Photocatalytic activity enhanced by photo-thermal conversion with recyclable hollow Fe$_3$O$_4$@TiO$_2$ nanoparticles

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Abstract. Photocatalytic nanoparticles have been applied in the utilisation of solar energy because of their excellent harvesting of solar energy for wastewater treatment and chemical synthesis. In particular, TiO$_2$ nanoparticles exhibit unique photo-catalytic performance due to their high specific surface areas and distinctive optical properties. However, the presence of nanoparticles in solar energy systems can cause secondary pollution and severely limit large-scale application of the nanoparticles in solar technology. In the present work, recoverable hollow Fe$_3$O$_4$@TiO$_2$ nanoparticles were synthesized via a modified hydrothermal method. The prepared nanoparticles exhibit superior photocatalytic activity for degrading organic pollutants (Rhodamine B), which is 33.1% higher than that of P25, and the effect of photo-thermal conversion in enhancing the photo-catalytic activity of this nanoparticles was studied, which has not been investigated in most of previous reports. This study not only reveals that photo-thermal conversion plays an important role in enhancing photocatalytic activity, but also provides an approach to significantly reduce material consumption in the design of solar devices and facilitate the efficient utilization of solar energy applications.

Keywords: photo-thermal conversion; Fe$_3$O$_4$@TiO$_2$ nanoparticles; purification; magnetic separation

1. Introduction

Renewable energy resources are critical to the development of a globally sustainable society [1]. The development of sustainable energy technologies, especially solar energy, has become extremely important for securing future energy sources [2]. Solar energy is a sustainable and inexhaustible source of energy which has the potential to replace fossil fuels. Furthermore, there is significant potential for solar energy to be converted into other forms of energy, such as electric, thermal, and chemical energy [3]. Among them, photovoltaics is a promising commercial technology which may allow for the generation of electrical power for a wide range of applications [4]. Photo-thermal systems have potential in a range of industrial applications, such as vapour generation and seawater desalination. Besides, photo-thermal conversion has also been employed to selectively kill cancer cells in medical sciences [5]. Photochemical conversion has significant promising for photocatalysis, which is essential for a wide range of applications [6].
For the photochemical utilization of solar energy, the photocatalytic activities of nanoparticles (NPs) are largely dependent on their photo absorption and carrier-generation properties, which are usually affected by the materials and their structures [7]. In addition to photochemical processes, researchers have recently found that nanofluids, dispersions containing nanoparticles, exhibit excellent photo-thermal conversion properties in direct-absorption solar collectors (DASCs) [8]. In this application, carbon nano-materials, metallic oxides, and metallic nanoparticles were used to enhance solar light absorption and photothermal conversion. Enormous aforementioned literature has illustrated that TiO$_2$ exhibits excellent catalytic properties for water purification under the solar illumination [9,10]. This photochemical conversion process was accompanied by a photo-thermal conversion process which has an effect on photochemical conversion [11,12]. A number of researchers focused on the synthesis of nano-materials with excellent light absorption properties to improve the photo-thermal conversion efficiency of solar devices. Jin et al. [13] investigated the photo-thermal conversion mechanism of gold NPs-based solar volumetric receivers. Ni et al. [14] have reported a photo-thermal platform that has the potential to be scalable for a wide range of solar-based applications such as power generation, distillation, and sterilisation.

In this work, we reported the preparation of hollow Fe$_3$O$_4$@TiO$_2$ nanoparticles via a modified hydrothermal method, which combine the properties of TiO$_2$ and Fe$_3$O$_4$ to provide a material that facilitates recyclable purification and separation. Initially, the Fe$_3$O$_4$@TiO$_2$ NPs were characterised by SEM, TEM and magnetic property analysis. Subsequently, the photo-thermal conversion combined photocatalytic experiments were carried out to study the degradation performance compared to P25. We observed the photocatalytic performance of Rhodamine B (RhB) under visible light to investigate the photocatalytic disinfection activity of the Fe$_3$O$_4$@TiO$_2$ NPs.

