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Synthesis and Characterization of CaF$_2$ Nanoparticles with Different Doping Concentrations of Er$^{3+}$

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Abstract: Calcium fluoride nanoparticles with various amounts of erbium ion dopants were prepared by CTAB/C$_7$H$_9$OH/C$_7$H$_{16}$/H$_2$O reverse micro-emulsion method. The nanoparticles were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), fourier transform infrared spectroscopy (FTIR), absorption and fluorescence spectra. The XRD patterns indicate a typical cubic fluoride structure and no other impurities. TEM results show the synthesized particles having uniform grain size and without agglomeration. FTIR spectra reveal that there are some amounts of -OH, NO$_3^-$ and other organic functional groups on the particle surfaces before the annealing process. Many absorption peaks and bands are present in the absorption spectra, corresponding to the rich energy levels of erbium ion. The Red-Shift of absorption bands and Blue-Shift of fluorescence peaks can be attributed to the weakened energy level split as a result of the decrease in crystal field strength.

Keywords: CaF$_2$; Nanoparticles; Doping; Erbium ions

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Introduction

As one of the traditional optical materials, calcium fluoride exhibits a series of advantages compared with oxide compounds, including lower phonon energy [1], melting point, and refractive index [2], as well as the higher optical transmittance and broader transmittance range [2]. Moreover, the typical fluorite structure of calcium fluoride enables high doping concentration of foreign ions. Thus, on the one hand, calcium fluoride with high purity is applied in the fields such as ultraviolet lithography, astronomical observation, aerial survey, detection and high-resolution optical instruments. On the other hand, calcium fluoride single crystal doped with rare earth (RE) ions works well as an important solid laser gain medium, such as Yb:CaF$_2$ [3-5] and U:CaF$_2$ [6-10] single crystal.

However, it is well known that the manufacturing of single crystals has many disadvantages, including long fabrication period, the need for special devices, restricted size for products, as well as the segregation of RE ions resulting in the limit at high doping concentration. To overcome these problems, a new method, which has drawn considerable attention from the middle 1990s [11,12], arises to fabricate transparent ceramics, replacing single crystals by sintering RE ions doped nanopowders. Aubry et al. [13] reported the fabrication of Yb:CaF$_2$ transparent ceramics, using the corresponding nanopowders as raw materials. However, it has been demonstrated [14] that the properties of the starting nanopowders are the crucial factor which influences strongly on the properties of transparent ceram-
ics. Thus, a number of synthesis methods were applied in the last several years: Li Yadong [15] synthesized RE:CaF$_2$ nanoparticles with diameter of 100~300 nm by hydrothermal method; Stark [16] prepared CaF$_2$ nanoparticles with diameter of 14 nm using flame synthesis, although the product yield was very low. In addition, Yb:CaF$_2$ [17] and Eu:CaF$_2$ [18] nanoparticles were also synthesized by wet chemical route in Igepal/cyclohexane/water reverse micelles system and polystyrene/THF solution, respectively.

Among the series of RE ions, the erbium element is the one interesting active ion having an intrinsic rich energy level, especially the up-conversion emission, and is believed to present high luminescence efficiency when incorporated into the low-phonon-energy CaF$_2$ matrix. The preparation of fine Er doped CaF$_2$ nanoparticles is expected to pave the way for the sintering of transparent ceramics, with potential applications in the fields such as lamps and display [19], the optical telecommunication [20], new optoelectronic devices [21] and biolabeling [22]. In this work, erbium doped CaF$_2$ nanoparticles were synthesized by a microemulsion method in a CTAB/C$_4$H$_9$OH/C$_7$H$_{16}$/H$_2$O micelles system. Details on the absorption and emission spectra are discussed.

**Experimental**

The starting materials used in the experiments were Ca(NO$_3$)$_2$·4H$_2$O (≥ 99.0%), NH$_4$F (≥ 96.0%), n-butyl alcohol (≥ 99.5%), n-heptane (≥ 97.0%), CTAB (Cetyltrimethyl Ammonium Bromide) (≥ 99.6%), Er(NO$_3$)$_3$·5H$_2$O (≥ 99.9%), and ethanol (≥ 99.0%). The reagents were all provided by SCRC (Sinopharm Chemical Reagent Co., Ltd, China). De-ionized water was purified by the ultra-pure water system at our laboratory.

For the microemulsion experiment, a CTAB/C$_4$H$_9$OH/C$_7$H$_{16}$/H$_2$O system was used to synthesize the nanoparticles. Microemulsions were made by dissolving 11 g of CTAB in 27 ml of n-heptane inside a 100 ml teflon beaker. This mixture was stirred magnetically until it was homogeneous and clear. A 10 ml of 0.4 mol/l Ca(NO$_3$)$_2$ and Er(NO$_3$)$_3$ aqueous solution was poured in slowly and was stirred for a short time. Finally, a 14 ml of n-butyl alcohol, as a co-surfactant, was added into the solution. In a similar way, the microemulsions containing fluoride ions were made by substituting the calcium nitrate aqueous solution with 10 ml of 1.0 mol/l NH$_4$F aqueous solution. These two kinds of microemulsions were then mixed and stirred at room temperature for 30 min and the Er:CaF$_2$ nanoparticles generated according to the following reaction: Ca$^{2+}$ + Er$^{3+}$ + F$^-$ → Er:CaF$_2$. The Er dopant concentrations were designed to be 0.2 mol%, 0.6 mol%, 1 mol%, 2 mol% and 6 mol%, respectively.

The emulsion mixture was centrifuged at a rate of 11000 rpm for 15 min, which caused sedimentation of the nanoparticles and allowed the removal of the mother liquor. The particles were then washed and centrifuged with ethanol and de-ionized water alternatively for several times. Finally the products were oven dried at 30℃ and lightly crushed in an agate mortar.

The direct precipitation method in aqueous solution was also applied for comparison with the microemulsion method. A solution containing the cationic precursors was made by dissolving nitrate salts in de-ionized water. Then this solution was added dropwise to the aqueous NH$_4$F solution which was stirred magnetically, leading to the formation of Er$^{3+}$ doped CaF$_2$ nanoparticles. The separation and drying procedure were same as that described above.

X-ray diffraction (XRD) measurements were performed on D/Max-RB (Rigaku, Japan) using Cu Kα radiation. The 2θ angular resolution was 0.04°. The diffraction patterns were scanned slowly over the 2θ range 25~60° at a rate of 2°/min.

Micromorphology of the obtained nanoparticles was observed by transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan) and the samples were prepared on a holey carbon-coater copper TEM grid.

The IR spectra were obtained by using Fourier transform infrared spectroscopy (FTIR, Nexus, Thermo Nicolet, USA) to investigate the influence of annealing at different temperatures. The emission spectra were recorded on a fluorescence spectrophotometer (FP-6500, JASCO, Japan) equipped with a Xe-lamp as the excitation source. The excitation wavelength was 483 nm. All experiments were performed at room temperature.

**Results and discussion**

Figure 1 shows the XRD patterns of CaF$_2$ nanoparticles doped with trivalent erbium ions of 0.2 mol%, 0.6 mol%, 1 mol%, 2 mol% and 6 mol%, respectively, comparing with JCPDS standard card (35-0816) of the CaF$_2$ crystal. The patterns of samples exhibit peaks well in accordance with the standard card without other phase, indicating that the Er$^{3+}$ doped CaF$_2$ nanoparticles were isostructural with CaF$_2$ crystal. The full width at half maximum (FWHM) of peaks shows a broadening trend with the doping concentration, which indicates the incorporation of Er$^{3+}$ facilitated the decrease in grain size and crystallinity. The XRD results also show the shifts in diffraction angles. This is the consequence of the incorporation of foreign ions into the lattice structure of host materials resulting in the changes of lattice parameters.

Figure 2 shows the TEM images of 0.2 mol% Er$^{3+}$
doped CaF$_2$ nanoparticles synthesized by the microemulsion method and direct precipitation method. The particles of CaF$_2$ with no agglomeration prepared by microemulsion were uniform in grain size of about 20 nm (see Fig. 2(a)). The nanoparticles with the same chemical composition prepared by aqueous solutions direct precipitation method was un-homogenous in grain size and severely agglomerated as presented in Fig. 2(b). The reaction by the micromulsions method took place inside the micro-micelles in which there were limited amounts of reaction reagents, namely, this method could control the grain growth in these micro-reactors. In the process of direct precipitation, conversely, the instantaneous local concentrations differed greatly when being mixed, resulting in the different numbers of nucleation and grain growth rate.

The IR absorption spectra were used to determine whether the surfactants and nitrates were removed completely from the product prepared by reverse microemulsion after washing. As shown in Fig. 3, the sharp peaks at 2856 cm$^{-1}$ and 2928 cm$^{-1}$ are assigned to the symmetric and antisymmetric stretching vibration of the -CH$_2$ groups. The broad peaks at 3453 cm$^{-1}$ and 1635 cm$^{-1}$ are assigned to the symmetrically stretching vibration and asymmetric stretching vibration of -OH, implying the presence of H$_2$O molecules. The peak at 1385 cm$^{-1}$ is the asymmetric stretching vibration of NO$_3^-$. Residual organics were also detected on the spectrum of the as synthesized powder around 1093 cm$^{-1}$. FTIR analysis shows that inorganic groups were not removed completely by the washing procedure; some of them are adsorbed on the surfaces of the particles due to the high surface energy originating from large surface area. Besides, as can be seen in Fig. 3, the FTIR spectra recorded on the synthesized powder after annealing at different temperatures are also presented. After annealing at 400°C, the traces of organics were removed and the amounts of nitrates were strongly decreased. With the increase in the annealing temperatures from 400°C to 600°C, the nitrates could not be detected any more. The intensity of the strong absorption bands related to the presence of water or hydroxyl groups in the as obtained powder decrease continuously with the increase in annealing temperature revealing a decrease in the amount of these molecules or groups.

The absorption spectra of CaF$_2$ powders with dif-
different Er\(^{3+}\) dopant annealed at 400°C are shown in Fig. 4. The effect of annealing on the characteristic absorption peaks of trivalent erbium ion is not obvious, in contrast with intensive absorption peaks attributed to the existence of -OH, -CH\(_2\), NO\(_3\) and organic groups in the range of IR as shown in Fig. 3. Experimental results indicate that there are many absorption bands and the absorption intensity increases with the dopant concentration. The band in the ultraviolet region between 340 and 380 nm with a maximum around 374 nm can be assigned to the \(^4I_{15/2} \rightarrow ^4G_{11/2}\) transition. The two bands between 390 and 500 nm with maximum around 402 and 480 nm can be assigned to \(^4F_{7/2} \rightarrow ^2H_{9/2}\) and \(^4I_{15/2} \rightarrow ^4F_{7/2}\) transitions. The remaining bands centered at 515, 648, 788 and 960 nm, as well as the broad absorption band around 1500 nm correspond to the following transitions of Er\(^{3+}\), \(^4I_{15/2} \rightarrow ^2H_{11/2}\), \(^4I_{15/2} \rightarrow ^4F_{9/2}\), \(^4I_{13/2} \rightarrow ^2H_{11/2}\), \(4I_{15/2} \rightarrow ^4H_{11/2}\) and \(^4I_{15/2} \rightarrow ^4I_{13/2}\), respectively. Furthermore, the absorption peak and band corresponding to the \(^4I_{15/2} \rightarrow ^4H_{11/2}\) and \(^4I_{15/2} \rightarrow ^4I_{13/2}\) transitions show somewhat a shift to IR, especially for the latter. This can be regarded as a consequence of weakened energy level split. It is well known that, in Er\(^{3+}\) doped CaF\(_2\) crystals, the cluster structures would appear when the dopant concentration is higher than 0.05 at \% [23] and the ions in clusters dominate when the dopant concentration is higher than 0.2 at \%, resulting in that the influences of crystal field of host is weakened strongly with the increase in doping concentration. Therefore the energy level splits of active ions are also weakened. However, shifts of other absorption peaks are not found or too weak to be observed. It may be inferred that the changes of crystal field strength would influence the high energy levels slightly more, relative to the low energy levels.

The annealing process has a strong influence on the emission spectra of Er\(^{3+}\) doped CaF\(_2\) nanopowders. The contrast of emission spectra of annealed powder at 400°C and un-annealed powder doped with 6 mol% Er\(^{3+}\) is shown in Fig. 5. The wavelength of excitation light was 483 nm. It can be seen from Fig. 5 that the emission intensity of the sample annealed at 400°C is stronger than that of the as-obtained nanoparticles, especially at the wavelength bands in the 525~570 nm region. The peaks centered at 540 nm and 546 nm can be attributed to the energy transfer \(^4S_{3/2} \rightarrow ^4I_{15/2}\), while the peaks centered at 552 nm and 558 nm can be assigned to the energy transfer \(^2G_{9/2} \rightarrow ^4I_{13/2}\). The broad bands are caused by the energy level split of \(^4I_{15/2}\) and \(^4I_{13/2}\) ground state. The relatively weaker emission intensity of as-obtained nanoparticles can be generally attributed to size and surface effects. It is known that the coordination of atoms on the surface is different from that in the bulk; atoms on the surface do not have a full coordination sphere which leads to a higher potential energy. Therefore, various chemical species can easily be adsorbed on the surfaces of the particles. Considering that our synthesis process was achieved with nitrate salt in water, the surface of the nanoparticles could be covered by residual NO\(_3\) and OH\(^-\) groups, as detected by FTIR spectroscopy. Such groups, with high phonon frequencies, are well known to quench efficiently the luminescence and resulted in the weak emission intensity of the as-obtained nanoparticles. Once they were heated up to 400°C, the treatment would remove the species adsorbed on the surfaces of the particles through their desorption and decomposition during the annealing process, resulting in the decrease in the amount of quenching centers; thus, the luminescence efficiency would improve and the decay time increased strongly.

![Fig. 4: Absorption spectrum of Er\(^{3+}\)-CaF\(_2\) nanopowders with different dopant concentration.](image-url)

![Fig. 5: Emission spectrum of Er\(^{3+}\)-CaF\(_2\) nanopowders with different dopant concentration.](image-url)
of dopant concentration from 0.2 to 6.0 mol%, the intensity of spectra did not show distinct enhancement as that of the absorption spectra. This observation could be related to the grain nano-scale size, as well as the cluster structure in the host CaF$_2$, leading to concentration quenching. Moreover, it is easy to evaluate that the fluorescence wavelength reveal a Blue-Shift with the doping amounts of Er$^{3+}$. This can also be attributed to the weak of energy level spilt mentioned above.

![Graph showing Er$^{3+}$ dopant concentration dependence of the emission of Er$^{3+}$:CaF$_2$ nanopowders annealed at 400°C.](http://dx.doi.org/10.1364/OL.29.001879)

**Conclusions**

CaF$_2$ nanoparticles doped with different amounts of erbium have been synthesized by the microemulsion method. The as-obtained particles, compared with those synthesized by direct precipitation methods, presented uniform morphology with mean grain size of about 20 nm. The incorporation of Er$^{3+}$ into the CaF$_2$ facilitates the decrease in grain size and changes of lattice parameter. The FTIR spectra indicate that there are still some amounts of NO$^-\text{3}$, -OH or water molecules and organic groups adhering to the particle surfaces. The absorption spectra show that the absorption intensity increases with the doping concentration. Red-Shift of absorption spectra and Blue-Shift of emission spectra can be attributed to the decrease in the field strength of the CaF$_2$ host. Annealing has a profound effect on the emission spectra. The emission intensity does not show an increasing trend with the increasing amount of Er$^{3+}$ dopant, but reveal a Blue-Shift of the emission peak at 725 nm.

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**References**


Effect of Hydrolyzing Agents on the Properties of Poly (Ethylene Glycol)-Fe₃O₄ Nanocomposite

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Abstract: Poly (ethylene glycol) (PEG) assisted hydrothermal route has been used to study the influence of the hydrolyzing agent on the properties of PEG-iron oxide (Fe₃O₄) nanocomposites. Iron oxide nanoparticles (NPs), as confirmed by X-ray diffraction analysis, have been synthesized by a hydrothermal method in which NaOH and NH₃ were used as hydrolyzing agents. Formation of PEG-Fe₃O₄ nanocomposite was confirmed by Fourier transform infrared spectroscopy (FTIR). Samples exhibit different crystallite sizes, which estimated based on line profile fitting as 10 nm for NH₃ and 8 nm for NaOH hydrolyzed samples. The average particle sizes obtained from transmission electron microscopy was respectively 174±3 nm for NaOH and 165±4 nm for NH₃ gas hydrolyzed samples. Magnetic characterization results reveal superparamagnetic characteristics despite a large particle size, which indicate the absence of coupling between the nanocrystals due to the presence of polymer in the nanocomposites. The conductivity curve demonstrates that σ_DC is strongly temperature dependent.

Keywords: Magnetite; PEG; Hydrothermal synthesis; Conductivity; Magnetization


Introduction

Magnetic particles have been widely studied because of their fascinating properties and wide range of potential applications in ferrofluids, information storage and medicine. Among magnetic particles, iron oxides (Fe₂O₃ and Fe₃O₄) have been extensively investigated [1-3]. The intrinsic properties of these particles are mainly determined by its size, shape, composition, crystallinity and structure [4-6].

Over the past decade, the Fe₃O₄ has been widely used in many applications such as magnetic recording, ferrofluids, magnetic separation, magnetic resonance imaging, and catalysis for a long time [7-12]. When the particle size of Fe₃O₄ is decreased to nanoscales, it exhibits superparamagnetic behavior [13,14]. This nanosize effect together with biocompatible properties of the material are considered of great potential for applications in biotechnology and biomedicine including bio-assays, magnetic resonance imaging (MRI), magnetically guided drug delivery, and hyperthermia [15-17].

Meanwhile, in bio-nanotechnology, the biocompatibility of most nanoparticles could be greatly improved by introduce poly(ethylene glycol) (PEG) to their surface. In general, attachment of PEG promotes water solubility, reduces toxicity, decreases enzymatic degradation, and increases the in vivo half-lives of small-molecule drugs [18]. PEG has frequently been used as a soft template for building 1D nanostructures due to its long-chain structure and selective absorption on...
preferred facets [19]. PEG with adsorbed by magnetic nanoparticles can prolong circulation time in a bloodstream. The modification of magnetite nanoparticles with PEG could be used to resist the protein adsorption and thus avoid their recognition by macrophage cells and simultaneously facilitate the nanoparticles uptake to specify cancer cells in a cancer therapy [20,21].

Size-controlled Fe₃O₄ nanoparticles were prepared via a facile solvothermal method by using mixed surfactants of SDS and PEG as protective reagents by Liu et al. [22]. They found that the mixture of SDS and PEG could act as a more efficient protective reagent than SDS or PEG alone. Quasi-hexagonal α-Fe₂O₃ nanoplates with lateral sizes of 40~60 nm and thickness of ca. 10 nm were fabricated by a facile poly (ethylene glycol 600) (PEG-600) assisted hydrothermal technique in combination with calcination method by Zhang et al. [23]. Zhen et al. [24] studied the PEG (Mwt = 400, 1000, 20,000) assisted hydrothermal synthesis of single-crystalline Fe₃O₄ nanowires. Dong et al. [25] synthesized the Fe₃O₄ nanoparticles via a simple technique at room temperature using PEG as a template.

