Preparation of In$_2$O$_3$@TiO$_2$ core-shell spherical nanocomposites with the enhanced photocatalytic activity under solar light irradiation

H M Zhao$^1$, H T Fu$^{*,1,2}$, C X Ge$^1$ and Q Xu$^1$

$^1$ School of Metallurgy, Northeastern University, Shenyang 110819, People’s Republic of China
$^2$ Key Laboratory for Ecological Metallurgy of Multimetallic, Ministry of Education, Northeastern University, Shenyang, 110819, People’s Republic of China

Corresponding author and e-mail: H T Fu, fuht@smm.neu.edu.cn

Abstract. In this study, we demonstrate In$_2$O$_3$@TiO$_2$ core-shell spherical nanocomposites prepared by hydrothermal method and sol-gel coating method. The In$_2$O$_3$ particles show quite a uniform particle size (~200 nm in diameter) and smooth surface. Porous TiO$_2$ polycrystalline is coated on the surface of In$_2$O$_3$ nanospheres as a shell. The thickness of the shell can be controlled by adjusting the molar ratios of In to Ti. UV-Vis spectra indicate that the adsorption peaks of pure In$_2$O$_3$ and TiO$_2$ nanospheres are located at 323 and 319 nm, respectively. The surface coating of TiO$_2$ can make the adsorption of nanocomposites shift to the long wavelength to ~340 nm. The photocatalytic activities of the pure In$_2$O$_3$, TiO$_2$, and the nanocomposites obtained with different molar ratios of In to Ti were evaluated by measurement of the degradation concentration of 30 ppm methylene blue (MB). The results show that the nanocomposites show higher photocatalytic performance than the pure oxides. The ratio at 1:10 exhibits the highest reaction rate constant (0.0152 min$^{-1}$), similar to other nanocomposites but higher than pure In$_2$O$_3$ nanospheres (0.0069 min$^{-1}$) and TiO$_2$ (0.0058 min$^{-1}$). This can be attributed to the large surface and tuned band energy structure for enhanced visible light absorption and the effective charge separation at the heterojunction of In$_2$O$_3$ and TiO$_2$. These findings may benefit to the new developed core-shell material as photocatalysts with enhanced efficiency for environmental applications.

1. Introduction

Photocatalysis is considered as an effective and low-cost way to solve the environmental issues, which become increasingly serious with the development of the industry.[1, 2] TiO$_2$, a traditional photocatalyst with high degradation efficiency, has attracted numerous attention since the evolution of oxygen and hydrogen from the TiO$_2$ electrodes has been reported by Fujishima and Honda in 1972.[3] Recently, it has been widely studied for the potential applications in air purification and photocatalytic degradation of organic pollutants due to its excellent chemical stability, low cost, and very low toxicity.[4-7] However, limited by the wide bandgap (~3.2 eV), TiO$_2$ is only excited by ultraviolet light which is <10% of the total solar spectrum irradiating to the surface of the earth.[8] Therefore, making TiO$_2$ responsive to visible light and enhancing the photocatalytic activity become major subjects for developing the TiO$_2$-based photocatalysts.[9-12] Many efforts have been made to extend
the photoresponse of TiO$_2$ to visible region, including elements doping (transition metals or non-metals) and nanoparticle surface modification (noble metals and transition metal oxides). Reseach proves that surface modification is more suitable to overcome the issues than element doping (suffering from thermal instability, photo-corrosion, lattice distortion, and an increase in the carrier-recombination probability). Coupling TiO$_2$ with other narrow bandgap semiconductors serving as the sensitizer is considered as an efficient way to absorb visible light.[9, 18]

Core-shell structures, as one of the most important ways for surface modification, have obtained intensive research interests due to representing diverse functions related components integrated into one unit and widely applying in renewable energy, advanced biomedicine, and environmental protection.[19-21] The successful applications of core-shell structures depend upon the availability of various shell frameworks with tunable composition, thickness, and structure over well-designed functional cores.[22] The core-shell structures, especially TiO$_2$ as shell, are also well applied in photocatalysis owning to their fascinating features. The cores play important roles in trapping photogenerated electrons and tuning the bandgap of the TiO$_2$ shell.[23-25]

