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Photocatalytic activity of magnetic core–shell CoFe$_2$O$_4$@ZnO nanoparticles for purification of methylene blue

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Abstract

Magnetic core–shell CoFe$_2$O$_4$@ZnO nanoparticles have been successfully synthesized by using coprecipitation method to provide easy separated nanomaterials and high photocatalytic activity performance. Core–shell nanoparticles with various CoFe$_2$O$_4$–to–ZnO molar ratio (1:2, 1:3, 1:4, 1:5) have been investigated over x-ray diffraction (XRD), transmission electron microscopy (TEM), UV-visible spectroscopy, and vibrating sample magnetometer. XRD spectra confirm the cubic spinel ferrite phase structure of CoFe$_2$O$_4$ and the hexagonal wurtzite phase of ZnO. The crystallite size is found within the range of 14.9–20.6 nm. TEM measurement confirms the good crystallinity of the samples. The magnetic hysteresis shows that CoFe$_2$O$_4$@ZnO has high saturation magnetization of about 30 emu g$^{-1}$ and coercivity of about 300 Oe. Photocatalytic investigation was carried out using methylene blue (MB) under UV irradiation. Our result yields the enhancement of MB degradation as ZnO content increases. The maximum photodegradation achieved by the core–shell nanoparticles is 57.2%, 60.5%, 65.5%, and 78.3% for molar ratio of 1:2, 1:3, 1:4, and 1:5, respectively. The enhancement of MB degradation can be attributed to the formation of internal structure between CoFe$_2$O$_4$ and ZnO in the form of heterojunction structure. The magnetic properties of core–shell lead to the easy separation between the magnetic core–shell nanoparticles and the final degraded solution by permanent magnet.

1. Introduction

The booming development of textile industry is a threat to environmental pollution. Industrial effluents containing several toxic organics not only pollute groundwater resources but also inflict a serious problem for human health. Therefore, the water treatment is the aim focus to resolve the problem [1–3]. It is well known that photocatalysis is one of the effective processes for water treatment. The main principle of photocatalysis is the movement of electrons to the surface caused by photogeneration of electron holes [2–6].

Photocatalysts use a material as an active agent to reduce the water pollutant via photodegradation. Photocatalysts use photon energy to carry out oxidation and reduction reactions. During photocatalytic oxidation, the materials absorb photon energy and excite electron from the valence band to the conduction band. The resulting electron and hole can then further react with oxygen (O$_2$) and water (H$_2$O) to form superoxide anion (O$_2^-$) and hydroxyl radical (OH), respectively [7]. TiO$_2$ and ZnO are two semiconductor materials which have been used mostly as photocatalyst materials [8–10]. These photocatalysts have the major drawback such as wide band gap i.e., 3.18 eV for anatase TiO$_2$, 3.03 eV for rutile [10], and 3.20 eV for ZnO [8]. ZnO has wide direct bandgap, high electron mobility, low cost, environment-friendly, and high UV light absorption [3–6, 8, 9, 11–16]. ZnO with the unique properties still has problems in separation and recycling after photodegradation process. Furthermore, the separation of these photocatalysts from treated water also becomes a restricted factor for the application in industrial scale because of inefficiency, expensive and time-consuming...
process [7]. Nanomaterials which possess both magnetic and photocatalysis properties would be a prospective solution to solve the subject [7, 11]. Core–shell heterojunction between semiconductor and magnetic material can be proposed to overcome the problem. The incorporation of magnetic material as a core and semiconductor as a shell produces catalysts that are easily separated using permanent magnet [3–5, 11], and the core–shell nanoparticles as photocatalysts material is possible to reuse.

Spinel ferrites are very promising magnetic materials because of their crystal structure, narrow band gap, high magnetic and electrical properties, high thermal and chemical stability [7, 17]. Cobalt ferrite (FeO$_4$) is hard magnetic material with high coercivity, high cubic magnetocrystalline anisotropic, high Curie temperature, and narrow bandgap [16, 18, 19]. The intercalation of CoFe$_2$O$_4$ nanoparticles not only brings out the recycling possibility but also leads to widening absorption band in range visible light, enhances the efficiency and easy separation after photodegradation [14–16].