Here, we report the synthesis of PEG-Fe₃O₄ nanocomposite. This is, to date, the first report using the adopted route for the synthesis of a PEG-Fe₃O₄ nanocomposite. Comprehensive physicochemical and magnetic characterization results are presented.

Experimental

Chemicals and Instrumentation

All chemicals, including FeCl₃·6H₂O (99%), FeCl₂·4H₂O (99%), NaOH PEG-400 (99%), and NH₃ gas (From HABAS, Turkey), were purchased from Merck and used as received without further purification.

X-ray powder diffraction (XRD) analysis was conducted on a Rigaku Smart Lab Diffractometer operated at 40 kV and 35 mA using Cu Kα1.

Fourier transform infrared (FTIR) spectra of the samples were measured with a Perkin Elmer BX FT-IR infrared spectrometer in the range of 400~4000 cm⁻¹.

Transmission electron microscopy (TEM) analysis was performed using a FEI Tecnai G2 Sphera microscope. A drop of diluted sample in alcohol was dropped on a TEM grid. Particle size distribution was obtained from several micrographs, counting a number of minimum of 150 particles.

Thermal stability was determined by thermogravimetric analysis (TGA, Perkin Elmer Instruments model, STA 6000). TGA thermograms were measured for 5 mg of powder sample at a heating rate of 10°C/min in the temperature range of 30°C~700°C under nitrogen atmosphere.

Electrical conductivity of the PEG-Fe₃O₄ has been studied in the range of 20~120°C with 10°C increment steps. The samples were used in the form of circular pellets with 13 mm diameter and 3 mm thickness. The pellets were sandwiched between gold electrodes and the conductivities were measured using Novocontrol dielectric impedance analyzer in the frequency range 1 Hz to 3 MHz. The temperature was controlled by a Novo-cool Cryosystem, between −100°C to 250°C. The dielectric data (ε’ and ε’’') were collected during heating as a function of frequency.

Room temperature VSM measurements have been conducted by using a quantum design vibrating sample magnetometer (QD-VSM).

Procedure

a) Synthesis of Fe₃O₄ NPs and PEG-Fe₃O₄ nanocomposite

In a typical experiment, 2.79 g of FeCl₃·6H₂O and 1 g of FeCl₂·4H₂O were added dropwise into a separate 50 ml two separate Teflon-lined stainless autoclaves, then 30 ml PEG-400, heated and melted, was injected to each autoclave. The hydrolysis was performed by the addition of 1 M NaOH solution (TE2) for the first autoclave and NH₃ gas (TE1) for the second until the pH of each solution is equal to 11. After continuous stirring, homogeneous solutions were obtained. The autoclaves were kept at 160°C for 12 h, then cooled to room temperature. The products were filtered and washed several times with distilled water and absolute ethanol, and finally dried in a vacuum oven at 50°C for 12 h.

Results and Discussion

XRD Analysis

Phase investigation of the crystalline products has been conducted using XRD and the patterns are presented in Fig. 1. The XRD patterns indicate that the products were iron oxide, Fe₃O₄, and broadening of the diffraction peaks were observed owing to the small crystallite size. All the observed diffraction peaks could be indexed by the cubic structure of Fe₃O₄ (JCPDS no 19-629) indicating a high phase purity of iron oxide. The mean size of the crystallites was estimated from the diffraction pattern by line profile fitting method using the equation (1) given in Ref 26, and 27 (equation given below). The line profile, shown in Fig. 1, were fitted for observed seven peaks with the following Miller indices: (111), (220), (311), (400), (422), (511), (440). The average crystallite size, D and σ, was obtained as 10±2 nm and 8±2 nm for TE1 and TE2 samples, respectively, as the result of this line profile fitting.
FTIR Analysis

FTIR spectra of as synthesized PEG-Fe₃O₄ nanocomposites by using NaOH (TE2) and NH₃ (TE1) as hydrolyzing agent; TE1 and TE2 are shown in Fig. 2. As prepared powder presents characteristic peaks of magnetite powder: metal-oxygen band, observed at ν₁ (590 cm⁻¹) corresponds to intrinsic stretching vibrations of the metal at tetrahedral site (Fe_{tetra} ↔ O), whereas metal-oxygen band observed at ν₂ (445 cm⁻¹) is assigned to octahedral-metal stretching (Fe_{octa} ↔ O) [28-33]. The FT-IR measurements reveal that the vibration band of C-O bond shifts from 1113 cm⁻¹ (as pure ethylene glycol) to 1095 cm⁻¹ for the nanocomposite which indicates that the O from C-O coordination bond of C-O bond shifts from 1113 cm⁻¹ (as pure ethylene glycol) to 1095 cm⁻¹ for the nanocomposite which indicates that the O from C-O coordination bond of Fe₃O₄ nanoparticles. The presence of C-O (≈1106 cm⁻¹), -CH₂ (≈2900 cm⁻¹) and -CH (≈2800 cm⁻¹) peaks were strong evidence that PEG was chemically bonded to the surface of nanoparticles. The surfactant molecules in the adsorbed state are influenced by the field of solid-state surface. As a result, the characteristic bands shifted to a lower frequency region. In the previous reports [34-38], it has been concluded that the functional head groups of the surfactant have coordination bond or strong interaction with nanoparticles, and thus kinetically control the growth rates of various facets of crystals, which can control the morphology. As a surfactant, PEG is one of the polymers with major interest in this area because it is nontoxic, nonflammable and easy to handle. The PEG with a uniform and ordered chain structure is easily adsorbed at the surface of metal oxide colloid has been reported. When the surface of the colloid adsorbs this type of polymer, the activities of colloid will greatly decrease and the growth rate of the colloids in some certain facet will be confined [39,40]. Therefore, the addition of PEG in the reaction system will modify the kinetics of the growth process, which leads to anisotropic growth of the crystal. Linear PEG used in the synthesis of series of nanoparticles and 1D material in solution [40].

TEM Analysis

TEM analysis performed to investigate the morphology of the PEG-Fe₃O₄ nanocomposites. Micrographs and size distribution histograms calculated thereof are presented in Fig. 3(a) and 3(b). Fe₃O₄ particles observed to have more edgy morphology including squares, polygons and parallelograms; particles also agglomerated. It is most likely due to the influence of the chemisorbed PEG on the growth of nanoparticles and eventually sticking/clustering particles together. Size distribution histogram is obtained by measuring at least 150 nanoparticles and is fitted by using a log-normal function as follows [41].

An average size, D_{TEM/log-normal}, of 173±3 nm and 165±4 nm was obtained for magnetite nanoparticles in TE2 and TE1 nanocomposites, respectively. Crystallite size obtained from XRD line profile fitting vs. particle size estimated from TEM, reveal the polycrystalline characteristics of observed particles.

Thermal analysis

Thermal stability of the precursor and final powders is analyzed by using TGA. To confirm the existence of PEG on the surface of Fe₃O₄ NPs and quantify the proportion of organic and inorganic phases, TGA was measured in the temperature range of 30~700°C and the thermograms are presented in Fig. 4. Pure PEG (as shown in Fig. 4c) combustion started at ~340°C and completely combusted at ~420°C [42]. PEG-400 shows approximately 100% weight loss in the 30~700°C temperature range of TG analysis. Degradation of PEG over the iron oxide begins at a much lower temperature. This behavior could originate from the fact that iron oxide particles behave as catalysts thus reducing the degradation temperature of PEG. Moreover, temperature range between degradation onset and offset points on the DTG curves for PEG is wider than that for the nanocomposite. This result might also be attributed to catalytic effects of nanoparticles for the degradation of PEG [43,44]. TE1 and TE2 nanocomposites (as shown in Fig. 4a and 4b) show a major weight loss of 16% and
Fig. 3 TEM micrographs and size distribution histograms (with log-normal fitting) of (a) TE2 and (b) TE1 samples.

Fig. 4 TGA thermograms of (a) TE1, (b) TE2 and (c) PEG.

22% over the temperature range of 30~700°C due to the decomposition and combustion of PEG respectively. These results imply that TE1 nanocomposite has 84% inorganic phase (Fe$_3$O$_4$) and TE2 nanocomposite has around 78% inorganic phase.

**Magnetization**

Under room temperature, M-H hysteresis curves of PEG-Fe$_3$O$_4$ nanocomposites measured up to 1.5 T are shown in Fig. 5. It reveals that magnetization curves are immeasurable coercively and remanence. Consequently, they do not show a hysteretic behavior. Besides, magnetization increases with external magnetic field strength, however, it does not reach to saturation even at 1.5 T. These observed properties are all typical features of superparamagnetic (SP) nanoparticles. Saturation magnetization (Ms) values of the nanocomposites are calculated from a plot of M vs. 1/H (M at 1/H≥0) as 54.6, 51.9 and 64 emu/g for TE1,TE2 and bulk Fe$_3$O$_4$, respectively, and appeared considerably lower than that of the bulk magnetite (92 emu/g) [45]. Here, we should notice that overall weight of the nanocomposites include the sum of the masses of magnetite and PEG coating. If we normalize these magnetization values to the mass of the magnetite only, derived from the TGA analysis in Fig. 3, Ms of sample TE2 becomes 59.5 emu/g and 69.3 emu/g of TE1, which are still lower than the theoretical Ms of bulk magnetization. However, reduced magnetization is generally observed in SP magnetite particles [32,45-48]. In the literature, the low magnetization values of SP particles can be explained by the spin canting and the presence of disordered spins at the surface [49]. As particle size decreases, effect of surface spins to the overall magnetization increases due to the presence of a considerably
high fraction of all spins on the surface. For instance, half of the overall spins can lie on the surface of the nanoparticles [49,50]. In addition to spin canting and presence of disordered spins at the surface, adsorption of surfactant molecules to the surface of magnetite particles can be another reason of low magnetization values in the nanocomposites. In general, we have observed in our previous works [32,48,51] as well as in this study also, that surfactant molecules are bound to the surface via oxygen atoms as revealed from FTIR data. As a result, some of the spins of the oxygen atoms close to the surface are pinned which weak the super exchange interaction between Fe-O-Fe atoms. Then, overall magnetization of the nanocomposite decreases.

Room temperature magnetization curves can be used to calculate average particle size of the nanocomposites with an assumption that they are weakly- or non-interacting SP particles. Magnetization of these particles can be described by the Langevin function which should be fit to the experimental data. Then, mean magnetic moment ($\mu$) of particles is found to determine average particle size (D). Accordingly, mean magnetic moments of TE1 and TE2 samples with normalized masses are calculated as 10.621 $\mu_B$ and, 7.743 $\mu_B$ respectively. When these values are inserted in $\mu = M_s \pi \rho D^3/6$, where $\rho$ is the density of the magnetite particles $\approx 5.18$ g/cm$^3$, average particle sizes are found to be 8.2 ± 2 nm and 7.7 ± 2 nm for the samples TE1 and TE2, respectively, and agrees with the crystallite sizes determined from XRD powder patterns.

**Temperature and frequency dependent conductivity and dielectric permittivity measurements**

The AC conductivity ($\sigma_{AC}$) curves of TE1 and TE2 samples as shown in Fig. 6. The $\sigma_{AC}$ is generally increasing with increasing temperature and frequency. The $\sigma_{AC}$ does not change so much with frequency at low temperatures but at higher temperatures, it increases exponentially with increasing temperature.

The $\sigma_{DC}$ conductivity of the TE1 and TE2 nanocomposites investigate from the frequency independent part of $\sigma_{AC}$ curves and obtained curves are demonstrated in Fig. 7. The conductivity curve demonstrates that $\sigma_{DC}$ strongly depends on temperature. These $\sigma_{DC}$ curves are fitted with Arrhenius equation as $\sigma_{dc} =$
Fig. 7  DC conductivity of PEG-Fe$_3$O$_4$ nanocomposites TE1 and TE2 samples versus reciprocal temperature.

$\sigma_0 \exp(-\frac{E_a}{k_B T})$ and the activation energies of $E_a = 0.251$ eV and $0.265$ eV are found for TE1 and TE2, respectively. These results are comparable with the $E_a$ of Carnosine coated Fe$_3$O$_4$ (0.312 eV) [30] and that of Alginic acid-Fe$_3$O$_4$ nanocomposite (0.151) [31].

Conclusion

In this investigation, iron oxide (Fe$_3$O$_4$) nanoparticles have been successfully synthesized by a PEG assisted hydrothermal method in which NaOH and NH$_3$ gas were used as hydrolyzing agents. Formation of PEG-Fe$_3$O$_4$ nanocomposite is confirmed by XRD and FTIR analysis. Samples exhibit different crystallite sizes, estimated based on line profile fitting as 10 nm for NaOH and 8 nm for NH$_3$ gas hydrolyzed samples. Average particle sizes, obtained from TEM analysis as 174$\pm$3 nm for NaOH and 165$\pm$4 nm for NH$_3$ gas hydrolyzed samples, indicate clearly that particles are polycrystalline. Magnetic characterization results reveal superparamagnetic character despite a large particle size, and magnetic domain size is estimated to be in the order of 8 nm for both samples, which evidence multi-domain character of the observed particles and the absence of coupling between the nanocrystals due to the presence of polymer in the nanocomposite. The conductivity curve demonstrates that $\sigma_{DC}$ strongly depends on the temperature. Since many intrinsic properties of magnetic nanoparticles are size-dependent, we believe that these nanoparticles with different sizes will have important applications not only in advanced magnetic materials and ferrofluid technology, but also in biomedical applications such as biomolecular separations, targeted drug delivery, cancer diagnosis and treatment, as well as magnetic resonance imaging. In addition, Fe$_3$O$_4$/PEG nanocomposite can also be used as thermoseeds for localized hyperthermia treatment of cancers.

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References

One-Step Cutting of Multi-Walled Carbon Nanotubes Using Nanoscissors

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Abstract: A novel, simple, and effective one-step method has been developed to cut the conventional long and entangled multi-walled carbon nanotubes (MWCNTs) with nanoscissors. The cutting process was carried out by the interactive collision of CNTs with the silicon carbide particles adhered on the abrasive papers. The final cut nanotubes have an average length of 200∼300 nm. The statistical length distribution result indicates that cutting by this method achieves high cutting efficiency for short duration of 2 min. Shortened nanotubes are found to be easily dispersed into aqueous and ethanol solutions. The cut MWCNTs/copper composite thin film fabricated by combined electrophoresis and electroplating techniques reveals that MWCNTs after cutting are well distributed and adhered to the Cu matrix. This method is not only fast and efficient but also no chemical waste, which will expand many potential applications of CNTs.

Keywords: Cutting; MWCNTs; Nanoscissors; Dispersion


Introduction

Carbon nanotubes (CNTs) have attracted enormous interest in nanoscience and nanotechnology over the past decade owing to their unique chemical, mechanical, and electronic properties [1-4]. The length of CNTs is of great importance for a variety of applications. Shortened CNTs are expected to have shorter dimension, richer chemistry, and to be more easily dispersed. They are promising in the application of future nanoscale structures and devices [5-8]. For example, Kalita et al. [5] demonstrated that short nanotubes performed much more properties in solar cell than that of a device with pristine and long MWCNTs. In addition, shortened CNTs also have potential applications in the field of field emission display, composite materials and hydrogen storage [6-8]. Besides, shortened CNTs can also be useful in controlled growth of CNTs with specific (n, m) type. Orgin et al. [9] cut a specific single-walled carbon nanotubes (SWCNTs) into several shorter segments and then the shorter SWCNTs could grown to longer lengths with the same (n, m) chirality.

Cutting methods of CNTs can be basically classified into three categories, namely mechanical, chemical, and a combination of both. Mechanical approaches for cutting nanotubes have focused on the use of ultrasonic treatment [10-12], ball-milling [13, 14], high-speed agitation [15], lithographic techniques [16], cryogenic crushing [17], and electron beam irradiation [18, 19]. However, it is almost inevitable that these processes are usually very energy consuming or involve expensive instruments. Chemical methods cut CNTs based on the idea of selective oxidation, wherein the higher reactivity of the defect sites along the length of nanotubes is more easily oxidized, for example, oxidation in oxidative acids [20], thermal oxidation [21], ozonolysis [22],...
and fluorination [23]. However, the chemical methods always influence the structure of CNTs because of oxidation involved during violent processes and they are sometimes hard to be controlled. The third kind of cutting CNTs combines mechanical and chemical methods such as sonication induced cutting in oxide media [2], or chemically driven nanoparticles cut CNTs via catalytic hydrogenation [24], but it always quite complicated and time-consuming.

In this paper, an efficient and reliable one-step method using nanoscissors is applied to cut MWCNTs. The cutting is promoted by interactive collision of CNTs with the silicon carbide particles adhered on the abrasive papers, which broke intramolecular C-C bonds by external force. This process requires short operation time of only several minutes for cutting CNTs. It’s more important that the cutting effect is limited to the collision points, so cutting of CNTs can be achieved without severe damage of the CNTs which is different from above-mentioned mechanical and chemical processes. Furthermore, the cut MWCNTs/Cu composite thin films are fabricated by combined electrophoresis and electroplating techniques. The present study provides a simple and effective method to cut MWCNTs which will broaden CNTs practical applications.

Experimental

MWCNTs fabricated by a chemical vapor deposition (CVD) method were purchased from Shenzhen Nanotech Port Co. Ltd., China. The samples were annealed as purified products. Annealing process was carried out by placing the pristine MWCNTs in a graphite-tube resistance furnace at 2000°C for 1 h under a high-purity argon gas atmosphere.

Experiments for the cutting of MWCNTs were conducted using a superfine SiC abrasive paper (antistatic abrasive paper, 5000 mesh size, Suisun Co. Ltd., Korea) as nanoscissors. A portion of nanotubes was uniformly placed between two pieces of abrasive papers. A constant pressure (25 MPa) was performed on the abrasive papers and maintained for 2 min. After that, the abrasive papers were removed and shortened MWCNTs were obtained.

After cutting, shortened MWCNTs/Cu composite thin films were prepared by combined electrophoresis and electroplating methods [25]. The additive of Mg(NO₃)₂ (10⁻⁴ mol/l) was added to CNT suspension of ethanol. A DC 10 V/cm was applied to electrophoresis for 1 min. The composition of the composite plating bath was 65 g/l CuSO₄·5H₂O + 196 g/l H₂SO₄ + 50 mg/l HCl. Electroplating was performed at 5 mA/cm² for 2 min.

Morphologies and structures of MWCNTs before and after cutting were characterized by field-emission scanning electron microscopy (SEM, Ultra 55, Carl Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). Dispersion in aqueous solution of MWCNTs before and after cutting was investigated by measuring zeta potential using a zeta potential/particle sizer instrument (NICOMP 380 ZLS, PSS.NICOMP, USA) at room temperature.