2. Materials and Methods

2.1. Chemicals

Iron(III) chloride hexahydrate (FeCl$_3$•6H$_2$O), Ascorbic acid, Polyacrylamide (PAM), Urea (AR,99%), Titanium(IV) Fluoride and C$_6$H$_5$Na$_3$O$_7$•2H$_2$O (Sodium citrate) were purchased from Aladdin Reagent (Shanghai, China). All the reagents were of the analytical reagent grade and were used as received. Deionized water was used through all the processes.

2.2. Synthesis of Fe$_3$O$_4$@TiO$_2$ NPs

1Mmol FeCl$_3$•6H$_2$O was stirred vigorously in 80ml deionized water for 10 min. Then, the suspension was mixed with 2Mmol C$_6$H$_5$Na$_3$O$_7$•2H$_2$O and 3Mmol urea. 0.8g PAM was added into the suspension and stirred vigorously 30 min. Then the mixed solution was transferred and sealed in a Teflon-sealed autoclave. The autoclave was kept at 200 °C for 12 h before being cooled in air naturally. Then the black precipitates Fe$_3$O$_4$ nanoparticles were washed with water and ethanol by magnetic attraction before oven drying at 50 °C for 12 h. In our synthesis system, citrate is used as a reducing reagent to provide the reducing atmospheres for the synthesis system as well as a coordination ligand to reduce the concentration of free iron ions in aqueous solution. The Fe$_3$O$_4$ nanoparticles were slowly mixed in the 8ml TiF$_4$ solution with the concentration of 0.04M and was stirred vigorously for 10 min. Later, the solution was transferred and sealed in a Teflon-sealed autoclave and add 70ml deionized water. The autoclave was kept at 180 °C for 48 h before being cooled in air naturally. Finally, the final Fe$_3$O$_4$@TiO$_2$ nanoparticles were separated from the reaction medium by magnetic separation.

2.3. Characterisation
Scanning electron microscopy (SEM) analysis was performed using a SUPRA 55 SAPHIRE SEM (ZEISS, Germany) at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) patterns of the Fe$_3$O$_4$@TiO$_2$ nanoparticles were obtained using a field emission microscope (JEM-2010, Japan).

2.4. Experimental procedure

The experiments were conducted at room temperature (298 K) with the humidity of 25%. The experimental setup for the photocatalytic activity determination with photo-thermal conversion process (Fig. 1). The main experimental components of the device contain a cylindrical receiver (acrylic beaker), a solar simulator (CEL-NP2000, Beijing AuLight Ltd. Co., China) and an electric scale (Practum313-1CN, Sartorius, Göttingen, Germany). Meanwhile, the photocatalytic activities of the hollow Fe$_3$O$_4$@TiO$_2$ NPs were evaluated by the degradation of RhB in a suspension during 20 min.

3. Results and Discussion

3.1. Characterisation

The SEM image (Fig. 2a) and TEM (Fig. 2b) image showed that the hollow Fe$_3$O$_4$@TiO$_2$ NPs are of uniform size and morphology. The XRD pattern of Fe$_3$O$_4$ showed the characteristic peaks of magnetite (Fig. 2c), thus confirming its chemical composition. In the range of 20° < 2θ < 80°, the diffraction peak at 25.5°, 38.3° and 55.4° are assigned to the (1 0 1), (0 0 4) and (2 0 0) reflections of TiO$_2$ (JCPDS No. 21-1272). The other diffraction peaks at the 2θ values of 30.5°, 35.4°, 42.8°, 53.6°, 57.2° and 62.5°, correspond well to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) reflections of the standard cubic phase of Fe$_3$O$_4$ (JCPDS No. 89-0691).

![Fig. 1. Mechanism for photocatalytic activity enhanced by photo-thermal conversion.](image)

![Fig. 2. Morphology of the prepared hollow Fe$_3$O$_4$@TiO$_2$ nanoparticles: (a) SEM images; (b) TEM images; (c) XRD pattern of the prepared hollow Fe$_3$O$_4$@TiO$_2$ nanoparticles](image)
3.2. Photocatalytic activity of the hollow Fe\textsubscript{3}O\textsubscript{4}@TiO\textsubscript{2} NPs