Many methods have been developed to synthesize CoFe$_2$O$_4$ nanoparticles, such as sol-gel, solid state reaction, sol-gel auto combustion, and coprecipitation [18–20]. Among those methods, coprecipitation is a cheap and simple method, in which the control of size and size distribution is obtained by controlling the relative rates of nucleation and growth during the synthesis process at room temperature [19, 21, 22]. For instance, synthesis, morphology, microstructure, and magnetic properties of core–shell type CoFe$_2$O$_4$@ZnO [13–16, 23], ZnFe$_2$O$_4$@TiO$_2$ [24], and Fe$_3$O$_4$@ZnO [3, 5, 11, 25] nanoparticles have been previously reported. The photocatalytic activity of CoFe$_2$O$_4$@ZnO core–shell nanoparticles have been also recently reported [14–16]. However, most studies reported that core–shell nanoparticles are obtained through high temperature process. For the best of our knowledge and the point of view of an energy consuming, only small number of researchers reported core–shell nanoparticles obtained through room and moderate temperature process. On the other hand, most studies have not reported the mechanism of kinetic model for the photocatalytic degradation activity of core–shell magnetic nanoparticles in detail. The aim of this study is facile synthesis of CoFe$_2$O$_4$@ZnO core–shell nanoparticles prepared through moderate temperature process for degradation methylene blue (MB) as an organic dye. The correlation between the microstructures, the magnetic properties and photocatalytic activity of CoFe$_2$O$_4$@ZnO core–shell nanoparticles is investigated in detail. The kinetic model for the photodegradation activity is also studied.

2. Experimental methods

Cobalt(II) chloride hexahydrate (CoCl$_2$.6H$_2$O), iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O), hydrogen chloride (HCl), sodium hydroxide (NaOH), were used. All pure analytical materials were purchased from Merck (Darmstadt, GFR) and used without further purification. The CoFe$_2$O$_4$ nanoparticles were synthesized using coprecipitation method, typically CoCl$_2$.6H$_2$O were dispersed into FeCl$_3$.6H$_2$O solution. Subsequently HCl solution was added into it. After 5 min stirred, the mixed solution was added dropwise into NaOH solution at temperature 60 °C for 2 h. Then, precipitate that has been washed 7 times were dried at 90 °C for 2 h. After stirred for 5 h, the solution was precipitated and washed. Later, the core–shell CoFe$_2$O$_4$@ZnO nanoparticles was obtained after calcinated at 60 °C for 12 h. The same things were done with the various CoFe$_2$O$_4$-to-ZnO molar ratio of 1:2, 1:3, 1:4, and 1:5, indicated as CFO@2ZnO, CFO@3ZnO, CFO@4ZnO, and CFO@5ZnO, respectively.

The structural and phase analyses of samples were performed using Shimadzu XD-3H (XRD), Jeol JEM 1400 (TEM). While magnetic and optical properties were analyzed using VSM (Riken Denshi Co. Ltd), UV–vis spectrometer. Core–shell doing MB decomposition was carried out using the following procedures: the catalyst was added into 100 ml MB solution (10ppm), then stirred in the dark for 30 min. At certain time, the solution is taken out just a few milliliters. It is placed on a magnetic table before analyzed using UV–vis spectrometer. The photocatalytic process was done for 3 h.

3. Results and discussion

The XRD spectrum of ZnO, CoFe$_2$O$_4$, and core–shell CoFe$_2$O$_4$@ZnO nanoparticles is shown in figure 1. ZnO has hexagonal wurtzite structure with crystalline peaks at 2θ = 34.4°, 36.8°, 47.5°, 56.4°, 63.1°, and 68.2° that can be respectively indexed to the planes of (002), (101), (102), (110), (103) and (112) (JCPDS standard data, Card No. 36-1451), as shown in figure 1(a). The XRD pattern of CoFe$_2$O$_4$ nanoparticles shows the existence of six clear distinctive peaks at 2θ = 30°, 35.3°, 43.2°, 53.2°, 56.8° and 62.5° of the spinel ferrite structure that are
matched to the (220), (311), (400), (422), (511) and (440) planes, respectively (JCPDS standard data, Card No. 22-1086), as shown in figure 1(b). The XRD pattern of core–shell CoFe₂O₄@ZnO nanoparticles still shows the existence of six clear distinctive peaks of the spinel ferrite. However, we found that all those diffraction peaks of ferrite undergo significant peak broadening and the decrease of peak intensity with the increase of ZnO concentration, as shown in figures 1(c)–(f), which mean that the crystallinity decreased.

The highest crystallinity for core–shell denoted by the sharp peak of core–shell nanoparticle is CoFe₂O₄@ZnO (1:5). After encapsulating by ZnO, peaks diffraction become broader while concentration zinc increase that indicates particles strain are change [5]. Strain of CoFe₂O₄ (CFO) is higher than CoFe₂O₄@ZnO. It might happen caused by distortion or crystal defect from the absorption of Zn and O on the interface. The crystallite size of nanoparticles can be determined using the Scherrer’s formula [5, 16]. Analysis of the crystallite size for each sample is presented in table 1. The crystallite size of CoFe₂O₄@ZnO decreased with the increase of ZnO concentration. Decreasing the crystallite size is caused by interstitial impurity when the atom Zn²⁺ which small radial ionic fills the space between the atoms of CoFe₂O₄ nanoparticles as called the crystal defect [13]. Meanwhile, crystal structure lattice of core–shell for hexagonal phase has appeared as deconstruction lattice which is approaching to the cubic lattice while ZnO increases. Deconstruction lattice caused by Miller’s mismatch plane between (311) plane of CoFe₂O₄ between (101) plane of ZnO which are responsible for heteroepitaxial growth of ZnO shell on the CoFe₂O₄ core nanoparticles [5].