Results and discussion

Figure 1 shows a schematic of the cutting process of MWCNTs using SiC abrasive papers as nanoscissors under 25MPa pressure. When the pressure is invariably applied on abrasive papers, it will produce a strong squeezing force which causes the interactive collision between CNTs, and shear force in radial direction will exert on CNTs, like pairs of scissors. As a result, the length of CNTs will be shortened. In brief, MWCNTs are squeezed and sequentially sheared by nanoscissors constituted of superfine SiC particles, and finally sheared off into short nanotubes.

![Fig. 1 Schematic of the cutting process using abrasive papers as nanoscissors.](image-url)
To understand the cutting process of MWCNTs with nanoscissors, it is firstly analyzed the results obtained from TEM images illustrated in Fig. 2. Figure 2(a) reveals that the diameter and length of the annealed MWCNTs before cutting are about 20–30 nm and 30 µm, respectively. In Fig. 2(b), a MWCNT is not yet sheared off by the SiC nanoscissors. The nanotube has distinctly twisted because of strong squeezing force. The inset to Fig. 2(b) shows a high resolution TEM image of the cut region. It can be clearly seen that there is a convex fold on the surface of the MWCNT, and the surface of the nanotubes creates part cuts on the outer graphitic layers due to the interactive collision of CNTs. The cross-section structure of a MWCNT after cutting is shown in Fig. 2(c). It is obviously observed that one end of CNT has been entirely sheared off as though it is torn by external force.

Figure 3(a) and 3(b) show SEM images of the same MWCNTs after cutting. These images illustrate remarkable changes in the lengths of MWCNTs after cutting. It is also observed that the long MWCNTs have been cut into different segments. Figure 3(b) shows a typical shortened CNT with a length of about 200–300 nm.

A statistical evaluation of the length distribution is performed using the MWCNTs lengths determined from SEM image (Fig. 3(a)). Histogram for shortened MWCNTs is shown in Fig. 4. The results clearly reveal significant shifts in the MWCNT population. After cutting, the most CNTs have lengths from 100 to 700 nm with an average length of 200–300 nm.

The quality of MWCNTs dispersion can be characterized by measuring their zeta potentials. It is well-known that untreated CNTs tend to have a potential very close to zero in neutral solutions (pH=7) [26]. As shown in Fig. 5, zeta potential results of MWCNTs before and after cutting are presented. Here, the mean values of MWCNTs’ zeta potential before and after cutting are about $-2.33$ and $-16.82$ mV, respectively. The more negative zeta potential values of short MWCNTs strongly support the fact that cutting MWCNTs is propitious to their dispersion in aqueous solution.
The increase of absolute value of zeta potential may be attributed to the contraction in length because long CNTs are even more tangled and aggregated compared with short CNTs. In order to intuitively investigate the dispersion of CNTs, MWCNTs before and after cutting dispersed in the ethanol solution are shown in the insert photographs of Fig. 5. MWCNTs after cutting are observed to have better dispersion than those before cutting. The MWCNTs before cutting agglomerate and precipitate at the bottom (insert photograph (a)). However, the MWCNTs after cutting are stable without aggregation for more than 2 weeks (insert photograph (b)). It can be due to the reduction of their lengths.

Conclusions

In this paper, we have developed a simple and effective one-step method to cut MWCNTs into short lengths with nanoscissors. After cutting, MWCNTs are homogeneously cut to short length of about 200~300 nm with a narrow length distribution. Due to without introduction of other functional groups into short CNTs during cutting process, the shortened CNTs are easily dispersible in water and ethanol without aggregation for several weeks. The cut MWCNTs/Cu composite thin films fabricated by combined electrophoresis and electroplating approaches reveal that MWCNTs after cutting are well distributed and adhered to the Cu matrix. Such cut CNTs with shorter lengths and easier dispersions will have many potential applications in many fields for CNTs.

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References


Development of an Amperometric Hydrogen Peroxide Biosensor based on the Immobilization of Horseradish Peroxidase onto Nickel Ferrite Nanoparticle-Chitosan Composite

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Abstract: Nickel ferrite (NiFe$_2$O$_4$) nanoparticles have been dispersed in chitosan solution in order to fabricate nanocomposite films. Horseradish peroxidase (HRP) has been immobilized onto this chitosan-NiFe$_2$O$_4$ nanocomposite film via physical adsorption. The size of the NiFe$_2$O$_4$ nanoparticles has been estimated using X-ray diffraction pattern and scanning electron microscopy (SEM) to be 40±9 nm. The chitosan-NiFe$_2$O$_4$ nanocomposite film and HRP/chitosan-NiFe$_2$O$_4$ bioelectrode have been characterized using SEM technique. The HRP/chitosan-NiFe$_2$O$_4$ nanocomposite bioelectrode has a response time of 4 s, linearity as 0.3 to 12 mM of H$_2$O$_2$, sensitivity as 22 nA/mM. The effects of pH and the temperature of the immobilized HRP electrode have also been studied.

Keywords: Biosensor; NiFe$_2$O$_4$; Horseradish peroxidase; Nanoparticle; Chitosan


Introduction

The rapid, accurate, reliable and reagentless sensing and detection of hydrogen peroxide is of great importance in textile/food and health care industries. Many techniques, including titrimetry [1], chemiluminescence [2], fluorescence [3] and spectrophotometry [4], tend to be complex, time-consuming and suffer from various interferences. Consequently, rapid and reliable methods for measuring H$_2$O$_2$ are greatly sought after. Electrochemical methods, especially using various amperometric H$_2$O$_2$ biosensors, have been extensively employed for the detection of H$_2$O$_2$. Several valuable efforts have been focused on the development of electrochemical biosensors based on horseradish peroxidase for the detection of H$_2$O$_2$. The performance of these biosensors depends on the methods of enzyme immobilization when fabricating enzyme-modified electrodes. Various immobilization techniques have been employed, including adsorption [5], cross-linking [6], layer-by-layer assembly [7], covalent binding [8], surfactant-enzyme complex formation [9], sol-gel entrapment [10], and the use of biological membranes [11] and nanomaterials [12].

Magnetic nanoparticles as special biomolecule immobilizing carriers are becoming the focus of research [13]. Magnetic nanoparticles have been used in biomedicine and immunology due to its special properties [14-16]. The applications of magnetic nanoparticles in the immobilization of biomolecules have been studied by Kau shik et al. [17] and Qu et al. [18]. Among magnetic nanoparticles, ferrites are a broad class of complex...
magnetic oxides of considerable technological importance [19, 20]. Nickel ferrite (NiFe$_2$O$_4$), with an inverse spinel structure shows good biocompatibility, noncytotoxicity, easy preparation and also ferromagnetism that originates from magnetic moment of anti-parallel spins between Fe$^{3+}$ ions at tetrahedral sites and Ni$^{2+}$ ions at octahedral sites [21, 22]. Due to their large surface-to-volume ratio, high surface reaction activity, high catalytic efficiency and strong adsorption ability, nanomaterials are utilized for biosensor applications. In a recent study, Luo et al. used chitosan/NiFe$_2$O$_4$ nanocomposite as an enzyme immobilization matrix for glucose biosensor application [23]. This study shows that GOx incorporated chitosan/NiFe$_2$O$_4$ nanocomposite is characteristic by an excellent electroanalytical response to glucose.

Due to the excellent film-forming ability, high permeability, mechanical strength, nontoxicity, biocompatibility, low cost and availability, chitosan has been found to be a workhorse biopolymer for the immobilization of biomolecules for biosensor applications. Much effort has been made to improve the performance of chitosan for application as biosensors. These adjustments include its structural modification, change in molecular factors, as well as the incorporation of metal oxide nanoparticles in the chitosan network structure [24, 25].

The motivation of our work is to construct and analyze a simple biosensor using HRP for the detection of hydrogen peroxide. Optimized experimental conditions for the fabrication and operation of the biosensor have been established. The resulting biosensor has some advantages such as high sensitivity, good repeatability and reproducibility.

Materials and methods

Materials

HRP (EC 1.11.1.7, RZ>3.0, 250 U/mg), and chitosan were obtained from Sigma. All other chemicals were of analytical grade and used without further purification.

Preparation of NiFe$_2$O$_4$ nanoparticles

Nanoparticles of NiFe$_2$O$_4$ were prepared through microwave-induced combustion. Analytical grade 1 g NiCl$_2$, 1 g Fe(NO$_3$)$_3$·9H$_2$O, and with 1 g glycine (NH$_2$CH$_2$COOH), were dissolved in deionized water in the desired ratio. The crucible containing the solution was heated in a microwave oven (CEM, MDS 81D, 650 W). Initially, the solution boils and evaporates followed by decomposition with copious evolution of gases (N$_2$, NO$_2$, CO$_2$). When the mixture reaches the ignition temperature it begins burning and releases a great deal of heat from the highly exothermic reaction [26]. This vaporizes the remaining liquid instantly, and forms a solid burning at over 1000°C. The entire process takes only 15 min to produce ferrite powders. Glycine serves as fuel, being oxidized by nitrate. The evolution of large amounts of gases helps dissipate heat, reducing oxide sintering [27, 28].

Preparation of NiFe$_2$O$_4$/Chitosan solution

Chitosan solution (0.5%) was obtained by dissolving 0.025 g of chitosan in 5 ml of 0.05 mol·l$^{-1}$ acetate buffer solution (acetate dissolved in doubly distilled water). The calculated amount of NiFe$_2$O$_4$ nanoparticles was dispersed in the chitosan solution by stirring at room temperature, followed by sonification. Finally, a highly viscous solution of chitosan with uniformly dispersed NiFe$_2$O$_4$ nanoparticles was obtained.

Construction of HRP/NiFe$_2$O$_4$/chitosan biosensor

Before each experiment, the GCE (3 mm diameter) was first polished on chamois leather with 0.05 µm alumina powders and then washed ultrasonically in doubly distilled water, anhydrous ethanol, and water, respectively. After these pretreatments, the cleaned GCE was dried in air. HRP/NiFe$_2$O$_4$/chitosan solution was prepared by mixing HRP in NiFe$_2$O$_4$/chitosan solution. To get the best amperometric responses of the biosensor, the composition of the HRP/NiFe$_2$O$_4$/chitosan were optimized. 10 µl of solution was dropped on the surface of the cleaned GCE. Then the electrode was dried at room temperature. Before experiment, the biosensor was immersed in 0.1 mM PBS (pH=8) to wash out the non-immobilized components from the electrode surface. When not in use, the biosensor was preserved at 4°C in a dry state.

Apparatus and measurements

X-ray powder diffraction (XRD) analysis was conducted on a Rigaku Smart Lab operated at 40 kV and 35 mA using Cu Kα radiation (λ=1.54059 Å). FEI XL40 Sirion FEG Digital Scanning Microscope was used in order to investigate the microstructure and morphology of the sample. Samples were coated with gold at 10 mA for 2 min prior to the scanning electron microscopy (SEM) analysis.

All electrochemical measurements were performed using a CHI Model 842B electrochemical analyzer. These measurements were carried out using a three electrode cell with glassy carbon electrode as the working electrode, a platinum (Pt) wire as the counter electrode, and saturated Ag/AgCl electrode as a reference electrode in phosphate buffer saline (PBS, 10 mM, pH 8) containing [Fe(CN)$_6$]$_{3−}$/4−. All amperometric measurements were carried out at room temperature. They were performed in stirred solutions by applying the de-
sired potential and allowing the steady state current to be reached. Once prepared, the enzyme electrode were immersed in 10 ml of a 10 mM PBS, pH 8 solution, and the amperometric responses to the addition of known amount of analyte solution were recorded, respectively. The data are the average of three measurements.

Results and Discussion

Construction of HRP/NiFe$_2$O$_4$/chitosan nanobiocomposite

The XRD powder patterns (Fig. 1(a)) of the prepared samples exhibited the reflection planes (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (620), (533) and (622) that indicate the presence of the spinel cubic structure matching well with the powder diffraction File No. 10-325 [29,30]. The mean size of the crystallites was estimated from the diffraction pattern by line profile fitting method using Eq. (1) given in reference 31 and reference 32 [31, 32]. The average crystallite size, $D$, was obtained as 40±9 nm as a result of this line profile fitting. Figure 1(b) shows that the as-synthesized NiFe$_2$O$_4$ NPs have large grain structures. The material becomes highly dense and large particles of 1μm are observed. The material is of a spongy nature with struts.

The porous film of chitosan contains pin holes as illustrated by the SEM micrograph in Fig. 2(a). Figure 2(b) shows that NiFe$_2$O$_4$ nanoparticles are uniformly embedded in the porous CH network. The surface of

![Fig. 1](image1.png)  
(a) XRD pattern of the NiFe$_2$O$_4$ particles prepared by microwave assisted route; and (b) SEM micrograph of NiFe$_2$O$_4$.

![Fig. 2](image2.png)  
(a) SEM micrographs of chitosan; (b) NiFe$_2$O$_4$/chitosan; and (c) HRP/NiFe$_2$O$_4$/chitosan.
HRP immobilized NiFe₂O₄/chitosan nanocomposite shows a homogeneous globular morphology (pocks due to the presence of HRP immobilized NiFe₂O₄ in chitosan can be clearly observed) (Fig. 2(c)) revealing the immobilization of HRP.

**Electrochemical behavior of HRP/NiFe₂O₄/chitosan modified electrode**

Electrochemical impedance spectroscopy (EIS) studies of chitosan film, NiFe₂O₄/chitosan and HRP/NiFe₂O₄/chitosan bioelectrodes have been conducted in the frequency range of 0.01-10⁵ Hz. In the EIS investigation, the semicircle part corresponds to the electron transfer limited process; its diameter is equal to the electron transfer resistance, Rₘ, which controls the electron transfer kinetics of the redox probe at the electrode interface. Figure 3 presents the representative impedance spectrum of the (a) Bare GCE, (b) chitosan, (c) NiFe₂O₄/chitosan, (d) HRP/NiFe₂O₄/chitosan and (e) HRP/chitosan electrodes in 10 mM PBS pH=8.5 solution, containing [Fe(CN)₆]⁴⁻/³⁻ (5 mM), respectively. It can be seen that the bare GCE exhibits an almost straight line that is characteristic of a diffusion limiting step of the electrochemical process. A well-defined semicircle curve was observed with both the chitosan film electrode (curve b) and NiFe₂O₄/chitosan nanocomposite film electrode (curve c). It indicates the impedance of the electrode increases in the presence of NiFe₂O₄/chitosan nanocomposite and chitosan film due to the non-conductivity of chitosan component in the film, which obstructed the electron transfer of the Fe(CN)₆⁴⁻/³⁻. The impedance of NiFe₂O₄/chitosan nanocomposite film is smaller than that of chitosan-GCE. This decreased impedance can be attributed to the conductivity of NiFe₂O₄ nanoparticles. An obvious increase in the interfacial resistance can be observed when HRP is entrapped in the NiFe₂O₄/chitosan film. The increase of Rₘ might have been caused by the hindrance of the macromolecular structure of HRP to the electron transfer. On the other hand, Rₘ of HRP/NiFe₂O₄/chitosan is smaller than that of HRP/chitosan, indicating the HRP/NiFe₂O₄/chitosan nanocomposite film allows greater permeation for Fe(CN)₆³⁻/⁴⁻ probe than the pure chitosan film.

Figure 4 shows various cyclic voltammograms
obtained for (a) chitosan, (b) NiFe$_2$O$_4$/chitosan and (c) HRP/NiFe$_2$O$_4$/chitosan electrodes in 10 mM PBS solution containing [Fe(CN)$_6$]$^{3-}/4^-$ (10 mM), at 10-100 mV s$^{-1}$. It can be seen that the anodic potential shifts towards positive side and the cathodic peak potential shifts in the reverse direction. Besides this, the redox peak currents are proportional to the square root of scan rate, $v_{1/2}$, indicating a diffusion electron-transfer process. It can be seen that the redox potential of NiFe$_2$O$_4$/chitosan electrode shifts towards the higher side than that of pure chitosan film due to the incorporation of NiFe$_2$O$_4$ nanoparticles. It appears that the NiFe$_2$O$_4$/chitosan nanocomposite electrode provides a biocompatible environment to the HRP; and NiFe$_2$O$_4$ nanoparticles act as an electron mediator resulting in an accelerated electron transfer between HRP and electrode [33].

The electrocatalytic behavior of HRP incorporated in the bionanocomposite has been evaluated by cyclic voltammetry. Since the proposed HRP electrode did not show direct electron transfer between immobilized HRP and GCE, K$_4$Fe(CN)$_6$ was used as the electron mediator. Cyclic voltammograms (CVs) of the HRP/CS/GPTMS-modified electrode in 0.02 mol l$^{-1}$ PBS (pH=7.0) are shown in Fig. 5. When 40 μmol l$^{-1}$ H$_2$O$_2$ was introduced, an obvious electrocatalytic response was observed with the increase of reduction current and the decrease of oxidation current. The response process of the biosensor may be expressed as follows:

$$H_2O_2 + 2Fe(CN)_6^{3-} + 2H^+ \xrightarrow{HRP} 2H_2O + 2Fe(CN)_6^{4-}$$

(Fig. 6(a)). By the use of composite solutions containing different HRP concentrations and a fixed NiFe$_2$O$_4$ concentration (2 mg ml$^{-1}$) for dropping on the surface of the GCE, the change of amperometric current with HRP amount under constant H$_2$O$_2$ concentration is shown in Fig. 6. The current response increases as increasing HRP concentration and achieves a maximum value at 8.0 mg ml$^{-1}$. With the increasing of HRP concentration from 8.0 to 10.0 mg ml$^{-1}$, the sensitivity reduces gradually. So, an optimum loading of 8.0 mg ml$^{-1}$ HRP was used for subsequent experiments.

Figure 6(b) shows the dependence of the current response of the modified electrode on the applied potential in the range from −0.3 V to 0 V under constant H$_2$O$_2$ concentration. With applied potential decreasing from −0.1 V to 0 V, the steady state current increases due to the increased driving force for the fast reduction of H$_2$O$_2$ at the lower potentials and approaches a maximum value at −0.1 V, then the response current decreases with applied potential decreasing from −0.3 V to −0.1 V. Therefore, −0.1 V was selected as the applied potential for amperometric measurement in subsequent experiments.

The effect of pH on the modified electrode response was investigated under constant H$_2$O$_2$ concentration and the results are displayed in Fig. 6(c). The biosensor response increases with increasing pH value from 5.0 to 8.0, and achieves a maximum value at 8.0, then decreases from 8.0 to 9.0. So pH=8.0 PBS was chosen as the supporting electrolyte for the further experiments.

The activity of the enzyme electrode has been investigated using 15 mM H$_2$O$_2$ solution in 10 mM PBS, pH=8.0 solution by amperometric measurements at temperature varying from 35 to 60°C, as shown in Fig. 6(d). It is observed that the response increases with rising temperature, reaching a maximum at 55°C, and then starts to decrease. This could have been caused by the denaturation of HRP or film instability at the higher temperatures.