To investigate the photocatalytic properties of the prepared hollow Fe\textsubscript{3}O\textsubscript{4}@TiO\textsubscript{2} nanoparticles, hollow Fe\textsubscript{3}O\textsubscript{4}@TiO\textsubscript{2} nanoparticles was used to catalyze the degradation of RhB under simulated solar light compared to P25. Fig. 3a showed the UV-vis absorption spectra of the RhB solution after different solar-light illumination times, the intensity of the initial absorption spectrum decreases gradually with solar-light illumination duration. Following the Beer-Lambert law, the concentration of RhB is directly proportional to the intensity of the characteristic peak [15]. Hence intensity changes of the absorption peak were used to evaluate catalytic activity. Furthermore, the RhB degradation dynamics was expressed by plotting \((\text{TRC}_f/\text{TRC}_0)\) as a function of time, as shown in Fig. 3b, the concentration of RhB decreases quickly as solar energy is converted into free carriers which promote the fast degradation of RhB. The photocatalysis kinetics of a semiconductor can be analyzed by the Langmuir-Hinshelwood first-order reaction model [16]:

\[
\ln\left(\frac{\text{TRC}_0}{\text{TRC}_f}\right) = kt
\]

where \(\text{TRC}_0\) is the initial concentration of RhB and \(\text{TRC}_f\) is the final concentration of RhB of the degraded RhB solution, \(k\) is the photo-degradation rate constant, and \(t\) is the solar irradiation time. Equation (4) affords the photo-degradation rate constant \(k\) through a plot of \(\ln(C_0/C_t)\) versus solar irradiation time \(t\). Fig. 3c illustrates the dependency of \(\ln(C_0/C_t)\) on time, and the slope of the best fit line affords \(k\). The total RhB concentration (TRC) of the degraded solution after 20 min of irradiation was calculated according to the Beer-Lambert law. The efficiency of RhB degradation (\(E_d\)) was calculated Equation:

\[
E_d = \frac{\text{TRC}_0 - \text{TRC}_f}{\text{TRC}_0} \times 100\%
\]

The reduction in the concentration of RhB is negligible under sun light radiation without photocatalyst.

3.3. The effect of photothermal conversion on photocatalytic activity

Making the most efficient use of solar light is the main purpose of the research in photocatalysis. The solar power intensity has a significant effect on the temperature distribution in suspension, so varying the solar power could help to investigate the effect of the solar illumination intensity on the photothermal conversion efficiency of the device. In this study, direct solar absorption enabled by Fe\textsubscript{3}O\textsubscript{4}@TiO\textsubscript{2} nanofluids was experimentally investigated. Photo-thermal conversion experiments were conducted at a constant Fe\textsubscript{3}O\textsubscript{4}@TiO\textsubscript{2} concentration and the temperature rise of the suspension with the solar illumination intensity increased from 1 to 5 suns (1, 3, and 5 suns) were showed in Fig. 4a. Raising the solar power intensity cause an increase in the bulk temperature of the suspension, and the unconspicuous temperature gradient indicated that the penetration depth of sunlight in the suspension.
was more obvious, which may results in a temperature gradient in the suspension. The photo-degradation rate constant of hollow Fe$_3$O$_4$@TiO$_2$ nanoparticles under different solar illumination intensity was showed in Fig. 4b. The photo-degradation line have different slope under different solar illumination intensity and the slope is increasing with the increase of solar illumination. All above states indicated that the effect of photothermal conversion enhance the photocatalytic activity.

Fig.4. (a) Temperature rise in bulk fluid and (b) photocatalytic performance at different solar intensities (1, 3, and 5 sun)

4. Conclusion

In this study, we presented a convenient and efficient approach to synthesise hollow Fe$_3$O$_4$@TiO$_2$ NPs. The prepared nanoparticles exhibit superior photocatalytic activity for degrading organic pollutants (Rhodamine B), which was 33.1% higher than that of P25, and the effect of photo-thermal conversion in enhancing the photo-catalytic activity of this nanoparticles was studied, which has not been investigated in most of previous reports. This study reveals that photo-thermal conversion plays an important role in enhancing photocatalytic activity, moreover, it provides an approach to significantly reduce material consumption in the design of solar devices and facilitate the efficient utilization of solar energy applications.

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