The microstructures of CoFe₂O₄ and CoFe₂O₄@ZnO were further investigated by TEM with selected-area electron diffraction (SAED) images, as shown in figure 2. The morphological analysis using TEM spectroscopy delineate nearly spherical shape formed with smaller and uniform grains of CoFe₂O₄, as shown in figure 2(a). The other morphology of CoFe₂O₄@ZnO does not clearly seem due to the intergrains agglomeration [5, 14, 16]. The morphology nanoparticle that encapsulated by ZnO shows the particle to be covered by a thin membrane which indicated the presence of ZnO as a shell, as shown in figure 2(b). It is typical of the core–shell like structure [15]. The agglomeration that appears due to the large interface strain shows the high grain reactivity of the magnetostatics interaction and the interaction exchange dipole moment of small particle size with wide specific

![Figure 1. XRD patterns of (a) ZnO, (b) CoFe₂O₄ and CoFe₂O₄@ZnO with concentration: (c) 1:2, (d) 1:3, (e) 1:4, and (f) 1:5.](image)

Table 1. The crystallite size of CoFe₂O₄ and CoFe₂O₄@ZnO nanoparticles with various ZnO concentration.

| Sample             | Crystallite size (nm) |
|--------------------|-----------------------|
| CFO                | 17.3                  |
| CFO@2ZnO           | 20.6                  |
| CFO@3ZnO           | 19.0                  |
| CFO@4ZnO           | 18.1                  |
| CFO@5ZnO           | 14.9                  |

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surfaces active \([5, 14]\). Interaction exchange dipole made by induced external magnetic field during the synthesis process which leaving the remanent magnetization in nanoparticles. The diffraction ring pattern shows a light-dark pattern arranged in a ring-like, as shown in figure 2. The SAED images of both samples show the spotty ring (discontinuous ring) patterns, revealing their crystalline spinel structure. Measured inter-planar spacing \(d_{hkl}\) from SAED patterns are in good agreement with the values in the standard data (JCPDS Card No. 22-1086). The diffraction rings are identified, from inner to outer, as the \((220)\), \((311)\), \((400)\), \((511)\), and \((440)\) planes, respectively, revealing spinel type structures of \(\text{CoFe}_2\text{O}_4\) nanoparticles, corresponding well with XRD data. After encapsulating by \(\text{ZnO}\), the reduce contrast of diffraction ring is caused by the decrease of crystallinity, as described previously.

The hysteresis loop of \(\text{CoFe}_2\text{O}_4\) and \(\text{CoFe}_2\text{O}_4@\text{ZnO}\) core–shell nanoparticles are shown in figure 3. The result indicates that the magnetic properties of nanoparticles are ferromagnetic. The hysteresis loop shows that the \(\text{CoFe}_2\text{O}_4\) nanoparticle is more magnetically active than \(\text{CoFe}_2\text{O}_4@\text{ZnO}\) core–shell since \(\text{ZnO}\) paramagnetic reduced the magnetic nature of \(\text{CoFe}_2\text{O}_4\) [15]. The hysteresis loop clearly indicates that low coercivity \((H_c)\) of \(\text{CoFe}_2\text{O}_4\) tend to be approaching the superparamagnetic properties. The saturation magnetization \((M_s)\) and the coercivity \((H_c)\) of \(\text{CoFe}_2\text{O}_4\) is 38 emu g\(^{-1}\) and 87 Oe, respectively, as shown in table 2. The \(M_s\) and \(H_c\) of \(\text{CoFe}_2\text{O}_4@\text{ZnO}\) core–shell nanoparticles is about 30 emu g\(^{-1}\) and about 300 Oe, respectively. The decrease of \(M_s\) and the increase of \(H_c\) after \(\text{ZnO}\) encapsulation is due to the paramagnetic properties of \(\text{ZnO}\). Trend in the relationship between the crystallite size and magnetic properties is predicted due to interfacial defect and the effect of agglomeration in the sample so that the tendency of clumping grains leads to the anisotropic energy become bigger and the coercivity becomes larger [16].