### Amperometric response of the biosensor to H$_2$O$_2$

The amperometric measurement of H$_2$O$_2$ at the enzyme electrode has been investigated and the calibration curve of the response current of the enzyme electrode to H$_2$O$_2$ concentration is shown in Fig. 7. The inset plot shows the response current of the successive addition of 0.3 mM H$_2$O$_2$. From Fig. 6, it can be observed that the linear range is up to 12 mM with a correlation coefficient (R) of 0.9932 and then a plateau is reached gradually at higher H$_2$O$_2$ concentrations. The biosensor has a good detection limit of 0.014 mM (signal-to-noise = 3), a high sensitivity of 22.42 nA/mM and a short response time (within ~4 s).
Fig. 6 (a) Effect of HRP concentration on the enzyme electrode in 10 mM PBS solution (pH=8.0); (b) Effect of the applied potential on the amperometric response of the enzyme electrode to 12 mM \( \text{H}_2\text{O}_2 \) in 10 mM PBS solution (pH=8.0); (c) Effect of pH on the amperometric response of 12 mM \( \text{H}_2\text{O}_2 \) in 10 mM PBS solution at an applied potential of \(-100 \text{ mV} \) vs. Ag/AgCl; and (d) Effect of temperature on the amperometric response of 12 mM \( \text{H}_2\text{O}_2 \) in 10 mM PBS solution (pH=8.0) at an applied potential of \(-100 \text{ mV} \) vs. Ag/AgCl.

Fig. 7 Typical current-time responses obtained with enzyme electrode at an applied potential \(-100 \text{ mV} \) to successive analyte addition in a stirred 10 mM PBS (pH=8.0). The calibration curve corresponding to the current response of different concentration of \( \text{H}_2\text{O}_2 \) is given as inset.

The apparent Michaelis-Menten constant \( (K_{\text{app}}) \), which gives an indication of the enzyme-substrate kinetics, can be calculated from the electrochemical version of the Lineweaver-Burk equation [35,36]:

\[
\frac{1}{I_{ss}} = \frac{I}{I_{\text{max}}} + \frac{K_{\text{app}}}{I_{\text{max}}}
\]

Where \( I_{ss} \) is the steady-state current after the addition of substrate, \( c \) is the bulk concentration of the substrate and \( I_{\text{max}} \) is the maximum current measured under saturated substrate condition. \( K_{\text{app}} \) was determined by analysis of the slope and intercept for the plot of the reciprocals of the cathodic current versus \( \text{H}_2\text{O}_2 \) concentration. The apparent Michaelis-Menten constant \( K_{\text{app}} \) in the present study is calculated to be 1.4 mM. This value is much smaller than reported in earlier work [34], indicating that the present electrode exhibits a higher affinity for \( \text{H}_2\text{O}_2 \). In Table 1 the analytical performance of this biosensor is compared with that of other biosensors in prior studies. The analytical characteristics of the enzyme electrode indicate that the immobilization of HRP mentioned above appears to be beneficial to the enhancement of the biosensor performance.

Reproducibility, selectivity and recovery studies

The reproducibility of the developed biosensor has
been investigated. Results show that the current response to 5 mM \( \text{H}_2\text{O}_2 \) is not lowered after the biosensor has been tested continuously for 20 times. To evaluate the electrode-to-electrode reproducibility, 5 enzyme electrodes were prepared under the same conditions independently. The R.S.D. (3.8%) obtained with the present method indicates an acceptable electrode-to-electrode reproducibility. The selectivity of this \( \text{H}_2\text{O}_2 \) biosensor was evaluated by \( \text{H}_2\text{O}_2 \) detection in the presence of some potentially coexisting compounds of \( \text{H}_2\text{O}_2 \) in biological systems, including uric acid and ascorbate. Experimental results revealed that 0.1 mM ascorbate, and 0.1 mM uric acid would not cause observable interference in the amperometric determination of 2 mM \( \text{H}_2\text{O}_2 \). Therefore, this \( \text{H}_2\text{O}_2 \) biosensor demonstrates good selectivity.

To demonstrate the analytical applicability of the biosensors, the recoveries of four \( \text{H}_2\text{O}_2 \) samples have been determined by the standard adding method. The results are satisfactory. As listed in Table 2, the recovery rate is in the range 95-101%.

## Table 2 Recovery studies of biosensor for determining \( \text{H}_2\text{O}_2 \).

<table>
<thead>
<tr>
<th>( \text{C}_{\text{original}} \text{(mM)} )</th>
<th>( \text{C}_{\text{added}} \text{(mM)} )</th>
<th>( \text{C}_{\text{found}} \text{(mM)} )</th>
<th>Recovery(%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.5</td>
<td>3.02</td>
<td>101.0</td>
</tr>
<tr>
<td>5.0</td>
<td>1.0</td>
<td>5.88</td>
<td>98.0</td>
</tr>
<tr>
<td>7.5</td>
<td>2.5</td>
<td>9.76</td>
<td>97.6</td>
</tr>
<tr>
<td>10.0</td>
<td>5.0</td>
<td>14.27</td>
<td>95.1</td>
</tr>
</tbody>
</table>

*Recovery(%)=\( \text{C}_{\text{found}}/(\text{C}_{\text{original}}+\text{C}_{\text{added}}) \).*

## Conclusions

In this investigation, we have fabricated a new hydrogen peroxide biosensor based on the immobilization of HRP into the NiFe\(_2\)O\(_4\)/chitosan nanocomposite. The experimental results clearly demonstrate that the immobilized HRP possesses excellent catalytic ability and well-retained activity. The developed biosensor is characteristic by its outstanding sensing performance, such as rapid response, wide linear range, and high sensitivity under optimum conditions.


Conductivity Study of Polyaniline-Cobalt Ferrite (PANI-CoFe$_2$O$_4$) Nanocomposite

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Abstract: In this investigation, the structural and electrical properties of nanocomposites of polyaniline (PANI) and cobalt ferrite synthesized by hydrothermal route are reported for the first time (with weight ratios of CoFe$_2$O$_4$/PANI 1:2 and 2:1). Synthesized nanomaterials have been characterized by XRD, FT-IR, SEM and TEM techniques. FT-IR results confirm the presence of CoFe$_2$O$_4$ and PANI in the samples. Their detailed conductivity measurements have been investigated. It has been found that PANI has a more effective conducting mechanism in CoFe$_2$O$_4$-PANI composites. These results are also consistent with the change in AC conductivity orders in composites.

Keywords: CoFe$_2$O$_4$/PANI; Hydrothermal; Nanomaterials; Permittivity; Magnetism


Introduction

Polyaniline (PANI) is a conducting polymer studied extensively due to its ease of preparation, good processibility, environmental stability and potential applications in the catalysis, biosensors, batteries, and electronic technology [1]. It can also be applied as a corrosion resistant and light-weight material [2]. The PANI composites containing nanoparticles are usually investigated due to their unique magnetic and electrical characteristics. Metal oxides with the spinel structure constitute an important class of materials exhibiting a wide variety of interesting electrical, magnetic, and optical properties [3]. Spinel ferrites which have a general structure of $[M^{2+}]_{tet}[Fe^{3+}]_{octa}O_4$ [4] exhibit noteworthy magnetic, electrical, and catalytic characteristics among magnetic materials [5,6]. When their particle size is in the nanometer range, the properties of spinel ferrites are improved remarkably [2]. Cobalt ferrite (CoFe$_2$O$_4$) belongs to the family of spinel-type ferrites and is one of the most technologically important ferrites for high-density magneto-optic recording applications, due to its high coercivity, moderate magnetization, very high magnetocrystalline anisotropy, chemical stability and mechanical hardness [7-11]. Cobalt ferrite can also be an alternative ceramic material for the development of novel magnetostrictive smart materials [12,13]. Recent studies on CoFe$_2$O$_4$ have demonstrated that it can be an appropriate material for the development of new technologies in the areas of strategic importance [10,14]. For example, CoFe$_2$O$_4$ acts as a thin absorber working at a high frequency band [15]. In addition, cobalt ferrite containing composites have been shown to exhibit an enhanced magneto-optical effect and a large magneto-electric effect [16,17]. Indeed, many recent publications have appeared in the literature on conducting and magnetic polyaniline composites containing nanoparticles such as Fe$_3$O$_4$ [18], Mn$_3$O$_4$ [19], ZnO [1], ZnFe$_2$O$_4$ [2] and NiFe$_2$O$_4$ [20].

Although many articles on the nanocomposites of...
PANI with magnetic nanoparticles have been published recently [2,19], there are very few studies on PANI-CoFe$_2$O$_4$ [21]. The dielectric properties and losses of a material are important since it is usually not possible to infer the connectivity of a composite system from transmission electron microscopy (TEM) and scanning electron microscopy (SEM) alone [22]. However, to the best of our knowledge, no study has been reported on dielectric behavior of PANI-CoFe$_2$O$_4$. In this study, synthesis, characterization and electrical properties of CoFe$_2$O$_4$-PANI nanocomposites have been investigated for the first time.

**Experimental**

**Chemicals**

Cobalt chloride (CoCl$_2$·6H$_2$O), iron chloride (FeCl$_3$·6H$_2$O), and NaOH were purchased from Merck; (NH$_4$)$_2$S$_2$O$_8$ (APS, as initiator) and cetyl trimethyl ammonium bromide (CTAB) were obtained from Sigma-Aldrich and were used as received without further purification. Aniline monomer, obtained from Sigma-Aldrich, was distilled twice under reduced pressure before use.

**Instrument**

X-ray powder diffraction (XRD) analysis was conducted on a Rigaku Smart Lab Diffractometer operated at 40 kV and 35 mA using Cu K$_\alpha$ radiation. Fourier transformed infrared (FT-IR) spectra were measured in transmission mode with a Perkin Elmer BX FT-IR infrared spectrometer. The powder samples were grounded with KBr and compressed into pellets. FT-IR spectra were measured with a Novocontrol cryosystem, which is applicable between 293 and 393 K. Static magnetic properties measurements were performed using a quantum design vibrating sample magnetometer (QD-VSM). SEM analysis was performed on FEI XL40 Sirion FEG digital scanning microscope, and samples were coated with gold at 10 mA for 2 min prior to analysis. TEM analysis was carried on a FEI Tecnai G2 Sphera microscope, with TEM sample preparation of having a drop of diluted sample in alcohol dripping onto a grid.

**Procedure**

**Synthesis of CoFe$_2$O$_4$ Nanoparticles**

In a typical experiment, stoichiometric amount of cobalt chlorides and iron (III) chloride (with 1:2 molar ratio) were completely dissolved in 20 ml distilled water under stirring. Then certain amount of NaOH was added until the pH value of the solution reached 11. After continuous stirring for an hour, a homogeneous solution can be obtained. The mixed solution was poured in to a Teflon lined stainless-steel autoclave (60 ml) with a filling degree of 60%. The autoclave was kept at 423 K for 12 h, and then cooled to room temperature naturally. The product was filtered and washed several times with distilled water and absolute ethanol, and then dried in a vacuum oven at 343 K for 6 h.

**Synthesis of CoFe$_2$O$_4$-PANI**

Detailed synthesis of PANI was reported in our previous study [19]. Briefly, 1 g of aniline was dissolved in a dispersion of 0.1 g Mn$_3$O$_4$ nanoparticles and 0.2 g CTAB in 50 ml water at room temperature. The polymerization was carried out at 273-278 K for 8 h after the drop-wise addition of 20 ml of 0.1 M HCl precooled APS solution into the mixture with constant stirring. The product was isolated by washing the reaction mixture with deionized water and ethanol, followed by drying under vacuum at 323 K for 4 h. The synthesis of CoFe$_2$O$_4$-PANI mixture was carried out in accordance to the description in the table listed in the Section of Figures and Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Code</th>
<th>CoFe$_2$O$_4$ (gm)</th>
<th>PANI (gm)</th>
<th>CoFe$_2$O$_4$/PANI (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>1A</td>
<td>0.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$/PANI</td>
<td>1A1</td>
<td>0.2</td>
<td>0.1</td>
<td>2:1</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$/PANI</td>
<td>1A2</td>
<td>0.2</td>
<td>0.4</td>
<td>1:2</td>
</tr>
<tr>
<td>PANI</td>
<td>–</td>
<td>–</td>
<td>0.2</td>
<td>–</td>
</tr>
</tbody>
</table>
Results and Discussion

XRD Analysis

The XRD patterns of the prepared CoFe$_2$O$_4$ (1A) (Fig. 1(a)) show six reflection planes: (220), (311), (400), (422), (511) and (440), which indicates the presence of the spinel cubic structure [23] and agrees with that reported in JCPDS Card No. 22-1086. The average crystallite diameter (L) was estimated by Scherrer’s equation, $L=\frac{0.9\lambda}{\beta\cos \theta}$ (where $\beta$ is the line broadening at the full-width at half maximum (FWHM) of the most intense peak (311), $\theta$ is the Bragg angle, and $\lambda$ is the X-ray wavelength) [24,25]. The result shows that the particle size of CoFe$_2$O$_4$ was calculated as $5\pm3$ nm.

By the addition of the PANI, the crystallinity decreases for 1A1 and 1A2 samples (Fig. 1(b) and 1(c)). An almost amorphous structure of PANI was observed in Fig. 1(d).

FT-IR Analysis

Figure 2(a)-2(d) shows the FT-IR spectra of the CoFe$_2$O$_4$ nanoparticles, PANI-CoFe$_2$O$_4$ composite (1A1 and 1A2) and pure PANI, respectively. Two absorption bands are observed at 566 and 493 cm$^{-1}$, which can be attributed to the coupling between Fe-O stretching modes of tetrahedral and octahedral sites as expected from normal spinel structure [26,27]. Figure 2(b) and 2(c) shows the IR spectra of PANI and PANI-CoFe$_2$O$_4$ mixtures. The peaks at 1564 and 1488 cm$^{-1}$ are attributed to the characteristic C=C stretching of the quinoid and benzenoid rings, and 1303 and 1246 cm$^{-1}$ are assigned to C-N stretching of the benzenoid ring. The broad peak at 1143 cm$^{-1}$, which is described by Quillard et al. as the “electronic-like band” [28], is associated with the vibration mode of N=Q=N (Q refers to the quinonic-type rings). The peak at 804 cm$^{-1}$ is attributed to the out-of-plane deformation of C-H in the p-disubstituted benzene ring [19].

TEM & SEM Analysis

A typical TEM micrograph was shown in Fig. 3(a) for CoFe$_2$O$_4$ nanoparticles. SEM micrographs of PANI-CoFe$_2$O$_4$ with different amount of PANI were shown in Fig. 3(b). The nanoparticles for both materials consist of spherical particles. For CoFe$_2$O$_4$ nanoparticles, the average particle size observed by TEM measurements was found to be 6.8±0.1 nm. This value is in good agreement with the value estimated from the XRD data. CoFe$_2$O$_4$ nanoparticles (1A) were found to be embedded in PANI as shown in Fig. 3(b).

Conductivity

AC Conductivity

The AC conductivity characteristic of 1A, 1A1 and 1A2 composites and pure PANI samples are measured between 293 and 373 K in 1Hz-3MHz frequency range (Fig. 4). All measurements are carried out from 293 to 373 K. The AC conductivity of 1A increases with increasing frequency exponentially and has same values for high frequencies at all elevated temperatures. Total conductivity $\sigma_T$ of ferrites (1A), PANI and their composites (1A1 and 1A2) can be analyzed with the equation of $\sigma_T = \sigma_{DC}(T) + \sigma(\omega)$ [29], which is due to their semiconducting nature at elevated temperatures and frequencies. The first term in this equation is $\sigma_{DC}$ which is related to the drift of electric charge carriers via band conduction mechanism and its temperature dependence relationship can be elevated by following Arrhenius relation: $\sigma_{DC} = \sigma_0 + \exp(-E_a/kT)$. The second term $\sigma(\omega)$ depends on frequency which related to the dielectric relaxation caused by the localized electric charge carriers. It obeys the empirical formula of

\[ \sigma(\omega) = \frac{\varepsilon_{\infty} - \varepsilon_{\infty}}{\varepsilon_{\infty} + 2} \]
Fig. 3  (a) TEM micrograph with log normal distribution of 1A; and (b) SEM pictures of 1A1 and 1A2.

Fig. 4  AC conductivity vs. frequency for all samples: (a) 1A; (b) 1A1; (c) 1A2; (d) PANI.
frequency dependence given by AC power law [30],
\[ \sigma = B(T)w^{n(T)} \]  
(1)
in which \( B(T) \) and \( n(T) \leq 1 \) are constants at a certain temperature. The logarithm of AC conductivity versus angular frequency curves for 1A were fitted according to Eq. 1, and the fitting curves are shown as continuous lines in Fig. 4(a). The temperature dependence of fitting parameters of \( n \) is shown in Fig. 5. The cobalt ferrite nanoparticles (1A) have a conduction mechanism of Overlap Large Polars (OLP), which is inferred from the variation of \( n \) with respect to temperature. In OLP conduction mechanism, \( n \) shows a decrease initially. After reaching a minimum it starts to increase again with temperature [30].

The AC conductivity curve of pure PANI has three different regimes at 293K. At higher temperatures it can be seen that the variation of conductivity by increasing frequency exists three regimes: it increases in Regime I, almost unchangeable in Regime II, and decreases in Regime III (see Fig. 4(d)). This behavior is in agreement with the evidence of Fig. 7 in ref [31]. The conductivity mechanism may be explained by dielectric properties in the next section. The conductivities of double- or half-weight cobalt ferrite composite (1A1 and 1A2) have almost the same order of magnitude comparing with that of PANI. Therefore the addition of cobalt ferrite into PANI does not have a significant effect at 293 K; but the trend of conductivity curves can vary at higher temperatures. PANI is more effective in conduction than CoFe\(_2\)O\(_4\) (1A), that is, the ratio of PANI to CoFe\(_2\)O\(_4\) in the composite is 1:2 (1A2).

**DC Conductivity**

The DC conductivity values derived from the extrapolation of AC conductivity curves at lower frequencies are shown in Fig. 6. The activation energies are obtained from the slope of the Arrhenius curves by using the following equation [32],
\[ \tilde{\sigma} = \sigma_o + \exp(E_\sigma/kT). \]  
(2)
in which \( \sigma \) is a temperature-dependent term and \( E_\sigma \) is the activation energy. The fitting curves in continuous lines are shown in Fig. 6. The obtained activation energies are as follows: 3.85 meV, 0.44 meV, 1.33 meV and 1.42 meV for 1A, 1A1, 1A2 and pure PANI, respectively.

At room temperature the DC conductivity of composites 1A1 and 1A2, as well as pure samples 1A and PANI are significantly increased with increase of PANI weight percentage (see Fig. 7). This indicates that PANI has a more effective conducting mechanism in CoFe\(_2\)O\(_4\)-PANI composites (1A1 and 1A2). This result is also consistent with the change in the order of AC conductivity in composites. According to the ref [31], the AC conductivity curves of PANI-DBSA/PVF composites would jump if the composite contains more than 20% weight of PANI. In another study, the critical filling ratio for PANI is found to be around 20% for Ce\(_2\)O-PANI composites [33].
Permittivity

The permittivity of the samples are shown in Fig. 8. At lower frequencies both $\varepsilon'$ and $\varepsilon''$ of CoFe$_2$O$_4$ (1A) initially decrease exponentially, and then increase with rising temperature. However, they all have the same characteristics at higher frequencies. For all samples the $\varepsilon''$ curves exhibit a sharp decrease at lower frequency, whereas, they become stable at higher frequency and also show independent trends on temperature (Fig. 8(e)-8(h)). However the $\varepsilon'$ values of PANI are negative, whereas, they are positive for CoFe$_2$O$_4$. The composites 1A2 predominated by PANI have negative $\varepsilon'$ values, and 1A1 predominated by CoFe$_2$O$_4$ have positive values initially, and then fluctuate at negative values, and finally become steady above 100 Hz (see Fig. 8(a)-8(d)).