In$_2$O$_3$, a semiconductor with a direct bandgap of 3.6 eV and an indirect bandgap of 2.8 eV, is proposed as an efficient sensitizer to extend the absorption spectra of oxide semiconductors from UV region to the visible region.[26, 27] As aforementioned, In$_2$O$_3$ as the core, coupling with TiO$_2$ can transfer electrons from an excited small bandgap semiconductor to another one in the case of proper conduction band potentials, which benefits the separation of photogenerated electrons and holes and further enhancing the photocatalytic activity. This can be attributed to the difference of bandgaps between In$_2$O$_3$ (~2.8 eV) and TiO$_2$ (~3.2 eV for anatase). More importantly, an efficient heterostructure for separation of photoinduced charge carries can be formed via the higher conduction band (CB) of In$_2$O$_3$ ($E_{CB} = -0.63$ V vs. NHE) than that of TiO$_2$ ($E_{CB} = -0.4$ V vs. NHE).[28, 29]

Based on this feature, different morphologies of In$_2$O$_3$-TiO$_2$ photocatalysts have been synthesized, including surface-modified nanoparticles, films, and so on.[30, 31] Among these materials, In$_2$O$_3$-TiO$_2$ core-shell structure is proposed as a promising structure for the purpose of speeding up electron transfer and preventing recombination of electron-hole pairs.[28] However, it is little reported on the core-shell structures with fast electron transfer, low recombination rate, and high surface area.

Herein, we demonstrate a simple method to fabricate porous In$_2$O$_3$-TiO$_2$ core-shell spherical nanocomposites by controlling the ratio of titanium precursors to In$_2$O$_3$ nanospheres in acetone solution. No high-temperature calcination for crystallization of porous TiO$_2$ is one of the highlights for this coating method. The products are characterized by several advanced techniques, such as XRD, TEM, SEM, and UV-vis spectroscopy. Finally, the photocatalytic activity of the as-prepared core-shell structures is evaluated by degradation of methyl blue under simulated solar light irradiation.

2. Experimental

2.1. Preparation of In$_2$O$_3$ nanospheres

The In$_2$O$_3$ nanospheres were prepared by hydrothermal methods and followed by calcination in air. In a typical procedure, 10 ml 0.2 M NH$_4$HCO$_3$ solution was generally mixed with the equivalent volume of 0.05 M InCl$_3$·4H$_2$O solution. 0.2 g Na$_2$SO$_4$ and 1 mmol citrate acid were added into the previous mixture solution. After vigorous stirring, the mixed precursor solution was transferred into a 20 ml Teflon-lined stainless autoclave, sealed and maintained at 160°C for 8 h, then cooled down to room temperature. The as-prepared products were collected by centrifuge and washed several times with ethanol and deionized water, respectively. Finally, the products were dried at 70°C for 12 h.

2.2. Preparation of In$_2$O$_3$@TiO$_2$ core-shell spherical nanocomposites

30 mg of In$_2$O$_3$ nanospheres was added in 150 ml acetone to form a suspension. Afterward, a certain amount of 0.5 vol.% titanium butoxide (TBT) ethylene glycol solution was added into the previous suspension. After sonication for a while and followed with standing for 8 h, the as-prepared particles were collected and washed for further use. For crystallization, the precursors were boiled...
in ultrapure water for 2 h. And then, the products were centrifuged and washed with DI water and ethanol for several times and dried at 70°C for several hours.

2.3. Characterization
The compositions of the as-prepared products were characterized by Phillips X’pert Multipurpose X-ray Diffraction System (MPD) in the 2θ range of 5-80°. SEM images were recorded with a Zeiss field emission scanning electron microscope. The composite morphologies were observed on an FEI tecnai G20 microscope (TEM), operated at an accelerated voltage of 100 kV. The Brunauer-Emmet-Teller (BET) surface area and pore size with the distribution of the products were obtained from nitrogen physisorption isotherms (adsorption-desorption branches) at 77 K on a Micromeritics ASAP 2020 instrument. The optical properties were obtained on a Shimadzu UV-2600 UV-vis spectrophotometer (Varian) with a 1 cm quartz cell.

2.4. Photocatalysis test
The photocatalytic activities of TiO$_2$ based core-shell nanocomposites were determined by measuring the decolorization of MO under simulated solar light irradiation in a batch reaction. The reactor volume is 250 ml. A 300W xenon lamp (PLS-SXE300C) equipped with AM 1.5G total reflection filters was used to obtain simulated solar light to trigger the photocatalytic reaction, and the lamp was positioned about 15 cm away from the reactant solution meniscus. The luminance of the light source over the reactant solution was 0.7 W/cm$^2$. A 100 ml solution of 30 ppm methylene blue (MB) was injected into the reaction system, while 0.020 g of the photocatalyst was added. Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure adsorption-desorption equilibrium. At given time intervals, 3 ml solution was sampled and filtrated to remove the catalysts. The filtrates were analyzed by recording the variations of the absorption band maximum (657 nm) of methyl orange using a Shimadzu UV-2600 UV-Vis spectrophotometer. After various time intervals, MB concentration could be estimated using the following equation:

$$\text{MB concentration}= \frac{C}{C_0} \times 100\%$$  \hspace{1cm} (1)

Where $C_0$ is the initial MB absorbance at 664 nm and $C$ is the absorbance obtained after various intervals of time. The reaction rate ($k$) could be estimated as the linear relationship between ln($C/C_0$) and time:

$$\ln\left(\frac{C}{C_0}\right)=kt$$  \hspace{1cm} (2)

To eliminate the effect of heating during irradiation, the reactor was equipped with reflux condensation. After decolorization, the supernatant of the solution was obtained via centrifugation, and then characterized by UV-Vis spectroscopy.