To recognize the catalytic behavior of core–shell, it is crucial to define energy gap of bands for each their component. The wide energy gap of \(\text{ZnO}\) and the narrow energy gap of \(\text{CoFe}_2\text{O}_4\) may forms the heterojunction of the band structure. This junction not only establish the Schottky barrier at the interface between core and shell but also demote the band-gap energy to form equilibrium band, thus enhancing the efficiency of the interfacial charge separation process with fast electron transfer-ability and prevent recombination electron-hole [4–6, 12–14]. The energy gap was obtained by using linear touch plot extrapolation. The energy gap decreases while \(\text{ZnO}\) content increases so that when the core–shell 1:5 has a smaller bandgap leads to the higher photocatalytic activity, as shown in table 2.

Photodegradation MB of \(\text{CoFe}_2\text{O}_4@\text{ZnO}\) (1:2) is clearly shown in figure 4(a). The result show that the peak absorption is fall off which means MB successfully decomposed at range wavelength of visible light. The photocatalytic degradation of MB with various \(\text{ZnO}\) concentration of \(\text{CoFe}_2\text{O}_4@\text{ZnO}\) core–shell nanoparticles is shown in figure 4(b). The photocatalytic degradation activity of \(\text{CoFe}_2\text{O}_4@\text{ZnO}\) core–shell nanoparticles increased with the increase of \(\text{ZnO}\) concentration. The core–shell with concentration of 1:5 has a smaller bandgap, leads to the higher photocatalytic activity. Furthermore, the Langmuir–Hinshelwood kinetic model for the photocatalytic degradation activity of \(\text{CoFe}_2\text{O}_4@\text{ZnO}\) core–shell nanoparticles is also studied, as shown in

\(\text{Figure 2. TEM and selected area electron diffraction (SAED) images of (a) } \text{CoFe}_2\text{O}_4\text{ and (b) } \text{CoFe}_2\text{O}_4@\text{ZnO} \text{ nanoparticles.}\)
Figure 5. To understand the correlation of the enhanced photocatalytic activity. The experimental data are posted into the equation of $\ln\left(\frac{C_t}{C_0}\right) = -(K_{app}t)$, where $K_{app}$ was the rate constant [2, 6]. $\text{CoFe}_2\text{O}_4@\text{ZnO} (1:5)$ is the highest rate constant which means faster photodegradation compared to others.

Figure 6. Schematic diagram of photocatalytic $\text{CoFe}_2\text{O}_4@\text{ZnO}$ core–shell nanoparticles under UV light is shown in figure 6. The electron–hole pair at $\text{ZnO}$ is separated under exposure to UV light and the electron move toward from the valence band to the conduction band then leave a positively charged (hole) in the valence band. After electrons released, oxygen molecules adsorbed by the surface of $\text{ZnO}$ will interact with the electrons in the conduction band to make superoxide radicals ($\cdot\text{O}_2^-$). Meanwhile, holes in the $\text{ZnO}$ valence band will move to the valence band $\text{CoFe}_2\text{O}_4$, then oxidized between holes and hydroxyl ions ($\text{OH}^-$) occur to form hydroxyl radicals ($\cdot\text{OH}$). Eventually, the $\text{MB}$ molecules decompose into simple organic molecules, and will further decompose into $\text{CO}_2$ and $\text{H}_2\text{O}$ [2]. Aside from being a barrier to the charge recombination, $\text{CFO}$ is also useful as a place to store up the charge. Specific surface area is very important in increasing photocatalytic activity (PCA) as a place of interaction between dyes and catalysts [2, 6]. $\text{CFO}@\text{ZnO} (1:5)$ constituted the optimum degradation while the crystal size is small and the specific surface, surface tension, the reactivity is higher than the other nanoparticles.

4. Conclusions

A multifunctional core–shell structure with $\text{CoFe}_2\text{O}_4$ as core and $\text{ZnO}$ as shell was successfully grown using co-precipitation method. The $\text{CoFe}_2\text{O}_4@\text{ZnO}$ core–shell nanoparticles is ferromagnetic material. Thus, the $\text{CoFe}_2\text{O}_4@\text{ZnO}$ core–shell with $\text{ZnO}$ concentration of 1:5 with high photocatalytic activity for degradation $\text{MB}$ is a compatible material to be used as a reusable catalyst and it can be easily separated from the suspension using an external magnet which avoids hazardous disposal of photocatalysts to the environment.
Figure 4. (a) UV-visible absorption spectra using CFO@ZnO (1:2) and (b) photocatalytic degradation of MB for CFO@ZnO nanoparticles with various concentration.

Figure 5. Rate constants of the photocatalytic degradation of core–shell nanoparticles.
Figure 6. Schematic diagram of photocatalytic CoFe$_2$O$_4$@ZnO core–shell nanoparticles under UV light.

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