![Permittivity plots](image)

Fig. 8 Real part of permittivity for: (a) 1A; (b) 1A1; (c) 1A2; and (d) PANI. Imaginary part of permittivity for: (e) Cobalt Ferrite; (f) 1A1; (g) 1A2; and (h) PANI.

The primarily negative permittivity may be attributed to the large plasmon resonance conductivity at relatively low frequency [34]. The unique negative permittivity observed at low frequency for PANI samples implicate their potential applications in high temperature superconductors [35].

There are several theories to explain the mechanism on how the dielectric properties of the composite depend on mixing polymer and host material dielectric properties [36]. The first one is the volume fraction average method which was applied to determine the effective dielectric constant,

$$
\varepsilon_{\text{eff}} = \varepsilon_1 \phi_1 + \varepsilon_2 \phi_2
$$

where $\phi$ is the volume fraction of the constituents.

The second equation is Maxwell equation, and the effective parameter is represented by

$$
\varepsilon_{\text{eff}} = \varepsilon_1 \frac{\varepsilon_2 + 2(1 - \phi_1)(\varepsilon_1 - \varepsilon_2)}{\varepsilon_2 + 2\varepsilon_1 + 2(1 - \phi_1)(\varepsilon_1 - \varepsilon_2)}
$$

It is based on a mean field approximation of a single spherical inclusion surrounded by a continuous matrix.
of the polymer [37]. The room temperature dielectric constants \( \varepsilon' \) and \( \varepsilon'' \) of constituents and composites are shown in Fig. 9 and Fig. 10, respectively. As a result, the volume fraction model can be more realistic to determine the dielectric properties of our composites. Although it is implied in the literature that the Maxwell equation is more realistic than volume fraction model [36], the latter has been found to be more accurate. Because of the large order of difference between the dielectric constants of constituents (\( \varepsilon' \) for CoFe\(_2\)O\(_4\) is 25, and for PANI is \( -2 \times 10^5 \), almost \( 10^4 \)-fold difference in dielectric properties of constituents may be explained by dominant dielectric properties of PANI/CoFe\(_2\)O\(_4\).
Conclusion

In this study, the synthesis, conductivity and permittivity characterization of the composite of CoFe$_2$O$_4$-PANI (with the weight ratio of 1:2 and 2:1) have been reported. The XRD study reveals the formation of cubic spinel structure; and all of the characteristic reflection peaks have a (311) reflection trend. It has also been found that volume fraction model shows more accurate results compared with the Maxwell equation.

Acknowledgment

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References

The Effect of Condensation on the Morphology and Magnetic Properties of Modified Barium Hexaferrite (BaFe$_{12}$O$_{19}$)

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Abstract: We present a comparison for the effect of condensation on the morphology and magnetic properties of oleic acid modified BaFe$_{12}$O$_{19}$ nanoparticles. Two different samples of BaFe$_{12}$O$_{19}$ nanoparticles were synthesized by dehydration (Z1) and rotary evaporation (Z2) method, respectively. Oleic acid was used as the surface modification agent to observe the morphological and magnetic changes. The nanoparticles were analyzed by XRD, FTIR, TGA, SEM, and VSM techniques for structural and physicochemical characteristics. Crystallographic analysis reveals the phase as hexaferrite and the average crystallite size of Z1 and Z2 is $21\pm3$ nm and $17\pm2$ nm, respectively. Rotary evaporator accelerates the condensation process in viscous gel (Z2). Due to the use of rotary evaporator, the coating with oleic acid for Z2 product has been accomplished very well, as compared with Z1. As a result, saturation magnetization of Z2 sample is much lower than that of Z1 sample.

Keywords: BaFe$_{12}$O$_{19}$; Nanoparticles; Rotary evaporatory; Condensation; Magnetic properties

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Introduction

With the fast advancement of wireless communication during the past few decades, microwave absorbing materials are becoming increasingly important for the applications outside special fields such as silent rooms, radar systems and military applications. Among these microwave absorbers, barium hexaferrite as a hard magnetic material, may be the most extensively investigated material among the family of hard ferrites having the general formula MeFe$_{12}$O$_{19}$, where Me=Ba, Sr, or Pb, due to of its two outstanding properties of having high saturation magnetization and high magnetic anisotropy field (1.7 T for BaFe$_{12}$O$_{19}$), which results in a high coercivity, remanence and a ferromagnetic resonance at around 50 GHz [1] and excellent chemical stability [2,3]. The ferromagnetic resonance coincides with large magnetic losses, making these materials suitable for microwave absorbers. Therefore, it has already found applications as permanent magnets, high density recording media, as well as microwave devices. Fine particles of BaFe$_{12}$O$_{19}$ are used in high density perpendicular magnetic recording media with dimensions in nanometers and have attracted much attention because of their different magnetic and electrical properties, comparing with those of their bulk counterpart and potential applications in various fields [4].

The size of the particles for better magnetic properties can be controlled during preparation, depending on the production technique, or post preparation, by mechanical [5,6] or thermal treatments [7-9]. Aerosol

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Infrared spectrometer in the range of 400 to 4000 cm\(^{-1}\) samples were recorded with a Perkin Elmer BX FT-IR instrument for several hours as a key factor for preventing formation of α phase in the sol-gel method [21]. Pre-heating between 400°C and 500°C for several hours was reported as a key factor to prevent formation of α-Fe\(_2\)O\(_3\) phase in the sol-gel technique [19]. In this way, samples with coercive field and magnetic powder were obtained when it is around 1:11 in the sol-gel technique [19], when ball milling was used optimum ratio is 1:12 [20], 1:10 in the coprecipitation route [11], and it is 1:4 in the hydrothermal method [21]. Pre-heating between 400°C and 500°C for 5 mg of powder sample at a heating rate of 10°C/min in the temperature range of 30°C~750°C under nitrogen atmosphere.

VSM measurements were performed by using a Vibrating sample magnetometer (LDJ Electronics Inc., Model 9600). The magnetization measurements were carried out in an external field up to 15 kOe at room temperature.

Procedure

The starting materials, iron (III) nitrate nonahydrate (Fe(NO\(_3\))\(_3\)·9H\(_2\)O), barium nitrate (Ba(NO\(_3\))\(_2\)), sodium hydroxide (NaOH), citric acid (C\(_6\)H\(_5\)O\(_7\),H\(_2\)O), and oleic acid (C\(_{18}\)H\(_{32}\)O\(_2\)) were purchased from Alfa Aesar, having analytical purity. Ba(NO\(_3\))\(_2\) and Fe(NO\(_3\))\(_3\)·9H\(_2\)O weighed in the stoichiometry of BaFe\(_{12}\)O\(_{19}\) to prepare the aqueous solution of each with the respective concentrations of 0.1 and 0.6 M by stirring at 50°C with Fe/Ba ratio of 11:1 and were gradually added into the citric acid solution under continuous magnetic stirring. The molar ratio of metal nitrates to citric acid was adjusted at 1:1. The pH of the solution was continually monitored and maintained at a value of 7 by the addition of the sodium hydroxide solution required. The temperature was raised to 65°C and the solution was then stirred for 2 h at 65°C. Then 30 ml oleic acid was slowly added to the solution and mixed again for 2 h. Afterwards, the final solution was divided into two parts. First part (Z1) solution was allowed to dehydrate in a vacuum oven at 180°C for 48 h. Second part (Z2) solution was magnetically stirred for 12 h at room temperature, and then it was transferred to a rotary evaporator and evaporated at 90°C for 3 h to remove surplus water until a viscous liquid was obtained. Thus, it was observed that rotary evaporator accelerated the condensation process in viscous gel (Z2). Due to the use of rotary evaporator, the coating with oleic acid for Z2 product was accomplished very well as compared with Z1. By increasing the temperature, the gel precursors were combusted forming brown loose powder precursors (denoted Z2p, Z1p). These powders were precalcined at 450°C for 4 h, followed by calcination at 1100°C for 1 h. The modified hexaferrite BaFe\(_{12}\)O\(_{19}\) nanoparticles were thus obtained.

Results and Discussion

SEM Analysis

The morphology of as prepared samples was analyzed by SEM and the micrographs are presented in Fig. 1(a).
and Fig. 1(b) for Z1 and Z2, respectively. Both samples exhibit nanoparticles with several different morphologies including polygonic, rod-like, and plate like morphologies [26]. Z1 exhibits particles with size in the range of 40 nm to 500 nm. Sample Z2, however, shows slightly narrow size distribution in the range of ca. 40 nm to 260 nm. When compared with the crystallite sizes obtained from the XRD line profile fitting, (Z1: 21±3 nm and Z2: 17±2 nm) it is obvious that the particles observed by SEM are secondary particles with polycrystalline character for both samples.

Fig. 1  SEM images of: (a) Z1 at different magnifications; and (b) Z2 at different magnifications.

**FT-IR Analysis**

Figure 2 shows the FTIR spectra for the gel precursors (Z2p, Z1p), oleic acid and samples calcined (Z1, Z2) at 1100°C. The spectrum of oleic acid exhibit sharp bands at 2924 cm⁻¹ and 2854 cm⁻¹ and 1405 cm⁻¹ the symmetric (νₛ C-H) and asymmetric (νₘₐ C-H) CH₂ stretching modes and stretching mode of COOH group of the oleyl group, respectively. These characteristic peaks of oleic acid disappear after the ligand-metal interaction. The intense peak at 1710 cm⁻¹ (oleic acid molecule) is derived from the existence of the C=O stretch, and the band at 1285 cm⁻¹ exhibits the presence of the C-O stretch. The O-H in-plane and out-of-plane bands appear at 1462 cm⁻¹ and 937 cm⁻¹, respectively [27-31]. A set of bands appear at 1381 and 848 cm⁻¹, which are attributed to the N-O stretching and bending vibrations of NO₃⁻, respectively [32-34].

When the oleic acid molecule is adsorbed as a surfactant, the adsorption will result in some change in the spectra of the surfactant. For example, the adsorption band at 1710 cm⁻¹ (oleic acid molecule), which is assigned to stretching vibrations of C=O of the carboxyl group, disappears in the spectrum of the final magnetic fluid [27,35]. All these results suggest the existence of both oleic acid molecule and oleate in the magnetic par-
particles, thus leading to the conclusion that physical adsorption and chemical binding were formed on the surface of magnetic particles, resulting in significant improvement in hydrophobicity after modification.

From Fig. 2, it can be seen that before modification (calcined at 1100°C), the adsorption bands at 448 cm⁻¹, 552 cm⁻¹ and 603 cm⁻¹ correspond to typical BaFe₁₂O₁₉ adsorption bands [36-40].

**XRD Analysis**

Phase investigation of the crystallized products (Z₁, Z₂) was performed by XRD and the diffraction pattern is presented in Fig. 3. The XRD powder patterns indicate that the products are M-type BaFe₁₂O₁₉ and the diffraction peaks are broadened owing to very small crystallite size. All of the observed diffraction peaks are indexed by the hexagonal structure of BaFe₁₂O₁₉ revealing a high phase purity of hexaferrite agree with those reported in JCPDS, card number 84-0757 (including minor Fe₂O₃ (for Z₁) card number 76-1821).

The mean size of the crystallites was estimated from the diffraction pattern by line profile fitting method using the equation (1) given in [41,42]. The line profile, shown in Fig. 3(a) was fitted for 27 observed peaks for Z₁ with the following miller indices: (100), (002), (102), (006), (106), (110), (107), (114), (108), (202), (203), (116), (1010), (118), (1011), (213), (216), (2010), (300), (217), (2011), (218), (307), (2010), (200), (1114), (2014) and including minor phase Fe₂O₃ was given with (*) on Fig. 3(a). Figure 3(b) was fitted for 22 observed peaks for Z₂ with the following miller indices: (100), (002), (102), (006), (106), (110), (008), (112), (107), (114), (200), (203), (116), (205), (118), (1011), (209), (300), (217), (2011), (200), and (2014). The average crystallite, size, D and σ, was obtained as for Z₁=21±3 nm and Z₂=17±2 nm, as a result of this line profile fitting. In Fig. 3(c), bulk (unmodified) BaFe₁₂O₁₉ is shown to compare the effect of surface modification on the size and particle size of oleic acid modified nanoparticles, which was observed to be smaller compared to the unmodified sample.

**TG Analysis**

Thermogravimetric analysis is carried out to evaluate the mechanism for the formation of hexaferrite phase and to observe the effect of heating on structural changes of the synthesized sample. Figure shows three thermographs indicating the weight losses at 100°C, 300°C and 650°C. The first peak at 100°C is due to the loss of residual water in the gel [26]. The second weight loss around 300°C is due to condensation and the de-
composition of the unreacted citric acid that remained after combustion [43]. The third peak extending up to 600°C is due to further condensation (the decarboxylation of BaCO₃ formed during the combustion, which has been reported to take place at 1055°C for pure carbonate and at around 800°C for a mixture carbonate and an iron oxide [26,43,44]. This peak could also be assigned to simultaneous formation of monoferrite, MFe₂O₄ (M=Ba, Sr) [26]).

![Fig. 4 TGA thermograms of precursor (Z2p, Z1p) and calcined (Z2, Z1) hexaferrite powders.](image)

**VSM Analysis**

Room temperature M-H hysteresis curves of bulk (i.e., as annealed) BaFe₁₂O₁₉ particles and oleic acid modified BaFe₁₂O₁₉ (Z1, Z2) are shown in Fig. 5. It is observed that bulk BaFe₁₂O₁₉ and Z1 has nearly the same saturation magnetization (Ms) and measured 61 emu/g while that of Z2 is 38 emu/g. Similarly, coercive fields of bulk and Z2 samples are 5 kOe and that of Z1 is 4.5 kOe. The reason of the weak magnetization of sample Z1 can be explained by the formation of the intermediate hematite phase (α-Fe₂O₃), see Fig. 3(c). The presence of this phase is relatively higher in Z1 compared to Z2, thus, it is quite reasonable to have low saturation magnetization. Existence of this intermediate phase is often observed when barium hexaferrite is synthesized with initial Fe/Ba molar ratio of 12:1. To avoid the formation this impurity, optimal Fe/Ba molar ratio should be choosen. It was reported that the optimum Fe/Ba ratio is 4:1 for hydrothermal route [45], 10 for co-precipitation [9] and 11 in the microwave induced combustion method [46]. Generally, formation of α-Fe₂O₃ can be prevented by choosing the Fe/Ba ratio in between 11.5:1 and 10:1, further decrease leads to the formation of another intermediate phase, barium monoferrite (BaFe₂O₄). Fortunately, this phase can be removed by HCl etching [47]. In this way, Sozeri et al. very recently succeed to synthesize high purity and high quality barium hexaferrite samples with an initial Fe/Ba molar ratio of 2:1 [48]. XRD pattern of sample Z1 also has a low intensity peak of hematite, fraction of which is very low and magnetization of this sample appeared to be very close to that of bulk sample [49].

![Fig. 5 Magnetic field vs. magnetization plots Z1, Z2 and bulk BaFe₁₂O₁₉ (unmodified).](image)

The reason of the low coercive field of the sample Z1 is due to its large particle size. SEM micrographs and crystallite size calculations from XRD patterns showed that Z1 has larger grains as ≈21±6 nm in average size. It is known that as the grain size increases, coercivity of the sample decreases. In fact, the coercivity is related to the reciprocal grain size rather than the grain size itself [47]. Pinning of the magnetization occurs at the grain boundaries, density of which decreases as grain size increases. Therefore, when the grain size greatly increases, the coercivity caused by grain boundary pinning would disappear, because each grain can be in multi-domain state.

**Conclusion**

The preparation of fine particles of BaFe₁₂O₁₉ was accomplished by gel to crystalline conversion method in the present study. Oleic acid has been used as a surface modification agent in order to observe the morphological and magnetic changes. Comparing the crystallite sizes obtained from the XRD line profile fitting, (Z1: 17±2 nm and Z2: 21±3 nm) it is obvious that the particles observed in SEM are secondary particles with polycrystalline character for both samples. Although the ratio of Fe/Ba was taken as 11:1, this study shows that BaFe₁₂O₁₉ nanocrystals synthesized by the rotary method is almost pure but BaFe₁₂O₁₉ nanoparticles synthesized by dehydration contains α-Fe₂O₃ as impurity. Due to the accelerated condensation process observed for Z2, the resulting thickness of oleic acid coating is high. Thus, saturation magnetization of Z2 sample is much lower (nearly half) compared to that of Z1.
Acknowledgements

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References

Synthesis of Multi-Walled Carbon Nanotubes/ZnO Nanocomposites Using Absorbent Cotton

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Abstract: This letter focuses on the synthesis of multi-walled carbon nanotubes (MWNTs) and MWNTs/ZnO nanocomposites using absorbent cotton. The MWNTs have been synthesized by a rapid heating of absorbent cotton at different temperature (400°C, 550°C, 600°C). The MWNTs/ZnO nanocomposites have been synthesized by heating mixtures of Zn(OH)\textsubscript{2}/H\textsubscript{2}O/absorbent cotton at different temperature (at about 550°C and 600°C). The X-ray diffraction (XRD) pattern and energy dispersive spectrum (EDS) clearly show that the pure MWNTs and ZnO nanocomposites (with a mean size of 35.9 nm) were synthesized. The scanning electron microscopy (SEM) images demonstrate that the structure of synthesized MWNTs was middle-hollow, with inner and outer diameter of around 10 and 80 nm. The ZnO nanocomposites that had grown on the walls of MWNTs were nonuniform and agglomerated, with an outer diameter of around 110 nm. The selected area diffraction (SAD) patterns and Raman spectrum indicate that the MWNTs were well-crystallised, and there are a few defects in the walls. Infrared absorption spectroscopy (IR) spectra suggest that the surface of MWNTs has been covered by ZnO.

Keywords: MWNT; MWNTs/ZnO nanocomposites; Characteristic


Introduction

In recent years, there has been an increasing interest in developing materials with low dimensional nanostructure such as nanotubes and nanocrystals due to their potential applications in nanoscale devices. Multi-walled carbon nanotubes (MWNTs) have attracted considerable attention owing to their chemical stability, unique electrical property, and extraordinary strength [1]. The commonest fabrication techniques are electric arc discharge [2,3], laser ablation [4,5], chemical vapor deposition (CVD) [6,7], and flame synthesis [8]. Although many efforts have been made in developing those methods above, high temperature, complicated control, and expensive or unrenewable materials are always needed.