3. Results and discussion
3.1. Morphology and composition
The composition of the In$_2$O$_3$@TiO$_2$ core-shell nanocomposites and pure In$_2$O$_3$ nanospheres were characterized by XRD techniques. Fig. 1 shows the XRD patterns of the pure In$_2$O$_3$ nanospheres (green line) and the nanocomposites obtained at various molar ratios of In$_2$O$_3$ to TiO$_2$. For pure In$_2$O$_3$ nanoparticles, the XRD pattern indicates the diffraction peaks of cubic In$_2$O$_3$ (JCPDS NO. 01-089-4595), which is in good agreement with the previous study.[28, 29] In the patterns of nanocomposites, the peaks corresponding to TiO$_2$ appear, and the diffraction peaks centered at 2θ = 25.3°, 48.6°, and 53.8° is consistent with the peaks of (101), (200), and (105) from anatase TiO$_2$.[28, 30] In addition, the intensity of the TiO$_2$ (101) peaks apparently increase with the ratios. No other peaks related to impurities are observed, which indicates the high purity of the products.

The morphologies of the pure In$_2$O$_3$ nanospheres and In$_2$O$_3$@TiO$_2$ core-shell nanocomposite are recorded by SEM and TEM, respectively. Fig. 2 a & b shows the SEM and TEM image of the pure
In$_2$O$_3$ nanospheres. It can be seen that the nanospheres with the diameters of ~200 nm are uniform and with smooth surfaces. Fig. 2 c-f shows the In$_2$O$_3$@TiO$_2$ core-shell nanospheres prepared at different molar ratios of In to Ti (from 1:5 to 1:15). The spherical particles with high contrast represent In$_2$O$_3$ as cores, and the low contrast part corresponds to porous TiO$_2$ polycrystalline as the shell. It can be seen that TiO$_2$ are well coated on the In$_2$O$_3$ nanospheres, and the thickness of the shell increases with the molar ratios of In to Ti (20, 40, 50, and 70 nm for the ratios of 1:5, 1:7, 1:10, and 1:15). The thickness of the shell may affect the future functional performance.

Figure 1. XRD patterns of pure In$_2$O$_3$ and In$_2$O$_3$@TiO$_2$ core-shell nanostructures with various molar ratios (from 1:5 to 1:15).

Figure 2. (a, b) SEM and TEM image of the pure In$_2$O$_3$ nanospheres; TEM images of In$_2$O$_3$@TiO$_2$ core-shell nanostructures obtained with various molar ratios of (c) 1:5, (d) 1:7, (e) 1:10, and (f) 1:15.

3.2. Optical properties
The optical properties of the nanoparticles prepared in this study, including pure In$_2$O$_3$ nanospheres and the In$_2$O$_3$@TiO$_2$ core-shell nanocomposites synthesized at various molar ratios of In to Ti, were measured and analyzed. The UV-Vis spectra of the nanoparticles are shown in Fig. 3. It can be seen
that there is no obvious surface plasmon resonance for pure In$_2$O$_3$ and TiO$_2$ particles in the rage of 200 to 800 nm. The peak of TiO$_2$ is located at 319 nm while the In$_2$O$_3$ are centered at 323 nm. This is in accordance with the literature.[32] After coating with TiO$_2$, the peaks of the nanocomposites are slightly shifted to long wavelength by ~20 nm. The adsorption peaks become broaden probably due to the larger size after coating.[18] In addition, the locations of the peaks are little changed with the ratios. Specifically, the peaks are centered at 342, 399 and 337 nm for the ratio of 1:10, 1:15, and 1:5, respectively.

\[\text{Figure 3. UV-Vis spectra of the pure TiO}_2, \text{ pure In}_2\text{O}_3 \text{ nanospheres, and the core-shell nanocomposites.}\]