Zinc Oxide (ZnO), with a wide direct bandgap (3.37 eV) at room temperature, is an important semiconductor material applied in conventional catalysis process. ZnO nanostructures have profound applications in optics, optoelectronics, and actuators due to many unique properties such as good optical activity, better sensitivity for UV light, high stability, catalytic activity, and low production cost [9-11]. In our previous work, ZnO nanoparticles have been successfully synthesized using plants [12,13]. Recently, ZnO nanocomposites grown onto MWNTs could reduce the threshold electric field because ZnO has smaller electron affinity than the MWNTs, and the MWNTs/ZnO nanocomposites junction is similar to a ZnO/metal junction allowing electrons to be easily emitted into a vacuum [14,15]. It is well known that cotton contains a large amount...
of vascular bundles, and their components are cellulose, hemicellulose, and lignin. The present work shows that MWNTs can be obtained by heating grass containing much tubular cellulose in the presence of a suitable amount of oxygen [16,17]. The treatments of removing protein and grease in the synthetic method of MWNTs from vascular bundles will be unnecessary if the absorbent cotton is used as the source of carbon. In this work, MWNTs and MWNTs/ZnO nanocomposites were synthesized using absorbent cotton as the source of carbon, and characterized using special technique explained under experimental section. To our knowledge, this is the first report on the synthesis of MWNTs and MWNTs/ZnO nanocomposites using absorbent cotton. The method of synthesizing MWNTs and MWNTs/ZnO nanocomposites using absorbent cotton may be adaptable to industry.

Materials and Methods

Materials

Absorbent cotton and ZnO powders were purchased from the market and used without any further purification.

Synthesis of MWNTs

0.9 g absorbent cotton was rolled out onto the crucible, put into the muffle furnace, heated to about 400°C rapidly, and kept at about 400°C for 3 min. Subsequently, the samples were cooled to room temperature. The heat treatment (at about 400°C was repeated many times and the products containing MWNTs were collected. Finally, the collected products were washed 3 times with ethanol and water to remove impurities, and oven-dried at 105°C for 72 h.

Similarly, the above processes were treated at 550°C, 600°C, respectively.

Synthesis of MWNTs/ZnO Nanocomposites

Absorbent cotton was added into the solution of Zn(OH)\(_2\) (3 g ZnO dissolved in 100 ml water), and shaken (300 rpm) at 25°C for 72 h. Afterward, the absorbent cotton with Zn(OH)\(_2\) was dried in an oven at 105°C for 24 h, and treated with the above processes (as shown in 2.2 fraction) at 550°C and 600°C, respectively.

Characterization

The products were characterized by the methods as follows: X-ray diffraction (XRD) patterns were carried out with the Al Kα line as the excitation source (hν=1486.6 eV) using a PHI 5000C (Perkin-Elmer, USA); scanning electron microscopy (SEM) images were performed using a JEOL JSM-840 operated at 20 kV; and energy dispersive spectra (EDS) were obtained using an Oxford EDX system attached to SEM. The products containing MWNTs were characterized further by the following methods: selected area diffraction (SAD) pattern was taken on high resolution scanning electron microscopy attached to SEM; Raman spectrum was obtained using a micro-Raman spectrometer (Nicolet Almega XR) with a 473 nm laser as an excitation source; Infrared absorption spectroscopy (IR) spectra (4000~400 cm\(^{-1}\)) were measured using a IR spectrometer (Nicolet Antaris II).

Results and Discussion

The XRD patterns of the powdered MWNTs and the MWNTs/ZnO nanocomposites synthesized in 600°C are shown in Fig. 1. From Fig. 1(a), the characteristic peak at 2θ=25.8° represents graphite peak corresponding to C of the MWNTs and reveals the crystallinity of the MWNTs [18]. Moreover, the peaks at other degrees are observed clearly in the profile. It indicates that some impurities were combined in the walls.

Fig. 1 XRD patterns of the products: (a) containing MWNTs, (b) containing MWNTs/ZnO nanocomposites.
of synthesized MWNTs. The diffractions of both MWNTs and ZnO could be observed in Fig. 1(b). Except the peak corresponding to C of the MWNTs, the XRD peaks reveal good agreements with ZnO (JCPDS 36-1451). The main dominant peaks for ZnO are identified at $\theta = 31.76^\circ, 34.43^\circ, 36.20^\circ, 47.48^\circ, 56.45^\circ, 62.77^\circ, 66.27^\circ, 67.88^\circ$ and $68.99^\circ$, which can be indexed as (100), (002), (101), (102), (110), (103), (200), (112), (201) planes of ZnO, respectively. The main diffraction peaks related to the impurities are not observed, it means that the MWNTs/ZnO nanocomposites were pure.

The ZnO nanocomposites grown onto the surface of MWNTs may be produced by the following process:

$$\text{ZnO} + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2$$

Absorbent cotton + Zn(OH)$_2$ → MWNTs + ZnO → MWNTs/ZnO

XRD results of ZnO show prominent 100, 002 and 101 reflections among which 101 is of highest intensity [19-21]. The diameter (D) of the ZnO nanoparticles was calculated using the Debye-Scherrer formula $D = K \lambda / (\beta \cos \theta)$, where $K$ is the Scherrer constant (0.9 in this study), $\lambda$ is the X-ray wave length, $\beta$ is the peak width at half-maximum, and $\theta$ is the Bragg diffraction angle. The XRD peaks show that the ZnO nanoparticles had a diameter of about 35.9 nm. Furthermore, the dominant peaks of ZnO were more intensive and narrower, which are in good agreements with the characteristic of the previously synthesized ZnO nanoparticles [12,22,23] and mean that a good crystalline nature of the ZnO have grown on the surface of MWNTs.

Figure 2 (a) shows the typical SEM images of the MWNTs. The walls are composed of graphite sheets aligned to the tube axis. The structures of individual MWNTs are middle-hollow. The outer and inner diameter is 80 and 10 nm, and the length of nanotubes observed is longer than 1 $\mu$m. As shown in Fig. 2(b), ZnO nanoparticles have grown on the surface of the MWNTs. The outer diameter of MWNTs/ZnO nanocomposites is about 110 nm.

To obtain the more details of the MWNTs, the structures of framework were characterized by SAD and Raman spectrum. The MWNTs are well-crystalline, which is resulted from SAD pattern in Fig. 3. The SAD pattern is characteristic of MWNTs, and the two elongated arcs and circle correspond to the planes of graphite carbon, which are consistent with the XRD results. The wall of the MWNTs is composed of high-quality graphite layers, but there are a few defects in the walls of the MWNTs. It was proved further by the Raman spectrum (shown in Fig. 4). The peak at 1580 cm$^{-1}$ (G-band) corresponds to an E2g mode of graphite and is related to the vibration of sp2-bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphite layer. Nanotubes with concentric multi-walled layers of the hexagonal carbon lattice display the same vibration. The D-band at around 1360 cm$^{-1}$ is associated with vibrations of carbon atoms with dangling bonds in
plane terminations of disordered graphite or glassy carbons. The inverse of the ID/IG intensity ratio between the G- and D- bands is a usual measure of the graphitic ordering and may also indicate the approximate layer size in the hexagonal plane, La [24,25]. In this work, the ID/IG ratio of the MWNTs is about 0.47. The length of nanotubes observed in SEM images is longer than 1 µm, which does not agree with the calculation using the formula L_a = 44(ID/IG)-1. This is consistent with the prior reports by Kang et al. [17].

![Fig. 3 SAD pattern of individual MWNTs.](image)

![Fig. 4 Raman spectrum of the products containing MWNTs.](image)

Here an important question emerged: are the tubelike carbon structures prepared with this method genuine multi-wall nanotubes or just a simple “open graphitic structures”. In botany, vascular bundles are a strand of conducting tissue extending lengthwise through the stems of plants, including ferns, fern allies, gymnosperms, and angiosperms. They have similar tubular structures, and the major compositions are also cellulose, hemicelluloses and lignin. In our experiment, four pieces of evidence are found which may support the result that the products are really MWNTs. First, XRD pattern of the MWNTs indicates that the characteristic peak at 2θ = 25.8° represents graphitic peak corresponding to C of the MWNTs and reveals the crystalline of the MWNTs. Second the high-resolution SEM image shows that the wall-to-wall distance is uniform, 80 nm, can be seen that the vascular bundles are still maintaining tubular structures, while it is nearly impossible for the open graphitic structures to obtain all such perfect structure. Third, the SAD pattern of the tube like carbon structures reveals that the products are single crystalline, which cannot form through a simple “open graphitic structures”. Fourth, the Raman spectrum exhibits no plane termination in the products combined with the straight figure. These evidences further confirm that the products are well-crystalline MWNTs.

During this approach, water is lost, first from that absorbed by the cellulose and then by β-elimination from the cellulose hydroxyls, which makes the tubular structures contract and realizes the formation of C=C double bonds. Simultaneously, the oxygen makes the pyrolytic reactions of the vascular bundles more rapid. The complex chemistry of the C-O-H system is also helpful in the synthesis of MWNTs. Base on these results and theories the formation of MWNTs is not the open graphitic structures.

As shown in Fig. 5, the influence of temperature on the synthesis of MWNTs and MWNTs/ZnO nanocomposites can be clarify briefly. The typical IR spectra of the samples which were obtained by heat treatments at about 400°C, 550°C and 600°C are shown in Fig. 5(a), (b), and (c). Figure 5(c) shows a typical IR spectrum of the finally obtained carbon nanotubes. The peak at 1569.5 cm⁻¹ is associated with the vibration of the carbon skeleton of the carbon nanotubes. The peaks at about 2368.7 and 2337.6 cm⁻¹ correspond to the C=C double bonds stretch vibration, originated from the surface of tubes [26]. The peaks at 1706.6, 1130.2 cm⁻¹ indicate the existence of carboxylic groups on the tubes. The peak at 3867.3 cm⁻¹ corresponds to the stretching vibrations of OH groups. With the increasing of temperature, the peaks corresponding to carboxylic groups became more and more narrow and weak. These results mean that the
carboxylic groups were eliminated step by step, and the cellulose was converted into the carbon skeleton of the carbon nanotubes with the increasing of temperature. From Fig. 5(d) and (e), the IR spectra of MWNTs/ZnO nanocomposites are helpful to understand further the formation of them, which reveal the different surface chemistry of MWNTs and the MWNTs/ZnO nanocomposites. In the high frequency region, the weak peaks around 3516.0~3948.0 cm\(^{-1}\) can be observed, which can be assigned to the stretching vibrations of OH groups. Compared with the IR spectra of MWNTs, the two peaks at 2368.7 and 2337.6 cm\(^{-1}\) became narrower, and the peaks around 1709.8~1060.5 cm\(^{-1}\) are lower in the composite than those of MWNTs. The result suggests that the surface of MWNTs has been covered by ZnO. Furthermore, peaks observed at low frequency region (around 500~700 cm\(^{-1}\)) in MWNTs/ZnO nanocomposites are assigned to the Zn-O. Compared with Fig. 5(d), the peaks are weaker than them in the Fig. 5(e), and it is in agreement with the variation (see Fig. 5(b) and (c)). In addition, most of peaks can’t be observed clearly which may be caused by noise.

![IR spectra of the products](image)

Fig. 5 IR spectra of the products: (a) containing MWNTs in 400\(^\circ\)C, (b) containing MWNTs in 550\(^\circ\)C, (c) containing MWNTs in 600\(^\circ\)C obtained finally; (d) containing MWNTs/ZnO in 550\(^\circ\)C, (e) containing MWNTs/ZnO in 600\(^\circ\)C.

The result of Raman spectrum indicates there are some defects in the walls of MWNTs, which have potential applications in catalysis by using as catalyst supports [27]. Some ZnO particles were just covered on the surface of MWNTs via physical adsorption. At the same time, ZnO particles also can enter the defects in the walls of the MWNTs. In the EDS spectrum of the MWNTs/ZnO nanocomposites, as shown in Fig. 6, the peaks of C, O and Zn are obviously observed. The peak of Cu resulted from the conductive adhesive. It means that the MWNTs/ZnO nanocomposites were pure.

![EDS spectrum of the products](image)

Fig. 6 EDS spectrum of the products containing MWNTs/ZnO nanocomposites.

### Conclusion

In this work, MWNTs and MWNTs/ZnO nanocomposites were synthesized using absorbent cotton and ZnO powders. The MWNTs and MWNTs/ZnO nanocomposites were characterized by XRD, SEM, EDS, SAD, Raman spectrum, and IR. The results indicate that the pure MWNTs were synthesized. The structure of synthesized MWNTs was middle-hollow, with inner and outer diameter of around 10 and 80 nm. The ZnO nanocomposites that had grown on the walls of MWNTs were nonuniform and agglomerated, with an outer diameter of around 110 nm.

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### References


Injector Quantum Dot Molecule Infrared Photodetector: A Concept for Efficient Carrier Injection

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Abstract: Quantum dot infrared photodetectors are expected to be a competitive technology at high operation temperatures in the long and very long wavelength infrared spectral range. Despite the fact that they already achieved notable success, the performance suffers from the thermionic emission of electrons from the quantum dots at elevated temperatures resulting in a decreasing responsivity. In order to provide an efficient carrier injection at high temperatures, quantum dot infrared photodetectors can be separated into two parts: an injection part and a detection part, so that each part can be separately optimized. In order to integrate such functionality into a device, a new class of quantum dot infrared photodetectors using quantum dot molecules will be introduced. In addition to a general discussion simulation results suggest a possibility to realize such a device.

Keywords: Quantum dot infrared photodetector; Injection; Quantum dot molecule; High temperature operation; Responsivity


Introduction

The detection of infrared radiation (3~30 μm) is of great interest for many applications such as astronomy, military, free space optical telecommunications, medicine and gas-detection. Since about four decades HgCdTe (MCT) photo-detectors are dominating the photo-detection in the long wavelength infrared (LWIR) spectral range. The main reason of this large success is the large quantum efficiency due to direct interband transition in a semiconductor bulk material with a long minority carrier lifetime, a high mobility and small effective mass of the electrons. But also the easy tunability of the detection wavelength by the change of the alloy composition within a lattice-matched material system makes MCT detectors perfectly suited for infrared detection. But the demand to fabricate large area focal plane arrays (FPA) pushed this technology to its limits, because an accurate control of the material composition is not trivial for large area devices. This is especially required for FPAs working in the LWIR and very long wavelength infrared (VLWIR) spectral range in order to achieve small values for the noise equivalent temperature difference (NEDT). As MCT detectors show a broad spectral response, the realization of multicolour infrared photodetectors is also not trivial due to spectral cross-talking effects [1,2].

The onset of highly advanced epitaxial growth of III-V materials opened a new chapter for the fabrication of infrared photodetectors. The possibility to grow of semiconductor optoelectronic devices within monolayer accuracy enables the tailoring of electronic properties beyond the restrictions given by nature as in the case of devices based on semiconductor bulk material. Quantum well infrared photodetectors (QWIPs) use intraband transitions to detect infrared radiation. These
transitions can be tailored by the material combination of the heterostructure or by the variation of the quantum well (QW) width. The major advantage of QWIPs is the relatively easy fabrication of homogeneous large area FPAs. The narrow-band response of QWIPs is also an advantage for multicolour applications because cross-talk between the colours can be inherently excluded, in contrast to multicolour MCTs. But nonetheless, MCTs show a better overall performance for operation temperatures above 60~70 K, due to thermionic emission of the quantum-mechanically confined electrons within the quantum wells [2].

A further reduction of the systems dimensionality should in principle reduce the thermionic emission and in contrast to QWIPs absorption of normal incident light is inherently allowed [3]. The first intersubband quantum dot infrared photodetector (QDIP) was demonstrated nearly 15 years ago by Pan et al. [4]. Until today much research effort has been spent on QDIPs in order to achieve a device performance similar to QWIPs but at significantly higher temperatures. Notable success has been achieved in the meantime by several groups [5-11,28]. The most important approach to increase the detectivity, is the introduction of barriers in order to decrease the darkcurrent and/or to place the quantum dots (QDs) inside a quantum well (QW), these are the so called dot in a well (DWELL) structures [14]. The improvement of the detector performance in the case of the DWELL structure can be by part explained by an improvement of the refill mechanism of QDs with electrons, but also by an enhanced extraction efficiency of the photoexcited electrons within bound to bound transitions [9]. Bound to bound transitions are inherently more sensitive to normal incidence light compared to bound continuum transitions, so that the improvement of the photoexcited carrier extraction increases the quantum efficiency [15].

It is well known from experiment that the thermionic emission becomes a significant limiting factor especially in the LWIR and VLWIR-spectral range [7]. The result is that the responsivity decreases with increasing temperature, so that the detectivity is not only declining due to an increasing darkcurrent. Large values for the responsivity are also demanded in order to increase the frame rates in FPAs, so that a strategy must be found in order to preserve a large responsivity also for high operation temperatures [9]. In the following first part of the paper a QDIP-structure will be proposed where the quantum dots (QDs) inside a quantum well (QW), these are the so called dot in a well (DWELL) structures [9,14,28]. The most important approach to increase the detectivity, is the introduction of barriers in order to decrease the darkcurrent and/or to place the quantum dots (QDs) inside a quantum well (QW), these are the so called dot in a well (DWELL) structures [14]. The improvement of the detector performance in the case of the DWELL structure can be by part explained by an improvement of the refill mechanism of QDs with electrons, but also by an enhanced extraction efficiency of the photoexcited electrons within bound to bound transitions [9]. Bound to bound transitions are inherently more sensitive to normal incidence light compared to bound continuum transitions, so that the improvement of the photoexcited carrier extraction increases the quantum efficiency [15].

In a first order approximatiion thermionic emission rate from a QD is proportional to \( \exp[-\varepsilon_{\text{QD}}/k_B T] \), where \( \varepsilon_{\text{QD}} \) denotes the ground state ionization energy, \( k_B \) the Boltzmann constant and \( T \) the temperature in Kelvin [12]. The electron capture by LO-phonon emission is on the other hand limited by the discrete spectrum of the QDs, i.e. the so called phonon bottleneck. As a result, very large values for the photoconductive gain are experimentally reported, i.e. in the range of \( 1 \sim 10^6 \) [13]. The consequence of a low capture probability and an enhanced thermionic emission at elevated temperature results in a QD depopulation [16,39].

As already mentioned in the introduction the electron capture probability can by increased by placing the QD-layer within a QW, i.e. a DWELL structure [9,14,28]. QW-width can be used to tune the final state of the transition and to achieve either bound to bound or bound to continuum transitions [15]. Especially at high temperatures an optimum QW-width must be found due to the trade-off between efficient electron capture and reemission, because with an increasing QW-width the activation energy of electrons in the QD ground-state (GS) becomes smaller, i.e. the onset of the 2D continuum shifts closer to the QD-GS [16], even if the QD-GS shifts to smaller energies with respect to the 3D-continuum of the bulk material [14]. The reemission of carriers from excited states (EXs) can decrease the resistance of the device at high temperatures [13,39].

In order to optimize the electron capture independently of the spectral response and quantum efficiency of the detector, the QDIP structure can be split into two parts, an injection part and a detection part. In principle the structure consists of a pair of stacked QDs. Figure 1(a) depicts the conduction band profile of such a configuration for a cut through the QD-centre along the growth direction. The heights of the QDs are denoted with \( h_1 \) and \( h_2 \), measured from the bottom of the wetting-layer WL to the tip of each respective QD.

In the injection part of the structure (injector-DWELL, blue box) a QW with the width \( d_1 \) (see Fig. 1(b) QW1) is placed below the QD-layer (QD1). This QW ensures that electrons are efficiently captured by the injector-DWELL. Barrier B covers the WL of the QD1-layer (WL1) and supports the capture of darkcurrent electrons [26].

The LWIR detection part of the structure is constituted by the detector-DWELL (as shown in Fig. 1, red-box). The two-dimensional (2D) system of the injection-DWELL, i.e. QW1 followed by WL1, is spatially separated from the detector part of the structure by a distance D in order to avoid carrier injection into the 2D-system of the detector-DWELL, i.e. the layers WL2 and QW2. An injection into QW2 would unnecessarily increase the darkcurrent, because thermal emission from 2D systems is very efficient due to the continuous density of states [16]. The close presence of a large 2D-carrier density can also enhance Auger-like
scattering mechanisms [18] and this can additionally increase the emission of electrons in the detector-DWELL from the bound states to the continuum.

The activation energy $\varepsilon_{QD1}$ of the QD ground state of the DWELL-injector should be larger than that of the DWELL-detector $\varepsilon_{QD2}$ in order to suppress thermionic emission. The capture efficiency of the DWELL-injector can be optimized with an appropriate choice of the width $d_1$ of QW1. The width $d_2$ of QW2 should be as small as possible in order to avoid thermionic emission of confined carriers in QD2 and QW2 should only be used to maximize the spectral response of the detector [9,15]. Further, the spectral response of the detector-DWELL can be designed by the variation of the GS activation energy $\varepsilon_{QD2}$.

The key-functionality of the structure is that electrons are first captured by QW1. Some of the captured electrons further relax into the QD1-layer. Due to the proximity of the QD1- and QD2-layer in the order of 1-3 nm, electrons can be injected well localized from the QD1- into the QD2-layer via resonant tunnelling or non-resonant tunnelling.

Resonant tunnelling is only possible in special cases where the energy levels between the electron tunnels perfectly coincide [34]. But in general, due to slight detunings, e.g. anti-crossing, resonant tunnelling can also be connected with acoustic phonon scattering [23,34]. Consequently, resonant tunnelling injection becomes more the exception than the rule for efficient electron injection into the detector-DWELL. Nonetheless resonant tunnelling is very fast, i.e. in the range of some tens of ps [24], when the involved states coincide energetically within a few meV [34].

Reischle et al. [24] found that non-resonant tunnelling rates increase exponentially with decreasing QD spacing and that tunnelling times are in the range of 500 ps for a barrier thickness of 3 nm. For very small inter-dot layer spacing an offset of 425 ps was observed, most probably due to Pauli blocking. These values must be seen as an upper limit, because they have been evaluated at 4 K and multi-phonon processes become more important at higher temperatures [31].

The electron capture by the injector-DWELL must be fast compared with the electron tunnelling from QD1- to the QD2-layer in order to achieve large injection efficiency. Carrier capture times in conventional QDIPs can reach values in the range of 1 ns [13,38], i.e. QDIPs without QWs. As already mentioned in the outline the introduction of QWs in QDIP-devices can increase the carrier capture rate significantly [9].

The electron capture time for a DWELL-configuration is in the range of 100 ps for a temperature of 200 K [28], i.e. it is shorter than the electron tunnelling time from the QD1- to the QD2-layer. QWELLs are also already successfully in use for injection interband QD-lasers with carrier relaxation times typically in the range of a few tens of ps [40]. In QDIPs this relaxation time is longer due to their unipolar nature and the smaller electron density in the devices, so that Auger-cooling does not happen [32] and the Auger-assisted tunnelling would be weak [18].

Another important design restriction for the proposed device is that the electron emission time from QD2 to the continuum should be smaller than the tunnelling time. This is necessary in order to ensure that the QD layer becomes permanently populated by electrons. The electron emission time at 200 K is in the range of some hundred ps [31], i.e. the same order of magnitude as the low temperature non-resonant tunnelling time mentioned before. This means that an efficient electron injection from the QD1- to the

Fig. 1 In order to optimize carrier capture and the spectral response of the quantum dot infrared detector independently, the quantum dot infrared photodetector can be divided in an injector (blue box) and detector part (red box). Each part is realized as a dot in a well (DWELL)-structure: (a) the top draft shows a cut through a couple of stacked quantum dots (QDs). In general the QDs have a different height $h_1$ and $h_2$. The activation energies $\varepsilon_{QD1}$ and $\varepsilon_{QD2}$ are defined as the energy difference between the QD-groundstate and the conduction band edge of the barrier-material. (b) the drawing on the bottom depicts a cut through the structure at a position without QDs. The quantum well QW1 with the corresponding width $d_1$ ensures an efficient electron capture of the DWELL-injector. The barrier B covers the wetting layer WL1 of the quantum dot layer QD1 in order to increase the electron capture efficiency of the injector. QW1 is clearly separated from the DWELL-detector by a distance denoted with $D$ in order to prevent an injection of electrons from the QW1 into QW2 with the width $d_2$. 

The electron capture by the injector-DWELL must be fast compared with the electron tunnelling from QD1- to the QD2-layer in order to achieve large injection efficiency. Carrier capture times in conventional QDIPs can reach values in the range of 1 ns [13,38], i.e. QDIPs without QWs. As already mentioned in the outline the introduction of QWs in QDIP-devices can increase the carrier capture rate significantly [9].
QD2-layer is principally possible, because the phonon-assisted inter-dot tunnelling rate increases with temperature. Small quantum dots have a larger capture time and as well as smaller emission efficiency [13]. This offers a possibility to balance the ratio between the QD1- to QD2-layer tunnelling time and QD2 bound to continuum electron emission time.

Under unbiased conditions, the Fermi-level of the structure is determined by the doping of the injector-DWELL. Since the activation energy $\varepsilon_{\text{QD1}}$ of the injector-DWELL is larger as the activation energy $\varepsilon_{\text{QD2}}$ of the detector-DWELL, the thermionic emission becomes roughly reduced by the factor $\exp[-(\varepsilon_{\text{QD1}} - \varepsilon_{\text{QD2}})/k_B T]$ compared to the case of a conventional doped LWIR-DWELL detector.

Under biased conditions QW1 and B supply the QD1-layer with electrons in addition to the doping. As a consequence the Fermi-level increases as a function of bias at low temperatures. At temperatures above 130 K thermionic emission becomes significant due to multi-phonon-absorption [31]. Without the capture of additional electrons, i.e. without applied bias voltage, the QD1-layer would empty at temperatures above 200 K [16].

The role of carrier capture by QW1 and the barrier B is to ensure a population of the injector-DWELL energy states at high temperatures, preferentially of the s- and p-states. Under such a situation the back-relaxation from the QD2- to QD1-layer becomes suppressed by Pauli-blocking [24].

It must also be noted that the density of states (DOS) below the steady state Fermi-level (if the Fermi-level is deeper than the GS of the detector-DWELL) is increased compared to the case of a conventional QDIP-device, i.e. the injector-DWELL acts as an efficient electron reservoir. The optimum doping for QDIPs was found to be in the range of one to two electrons per QD [30]. The doping of QDIPs is in principle also limited by the small DOS of the QD-GS. The proposed device can in principle circumvent this limitation.

In principle the stacked QDs can be denoted as a quantum dot molecule (QDM) [18]. In order to simplify the discussion in the following, the proposed structure will be denoted as injection quantum dot molecule infrared photodetector (IQMIP).

Device simulation

In the following study a possible realization of an IQMIP-device will be presented in the (In,Ga)As/(Al,Ga)As/(In,Al)As material system. It is not the aim of the paper to analyze the electronic structure in detail, rather than to propose a general concept in order to improve the operation temperature of QDIPs. More information about QDMs can be found elsewhere [18-25].

The device simulation was performed with the free software NEXTNANO [29] by the use of the 8-band kp-method implemented in a 3D grid with a spatial resolution of 0.25 nm. The material parameters have been taken from Vurgaftman et al. [17]. The QDs have been modelled by truncated pyramids with a lateral size of 18 nm and a height of 6 nm.

The left part of Fig. 2 shows a detailed scheme of the structure, whereas on the right side the conduction band structure can be seen once for a cut through the wetting WL and once through the stacked QDs.

The barrier material consists of Al$_0$$_{15}$Ga$_0$$_{85}$As. This material was chosen in order to improve the GaAs-QWs offer a stronger confinement. In the injector-DWELL a 5 nm thin GaAs-QW (QW1) is placed below the QD1-layer. The WL of the QD1-layer is covered by a 1 nm thin Al$_{0.42}$Ga$_{0.58}$As-layer [26].

The fabrication of asymmetric QDMs was already successfully demonstrated by Bracker et al. [35], where the “indium flush” method has been applied [36], i.e. the quantum dots are only partially capped after growth with a subsequent annealing step before they are then completely capped. This technique enables to engineer the height of the quantum dots. The energetic configuration of the QDM can be designed by the height of the QDs. But within the calculations it turned out that with this approach the energetic spacing between the two GS energies was limited when realistic quantum dot heights had been used. Therefore a modified approach has employed where the QDs are realized by different alloy compositions [33], i.e. the QD1-layer is realized by Al$_{0.03}$In$_{0.97}$As and the QD2-layer by In$_{0.5}$Ga$_{0.5}$As. The small migration rate of Al adatoms should force the formation of small QDs with a large density, increasing the quantum efficiency [27]. The reason not to use AlInAs QDs for the QD2-layer was that the composition of InGaAs-QDs is easier to control. QW2 is composed of GaAs and its thickness can be used in order optimize the quantum efficiency and the responsivity independently of the carrier injection [15].

Figure 3 shows the result of a simulation performed by the use of the 8-band kp-method. The strain-distribution in the structure was taken into account by the minimization of the elastic energy. The influence of the strain on the conduction band as well as piezoelectric effects has been fully included.

Depending on the spatial dominance of the wavefunction the confined states can be assigned either to the injector- or the detector-DWELL. The energy difference between the two GSs $\varepsilon_{\text{QD1}} - \varepsilon_{\text{QD2}}$ is 73 meV, i.e. slightly larger than twice the LO-phonon energy of InAs-QDs [32], so that the application of a bias voltage can bring the GS of the injector-DWELL into a two-LO-phonon
resonance with that of the detector-DWELL. In a QD-system the LO-phonon energy is not fixed at a single distinct value, i.e. different LO-phonon energies are possible: from the barriers, the WL, the QDs, and their respective facets. But also the broadening of phonons, due to strain and inhomogeneities can potentially enlarge the energetic window of two phonon assisted tunnelling [32].

At temperatures above 130 K electron injection into the detector-DWELL should mainly occur also non-resonantly via EXs [24]. But a closer look to the results (see Fig. 3a) of the simulations offers an interesting feature of the structure: the p-state of QD2 hybridizes into bonding (p2-b) and anti-bonding states (p2-a) [20,21,38]. The corresponding energetic splitting of the states is only in the range of 2~3 meV, i.e. a carrier transfer between the QD1- and QD2-layer can occur by absorption of two to three acoustical phonons. The wavefunctions of the p2-b and p2-a states are shown in Fig. 4. It is interesting to see that the p2-a state is also significantly localized in the QD1-layer, but for the electron to become localized primarily in the QD2-layer a transition to the p2-b by phonon-scattering would be necessary. The probability of such a transition increases with temperature. In principle it does not make a large difference if the electrons are injected into the GS or the p-state, because once the electrons are injected into higher EXs of QD2 the electrons can further relax towards ground-state within a relatively short time-range of 30~60 ps [41].

If an electric field is applied to the structure the electron injection from the QD1- to the QD2-layer becomes additionally supported and as mentioned before, if the electron capture of the injector-DWELL works, efficient Pauli blocking prevents the back-scattering of electrons from the detector- to the injector-DWELL.

The p-states of the injector are 26 meV below the GS of the detector-DWELL, i.e. the density of states below the GS of the detector-DWELL is eight. This means that the electron-reservoir is significantly increased compared with the case of simple QDIP-devices.

The transition energy between the GS of the detector-DWELL and the quasicontinuum, i.e. the WL-states (see Fig. 3a, green line) is around 120~170 meV. The thermal activation of photoexcited electrons from the 2D-continuum of the WL to the continuum is very efficient at high temperatures [16,30].
It is clear that the absorption spectrum of the injector-DWELL superimposes with the spectrum of the detector-DWELL. In order to realize multicolour-devices the spectrum must be optimized in order to minimize cross-talk effects. This can maybe be achieved with of the spectral dependence of the device on the bias voltage.

The inhomogeneous size distribution of the self-assembled QDs can be a limiting factor for some concepts presented within this paper. Different approaches are in use in order to decrease the size distribution of the QDs, e.g. the Indium flush method [21,36]. The use of this technique allows engineering the height of the QDs, but the size distribution of the lateral dimension stays unaffected. Consequently a different solution must be found in order to limit the influence of the lateral QD dimension variation. Stacking of QD is connected with a strong correlation via strain between the seeding QD-layer and the stacked QD layer [37]. This correlation is supposed to drive the size ratio between stacked QDs. Such a correlation reduces the influence of the inhomogeneous size distribution of self-assembled QD on the relative spacing between the GS of QD1 and QD2. In order to investigate this assumption, the lateral size of the both QDs was reduced from 18 to 15 nm. The height was held constant due to the possibility to engineer it by the indium flush method. Figure 5 shows the result of this simulation. It can be seen that the energy difference between the s- and p-shell of the respective QDs is in the range of 1.2-1.7 meV.

Fig. 5 Simulations with different lateral quantum dot (QD) dimension have been performed in order to investigate the influence of an inhomogeneous size distribution, i.e. for 18 and 15 nm. The height of the QDs was kept at 6 nm for both simulation-runs, due to the possibility to employ the Indium-flush technique in order to achieve these dimensions. It can be seen that the energy difference between the s- and p-shell of the respective QDs is in the range of 1.2-1.7 meV.

Conclusion

In order to improve the operation temperature of a QDIP the device functionality can be separated in an injection and detection part. The electron injection can be realized by a QDM consisting of a double DWELL-structure. The GS of the injection DWELL is designed to be lower in energy than that of the detection-QWELL. This offers the possibility to inject carriers with the assistance of phonons into the detector-DWELL. The direct consequence of this design is that the static Fermi-level can be reduced in the active region compared to conventional doped LWIR-QDIPs. An optimal design of the detector-QWELL should also minimize the reemission of electrons in order to maintain large values for the responsivity also at
elevated temperatures.

As a proof of principle, a possible example to realize an IQMIP-device was presented in the InAlAs/InGaAs/GaAs material system. Different possible injection paths have been identified, i.e. resonant 2-LO phonon assisted injection between the GSs, acoustical phonon assisted tunnelling via the bonding and antibonding p-states of QD2, but also non-resonant tunnelling via EXs in general. Further, design restrictions have been roughly sketched, i.e. the electron capture time of the injector-DWELL should be faster than the tunnelling time between the QD1 and QD2-layer in order for efficient injection to occur. Additionally, the tunnelling time should be faster than the thermal emission time of electrons from the QD2-layer to the continuum. In principle, thermionic emission can be prevented by the use of small QDs, but also here a compromise must be found, because the reduction of the QD size reduces also the activation energy.

Optimal parameters and modification in the design must be found in a thorough experimental study, i.e. the non-resonant and resonant injection should be studied first as a function of temperature, and the energy difference between the GS of the injector- and the detector-DWELL.

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Fabrication and Optical Properties of Silicon Nanowires Arrays by Electroless Ag-catalyzed Etching

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Abstract: In order to realize ultralow surface reflectance and broadband antireflection effects which common pyramidal textures and antireflection coatings can’t achieve in photovoltaic industry, we used low-cost and easy-made Ag-catalyzed etching techniques to synthesize silicon nanowires (SiNWs) arrays on the substrate of single-crystalline silicon. The dense vertically-aligned Si NWs arrays are fabricated by local oxidation and selective dissolution of Si in etching solution containing Ag catalyst. The Si NWs arrays with 3 µm in depth make reflectance reduce to less than 3% in the range of 400 to 1000 nm while reflectance gradually reached the optimum value with the increasing of etching time. The antireflection of Si NWs arrays are based on index-graded mechanism: Si NWs arrays on a subwavelength scale strongly scatter incident light and have graded refractive index that enhance the incidence of light in usable wavelength range. However, surface recombination of Si NWs arrays are deteriorated due to numerous dangling bonds and residual Ag particles.

Keywords: Si nanowires; Ag-catalyzed etching; Broadband antireflection; Surface recombination

Introduction

As a promising candidate for conventional fossil energy, high-efficiency and low-cost silicon photovoltaic devices still meet some challenges such as non-abundant utilization of solar spectrum [1] and various carrier recombination [2] in spite of rapid development over the past few decades. In order to improve the performances of photovoltaic devices, novel ideas and advanced technologies should be applied to present devices. Considering of fast progress in the field of nanotechnology, low dimensional silicon nanostructures with tunable opto-electronic properties have great potential in photovoltaic conversion. For example, silicon nanowires (Si NWs) arrays have been proven to enhance optical absorption [3] and their radial pn junction where solar cells offer efficient carrier collection [4]. Compared with common pyramids and antireflection coatings on single-crystalline silicon solar cells, density-graded porous Si NWs arrays with subwavelength pattern exhibit broadband antireflection effects [5]. Similar to other subwavelength structures (SWS) such as moth eye [6] and surface-relief grating [7], Si NWs arrays have gradient refractive index (RI) and its antireflection is based on optical-constant gradient mechanism [8]. As most practical photovoltaic modules use c-Si materials with limited spectrum, optimized reflectance of Si NWs arrays help promote their output power. Up to now, main fabrication techniques of Si NWs arrays include bottom up approach by solution processing, physical or chemical vapour deposition and top down approach by dry or wet etching [9]. In particular, electroless Ag-catalyzed etching (EAE) which uses HF solution containing Ag particles to selectively etch silicon surface...
Experimental details

The typical fabrication of Si NWs arrays on Si substrates includes four steps: I) the commercial p-type (100) CZ-Si wafers with resistivity of ~1.5 Ω·cm and thickness of 200 µm were cut into 2×2 cm² squares, and then they were dipped into 1:8 HF/HNO₃ solution for 2 minutes at room temperature to remove surface sawdamage and rinsed with deionized water thoroughly; II) Ag-particles catalyst layers were plated on the cleaned surfaces by immersing the Si substrates into the mixture of 4.6 M HF and 0.01 M AgNO₃ aqueous solution at 30° for 1 minutes; III) the Si pieces wrapped by Ag thin films were etched with aqueous solutions of 4.6 M HF and 0.02 M H₂O₂ at 30° for different etching times; iv) the samples were successively immersed into diluted HNO₃ to remove residual Ag, rinsed with deionized water and dried by blowing N₂. All chemicals were analytical reagent grade and the resistivity of deionized water was 18.2 MΩ·cm.