3.3. Photocatalytic activity

The photocatalytic activities of the pure In$_2$O$_3$ nanospheres and the core-shell nanocomposites were measured by the degradation of 30 ppm MB solution. Fig. 4 shows the corresponding concentration changes of the MB solution and the reaction rate constant as a function of simulated solar light exposure time. In the case of pure In$_2$O$_3$ and TiO$_2$ as photocatalysts, ~70% and 74% degradation of MB can be obtained in 250 min after exposure to the solar light. In comparison, the as-preparation In$_2$O$_3$@TiO$_2$ core-shell nanocomposites show that the degradation of > 95% MB can be achieved under similar conditions. It should be noted that the photocatalytic activities under solar light irradiation of all the hybrid nanocomposites are superior to those of pure In$_2$O$_3$ and TiO$_2$. However, the photocatalytic performances of the nanocomposites are similar. Specifically, nearly 100% degradation of MB can be obtained at the molar ratio of 1:10, which shows the best photocatalytic activity towards the degradation of MB under solar light illumination, followed with the In$_2$O$_3$@TiO$_2$ core-shell nanocomposites with the ratios of 1:5 and 1:15. It can be noticed that smaller amount of TiO$_2$ coating improves the photocatalytic activity of the whole In$_2$O$_3$@TiO$_2$ core-shell nanocomposites. Fig.4b shows the reaction rate constants of all tested samples, and the core-shell nanocomposites at the ratios of 1:10 shows the highest rate constant among all the samples. The photocatalytic activity and the kinetic rate constants of all the different photocatalysts follow the order: 1:10 core-shell structure (k = 0.0152 min$^{-1}$) > 1:5 (k = 0.0146 min$^{-1}$) > 1:15 (k = 0.0127 min$^{-1}$) > pure In$_2$O$_3$ (k = 0.0069 min$^{-1}$) > pure TiO$_2$ (k = 0.0058 min$^{-1}$). This may be related to the surface area and the thickness of various amounts of TiO$_2$ coating. The surface areas measured by BJH method via adsorption isotherm are 168, 177, 171 m$^2$/g, which are close to that of pure TiO$_2$ (180 m$^2$/g)[33] but much higher than that of pure In$_2$O$_3$ nanospheres (120 m$^2$/g). The similar surface area of the nanocomposites and pure TiO$_2$ is because the contribution of the surface area is mainly from TiO$_2$. Normally, the large surface area can provide more adsorption site of dye molecules, and further increase the photocatalytic activity. The increase of the shell thickness is little affected the photocatalytic performance, which supports the relationship between performance and surface areas.
Figure 4. (a) Degradation rates of MB in the presence of the photocatalysts under simulated solar light irradiation. (b) Apparent rate constants of different photocatalysts.

3.4. Mechanism
The factors affecting the photocatalytic activity are diverse, such as surface area, bandgap energy, particle size, and the electron-hole recombination rate. The catalytic properties under solar light irradiation are mainly dependent upon the bandgap structure for the core-shell nanocomposites.[34] When In$_2$O$_3$ nanospheres are coupled with TiO$_2$ particles, the Fermi level of TiO$_2$ and In$_2$O$_3$ must align in equilibrium due to the existence of the In$_2$O$_3$/TiO$_2$ heterojunction.[35, 36] Under solar light irradiation, the photo-generated electrons transfer from the conduction band of In$_2$O$_3$ to the conduction band of TiO$_2$ under the built-in electric field, and the concentration gradient activated and yielded charge carriers, while the photo-generated holes accumulated in the valence band of In$_2$O$_3$. The negative electrons in the valence band of TiO$_2$ reacted with O$_2$ molecules in the aqueous solution and form the superoxide ions (O$_2^-$) and hydrogen peroxide (H$_2$O$_2$), while the holes react with OH$^-$ and produce reactive hydroxyl radicals (•OH).[29, 31]

4. Conclusions
In this study, the In$_2$O$_3$@TiO$_2$ core-shell spherical nanocomposites have been synthesized via a hydrothermal method for preparation of In$_2$O$_3$ nanospheres and sol-gel method for coating TiO$_2$ shell. The coating method shows several unique advantages, such as rapid and effective surface coating for materials and morphologies, no need of high temperature (>100°C), and potential for scale-up production. The core-shell nanocomposites have been proved as excellent solar-light-driven photocatalysts showing superior photocatalytic activity to the pure TiO$_2$ and In$_2$O$_3$ nanospheres. The red-shift of the nanocomposites, compared with pure TiO$_2$ nanoparticles, is attributed to the combination of the narrow bandgap of In$_2$O$_3$. The existence of the In$_2$O$_3$/TiO$_2$ heterojunction and the matched energy bands of this core-shell structure benefit the charge transfer and suppress rapid recombination of photo-generated electrons and holes. This study offers potentially advanced core-shell nanocomposites in photocatalysis for practical use.

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