A FEI QUANTA 250 FEG field emission scanning electron microscope (SEM) and JEM 2010F transmission electron microscope (TEM) were used to observe the surface and cross-sectional morphologies of Si NWs arrays on Si wafers as well as the morphology of a single nanowire. A TU 1901 UV-VIS spectrophotometer with an integrating sphere was used to measure the reflectance of Si NWs arrays in order to determine their broadband antireflection effect. A WT-2000 minority carrier lifetime tester with microwave photoconductivity decay technology (MW-PCD) was employed to characterize surface recombination of the samples.

Results and discussion

Figure 1 shows the SEM images of Ag-particles layers plated on the surface of Si wafers as above mentioned step II. The Ag film consists of white and bright denticles which lie loosely upon the substrates (see Fig. 1(a)). The thickness of the film is about 1.2 µm according to the cross-sectional image shown in Fig. 1(b). The high-magnified image (see Fig. 1(c)) indicates that there formed interconnected network which composed of Ag patches. When the etching process of H₂O₂ and HF in step III is skipped, the morphology after removing Ag residuals was shown in Fig. 1(d), where the pits and hills are randomly scattered. As discussed by Ogata [14], the plating of Ag catalysts in etching solution was a galvanic procedure in which the Ag ions input holes into the valence band of the Si wafer due to the difference of Fermi levels of these two substances and the reduced Ag particles formed nuclei in micro- or nanorange on the surface of the substrate. The Ag nuclei subsequently connected together and made up the dendrite-like structures on the networks. Such distribution of Ag catalysts leads to the appearance of uneven plane whose formation will be indicated in details later. The AgNO₃ and HF solution in step II mainly plays a role in plating Ag process but the etching speed is very slow. As a result, the H₂O₂ and HF etching was employed after Ag catalysts were plated.

The surface and cross-sectional morphology of the sample etched as step III for 10 minutes are shown in Fig. 2(a) and (b). The textured surface is composed of dense one-dimensional nanowires that have bright contrast with substrate and are uniformly spaced by pits among them. The depth of the Si NWs arrays and diameters of pits are separately about 500 nm and 200-500 nm. Almost all nanowires are vertical to substrate in the direction of (100) and few nanowires collapse because of failure to support their weight. The depth of the Si NWs arrays increases with the increasing of etching time. For example, Si NWs arrays etched for one hour have the thickness of 3 µm (see Fig. 2(c)). As revealed in the TEM image of a single nanowire (Fig. 2(d)), the width of the nanowire is about 200 nm and one end of the nanowire are a little bigger than the other end.

Although up to now the mechanism of Ag-catalyzed etching procedure is still unproven by experiments in details, the evolution and fabrication of Si NWs arrays can be deduced according to the growth theory proposed by Peng [15].

While the Ag nuclei on nanoscales was plated on the surface of Si substrate in etching solution, the holes input to valence band of Si by previous Ag ions help oxidize Si surfaces underneath the Ag nuclei. The silicon oxide formed in the process of local oxidation was immediately dissolved in the solution owing to HF etching and this leaded to the appearance of pits or pores which the Ag particles entered. The schematic diagram of the whole etching process is indicated as Fig. 3 and...
the overall reaction was under way as follow: $4\text{Ag}^+ + \text{Si} + 6\text{F}^- \rightarrow 4\text{Ag} + \text{SiF}_6^{2-}$. Owing to the unique preferential catalyzation of the Ag catalyst at the bottom of the Ag/Si interface, longitudinal etching perpendicular to the surface was much faster than the lateral etching parallel to the surface. As a result, the Ag-catalyzed etching selectively proceeded along the crystallographic orientation of the surface and the arrangement pattern of the Ag catalyst on the surface of Si decided on the porosity and dimension of the Si NWs arrays.

As we all know, coarse surfaces shine less than flat ones and nanostructured surfaces with high roughness often appear black which indicates low reflectance. Our samples textured with Si NWs arrays have completely black surfaces and reflectance measurements are given in Fig. 4. For the sample that was etched without HF and $\text{H}_2\text{O}_2$, the reflectance is generally more than 25% in the whole band and is especially high in short-
wavelength range. The effectless antireflection is attributed to low surface roughness since pits are shallow as shown in Fig. 1(d). In addition, the high reflectance in short-wavelength range is because refractive index of Si substrate is higher in this range than the average value.

For the 3 µm deep Si NWs array etched for one hour by HF and H$_2$O$_2$, the reflectance curve tends to be plane and its values are no more than 3% from 400 nm to 1000 nm. Such excellent antireflection effects are based on the interaction between incident light and the Si NWs arrays (Fig. 5). The diameters and spacing of Si NWs are smaller than the wavelength of incident visible light, so the diffuse scattering of incident light is strong. Light propagates along a curved path in the inhomogeneous mixtures of Si substrates and air on a subwavelength scale. According to effective medium theory (EMT) first proposed by Garnett [16], the Si NWs arrays can be approximated to multilayer “effective medium” (EM) and the effective refractive index (RI) of EM increases with decreasing of volume fraction of the materials. Thus, the RI of the Si NWs arrays gradually increases from 1 at the top near the air to about 3.5 at the bottom near the Si substrates. Such materials with gradient-index reduce surface reflection to an ultra-low level because an interface between any two adjacent EM with matching RI almost doesn’t shine. Whether light incident on the surfaces of Si NWs arrays is short-wavelength or long-wavelength, their RI profile is always graded. Therefore, ultra-low surface reflectance and broadband antireflection effect are accomplished by index-graded Si NWs arrays on subwavelength scale. The weighted average reflectance $R_w$ which considers solar spectrum from 400 nm to 1000 nm is calculated to be 2.8% according to the definition $R_w = \int F(\lambda)R(\lambda)d\lambda$ where $F(\lambda)$ is incident photon flux.

With the increasing of etching time of HF and H$_2$O$_2$ in step iii, the reflectance is firstly suppressed in short-wavelength range for shallow texture like the sample etched for 5 minutes and then suppressed in long-wavelength range for deep texture like the sample etched for 10 minutes. In the light of the graded-density surface texture model provided by Stephens [17], the reflectance of index-graded textures on subwavelength scale depends on the ratio of $d$ (depth of textures) and $\lambda$ (incident wavelength) and the exponential relationship was given as $R(d, \lambda) = R_0(\lambda)\exp[-C(d/\lambda)]$ where $R_0(\lambda)$ is the reflectance of flat surface and $C$ is a constant. For the texture like the sample etched for 5 minutes, its depth is much smaller than 500 nm considering of monotonic increasing relationship between depth and etching time. Thus, $d/\lambda$ in short-wavelength range is larger than in long-wavelength range and the former in the reflectance spectra decreased faster than the latter. The depth of the texture etched for 10 minutes is...
about 500 nm as shown in Fig. 2(b), so the reflectance in long-wavelength range rapidly decreased due to the rise of d/λ. The possible physical reason for different reflectance trends of index-graded textures in different range is that shallow texture only scatters short-wavelength light effectively and deep texture simultaneously scatters both short- and long-wavelength light.

In spite of good antireflection properties, the Si NWs arrays by Ag-catalyzed etching are extremely rough and this must facilitate surface recombination. Therefore, we measured the effective lifetime (τeff) of the samples by means of MW-PCD technique to investigate influence of etching on surface recombination and the results are displayed in Tab. 1. According to MW-PCD principles [18], τeff is related to bulk lifetime (τb) and surface recombination velocity (SR) of the samples. Ag-catalyzed etching processes only change surface conditions and have no effect on τb, so τeff solely depends on SR. As seen from Tab. 1, τeff decreases with the increasing of etching time and this means that SR increases with the increasing of the depths of textures. The deterioration of surface recombination is attributed to two possible reasons: enormous dangling bonds that continuously increased during etching and residual silver that is a deep-level impurity. They create many recombination centers in the forbidden band near the surface and cause serious surface recombination.

### Table 1 The minority carrier lifetime of the samples etched by HF and H2O2 for different times.

<table>
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<tr>
<th>Etching time (min)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>60</th>
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</thead>
<tbody>
<tr>
<td>τeff (µs)</td>
<td>1.577</td>
<td>1.538</td>
<td>1.471</td>
<td>1.259</td>
</tr>
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</table>

Obviously, serious surface recombination of Si NWs arrays will compensate for optimal antireflection if Si NWs are applied to replace pyramids and used as textures on conventional C-Si solar cells. Therefore, the key to reach high efficiency for Si NWs-textured solar cells will be compromised between surface antireflection and recombination. Furthermore, good passivation of Si NWs arrays textures is essential to reach high efficiency.

### Conclusion

Si NWs arrays were produced by Ag-catalyzed etching techniques on single crystalline Si substrates. The Ag particle film plated on the Si substrates is made up of dendrites-like structures and its arrangement causes the appearance of the pits and nanowires. The ultralow reflectance below 3% and broadband antireflection effect from 400 to 1000 nm are realized. The excellent antireflection properties are attributed to index-graded profiles of the Si NWs arrays on subwavelength scales and suppression of reflection for different wavelength range depends on the ratio of textures depths and incident wavelength. However, surface recombination of Si NWs arrays deteriorates due to numerous dangling bonds and residual Ag particles.

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Nanoimprint Lithography: A Processing Technique for Nanofabrication Advancement

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Abstract: Nanoimprint lithography (NIL) is an emerging micro/nano-patterning technique, which is a high-resolution, high-throughput and yet simple fabrication process. According to International Technology Roadmap for Semiconductor (ITRS), NIL has emerged as the next generation lithography candidate for the 22 nm and 16 nm technological nodes. In this paper, we present an overview of nanoimprint lithography. The classification, research focus, critical issues, and the future of nanoimprint lithography are intensively elaborated.

A pattern as small as 2.4 nm has been demonstrated. Full-wafer nanoimprint lithography has been completed on a 12-inch wafer. Recently, 12.5 nm pattern resolution through soft molecular scale nanoimprint lithography has been achieved by EV Group, a leading nanoimprint lithography technology supplier.

Keywords: Nanoimprint lithography; Soft molecular scale; Nanofabrication


Introduction

Nanofabrication, as one of the key domains of nanotechnology, has received intensive attention in the scientific community. There are three approaches to nanofabrication: top-down, bottom-up and their hybrid approach. Top-down approach is referred to fabrication of smaller devices by using larger ones to direct their assembly, which has been developed based on the conventional IC fabrication process. Bottom-up process is to apply smaller components into more complex assemblies. More importantly, combined top-down with bottom-up is usually applied in nanofabrication.

Nanoimprint lithography (NIL), invented by Stephen Chou et al., has been regarded as a possible alternative to optical lithography due to its low cost, high throughput and high resolution [1-8]. Since its invention, lots of research has been conducted in order to further develop NIL as a technology. To date, thermal embossing, laser-assisted, step and flash and UV nanoimprint lithography have been incorporated into the field of NIL. Since 2003, nanoimprint lithography has been accepted by International Technology Roadmap for Semiconductor (ITRS) as the next generation lithography candidate, and now has been added to 22 nm and 16 nm nodes. The resolution of nanopattern by nanoimprint lithography could reach sub-5 nm [9].

In this paper, we will elucidate fundamental theory and discuss some critical issues in nanoimprint lithography. Important research achievements are also presented in this review paper.

Classification of nanoimprint lithography

A schematic of the process of nanoimprint lithography is shown in Fig. 1. First, the substrate is coated with the polymer layer or functional layer, and the mold is pressed onto the polymer layer. After curing the polymer, the imprint mold is released from the layer. As a result, micro/nano patterns are transferred onto the layer. Usually, the patterns on the layer are etched by reactive ion etching process.
Fig. 1 Schematic illustrations for hot embossing and UV-nanoimprint lithography.

The main nanoimprint lithography technology is based on hot embossing lithography, UV-lithography and soft lithography. Depends on the kind of mold used, hard nanoimprint lithography and soft nanoimprint lithography are defined accordingly. SiO$_2$, Ni, Si, Si$_3$N$_4$, SiC molds are usually used for hard nanoimprint lithography. Polymer materials, such as PDMS, PMMA, PUA, PVA, PVC, PTFE, ETFE, are main the components for the fabrication of soft molds. Depends on the curing approach to the spin-coated polymer, we have the differentiation into hot embossing lithography, UV nanoimprint lithography and hot-UV nanoimprint lithography. Based on the imprinted area, the full-wafer nanoimprint lithography and step-and-repeat nanoimprint lithography are defined. Roll-to-roll nanoimprint lithography process is suitable for mass fabrication, and has application in the state-of-the-art flexible nanodevices. The classification of nanoimprint lithography is indicated in Fig. 2. The details of the process could be obtained from the relevant literature.

Research field of nanoimprint lithography

Nanoimprint lithography technology encompasses the integration of subject areas including electronic engineering, machine engineering, control engineering, materials, physics and chemistry. Research and development on novel methods, process controlling, fabrication of equipment, as well as devices and system is therefore becoming more and more important. The goal is to develop fabrication equipment and process, resulting in low cost, high efficiency and superior quality of the product. In the development of nanoimprint lithography, the basic processes and applications are highlighted. The basic processes include mold fabrication, the functional materials (imprint resists and transferred layer), controlling and optimization of imprint process and the development of imprint machine. The application fields of nanoimprint lithography are in electronic devices (high density memory), photoelectric devices (solar cells, light emitting diodes), optical components (polarizers, lasers, TFT-LCD, plasma sensors) and biological fields (biochips and microfluidic devices) [10-17]. The whole framework of nanoimprint lithography is outlined and shown in Fig. 3.

Critical issues in nanoimprint lithography

Nanoimprint lithography process can be divided into three steps: (1) mold fabrication and treatment, (2) imprint process, (3) subsequent etching (if required). The processes involved are mold fabrication, photore sist, process control and high-quality etching. To obtain small uniform nanopatterns, any process control in nanoimprint lithography is critical and become a series of related key technologies.

Mold

Mold is a functional unit for nanoimprint lithography. The fabrication of mold (hard or soft mold) and mold treatment are the key technologies are the prerequisite for the success of nanoimprint lithography. Imprint mold (stamp, template) material used in hot nanoimprint lithography has high hardness, compression strength, tensile strength, low thermal expansion coefficient, good corrosion resistance and other properties, to ensure that the template can wear, deformation, maintain an accuracy and have longer life. Silicon, quartz, silicon nitride, and diamond can be selected as molds for nanoimprint lithography, and the soft polymer (e.g., PDMS) is suitable for large area imprint lithography.

Usually, the nano-structure mold is fabricated by
Before exposure, the substrate is spin-coated with a layer of electron sensitive resist, followed by exposure and development, resulting in the formation of nanostructures on the photoresist film. The patterns on the resist are transferred onto the substrate, and there are mainly two technical approaches, one is carried out by reactive ion etching, the other is the combination of lift-off process and reactive ion etching, as shown in Fig. 4.

Figure 6 shows a micrograph of the replicated soft mold. Its nanopillar arrays composed of h-PDMS were formed on the PDMS surface and the diameter is ~80 nm, which is consistent with the pitch of the AAO master (not shown here). The resulting patterns were shown in the SEM image of Fig. 6.

The replication based on AAO master offer a simple and an alternative to soft mold. The replication process and technology can also applied in other replication processes.

During nanoimprint lithography process, the template is contacted on the surface of the photoresist. Therefore, the adhesion between the template and the photoresist is a critical element. If adhesion is too strong, the pattern will result in defects, and also contaminates the mold and decrease the lifetime. The strength of adhesion between the photoresist and the nano-imprint template can be determined by their surface: low surface energy will determine the ease for electron beam lithography.
for separation. Anti-adhesive treatment is necessary to decrease the risk of defect. In our research [21], a self-assembled monolayer (SAM) of 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane (FDTS) is formed by vapor phase instead of liquid phase to decrease the surface energy. Our developed method of anti-adhesive mold is simple and can obtain nanopatterns over large area.

**Resist**

Photoresist used in nanoimprint lithography is different from the conventional optical lithography of the photoresist. The resist has the following properties: inherent properties of the resist (with a good substrate adhesion, low shrinkage, low viscosity), coating properties (controllable thickness in the 50~500 nm, smooth surface, surface roughness is less than 5 nm) and good resistance to etching (at least 1:3 etch selectivity, relative to Si or SiO$_2$) [22-25].

**Defect**

In nano-imprint process, due to the environment, materials, or processes, for example, air bubbles, the mold deformation, uneven coating, unparallel between the substrate and the mold, and so on, will produce a variety of defects [26-27]. How to control and avoid the emergence of various defects in imprint lithography and improve the quality of imprint pattern is therefore key issues.

**Overlayer**

As the performance of electronic devices increases, the use of integrated chips becomes mandatory. If nanoimprint lithography is adopted in the IC product line, the use of the overlayer technology must be resolved. Currently, the overlay process is aimed at the field of nano-imprint, which is the most difficult and important issue. The application of Moiré fringe alignment method can obtain higher alignment accuracy, which can reach a precision of 20 nm [28].

**3D pattern**

Three-dimensional (3D) structure in the microsystem field has a very important prospect. Small structure, light weight, high sensitivity, low cost and superior performance of the device can be fabricated by 3D fabrication technology. It has greatly promoted the development of the product miniaturization and portability, increasing the device and the function of the system density, information density and interconnection density, and more importantly, it can greatly save materials and energy.

A unique benefit of nanoimprint lithography is the ability to pattern 3D structures. Multi-layer interconnect structure fabricated by nanoimprint lithography, its unique physical transfer process can not only reduce costs, with high resolution, but significantly reduce the number of processing steps in the formation of complex
three-dimensional structures [29].

The future of nanoimprint lithography

Since the publication of the first imprint article in 1995 by Stephen Chou, the number of research papers published has grown tremendously, as shown in Fig. 7. From a few papers per year in the late nineties, it is now increased to about 400 per year.

In Fig. 8, we list the distribution of published NIL papers on various countries, including the United States, Japan and South Korea, the top three ranked nations for published literature. It is noted that the United States has published more than 660 articles in the subject area of NIL.

NIL is a simple, low-cost nanofabrication technique. It has been widely used in biomedical devices, high-density storage, photonic crystals, polymer electronics, solar cells, sensors and high-precision printed circuit board production. For NIL to be used effectively for industrial applications, the issue of efficiency, cost, and quality must be addressed. For example, the fabrication of nanoimprint molds is largely dependent on other lithography techniques, which makes it a lingering barrier for nano-patterning. In some sense, nanoimprint lithography is still an infant. A lot more work has to be done in order to make NIL fully blossom in wider industrial application.

Conclusion

Nanoimprint lithography involves the mechanical replicas of patterns, which is neither limited by diffraction, scattering effects nor secondary electrons. It is a very promising technology for the production of micro/nano structures on the wafer level. This paper reviews the current state and development of nanoimprint lithography and highlights some critical issues in this nanofabrication technique.

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References


