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Recyclable photo-thermal conversion and purification systems via Fe_3O_4@ TiO_2 nanoparticles

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ABSTRACT

In recent years, nanoscale particles have been applied in the utilisation of solar energy due to their excellent properties. In light of the multiple functions of composite nanoparticles, some solar-assisted systems have been developed and exhibited comprehensive photoelectric and photo-thermal transformation effects. However, the presence of nanoparticles in these systems can cause secondary pollution and severely limit large-scale application of the solar technology. Herein we developed a recyclable photo-thermal conversion and purification system based on Fe_3O_4 nanoparticles decorated with TiO_2 nanoparticles, which could be separated from water under the action of a magnetic force. Under the solar illumination power of 1 sun (1 sun = $1000\,W{\cdot}m^{-2}$), thermal receiver efficiency of 76.4% and Rhodamine B degradation efficiency of 85% were obtained with a 0.1 g/L Fe_3O_4@TiO_2 nanofluid. With the increase of the solar illumination power, the degradation efficiency has been increased to 94%. The recovery rate and efficiency could be controlled by adjusting the magnetic field strength and the magnetic property of Fe_3O_4@TiO_2 nanoparticles. This study provides an approach to not only significantly reduce material consumption in the design of solar devices, but also to realise broad solar energy applications for water purification and photo-thermal conversion.

1. Introduction

Renewable energy resources such as wind, geothermal and solar energy are critical to the development of a globally sustainable society [1–3]. Solar energy is a kind sustainable and inexhaustible energy which is likely to replace fossil fuels [4–6]. Furthermore, it is significant promising for solar energy to be converted into electric, thermal, and chemical energy [7–11]. Photo-thermal systems have potential in industrial applications such as vapor generation at low temperatures which can be used for seawater desalination [12]. Photochemical conversion has significant potential for photocatalysis, which is essential for a wide range of applications [13,14]. The interest in photochemical research has been generated by convergence of significant developments in engineering applications, such as electrical energy production, environmental restoration, and photocatalysts [15]. Among a variety of oxide semiconductor photocatalysts, TiO_2 has been confirmed to be one of the most suitable material for photocatalytic purification of polluted air and wastewater, particularly of organic contaminants with low concentration, due to its strong oxidising power and long-term stability [16,17]. As a photocatalyst, TiO_2 nanoparticles (NPs) have been attracting considerable attention, especially for the treatment of organic contaminants in water [18,19].

The excellent properties of TiO_2 NPs have been shown to be associated with their crystalline structure, size and morphology [20]. To study their photocatalytic performance, various morphologies and structures of TiO_2 NPs have been synthesised. For example, Dou et al. [21] have reported the preparation of TiO_2 NPs and investigated the effect of their morphology on their photocatalytic activity the removal of mercury in aqueous solutions. Zhang et al. [22] have reported that necklace-structured TiO_2/SnO_2 hybrid nanofiber photocatalysts could be prepared by the electrospinning method, resulting in increased photocatalytic activity. Zhuang et al. [23] reported a new insight into understanding the relationship between photoactivity, defects and heterogeneous catalytic reaction mechanisms. All of the aforementioned literatures illustrate that TiO_2 exhibits excellent catalytic properties for water purification under the solar illumination. This photochemical conversion process was accompanied by a photo-thermal conversion process, which has an effect on photochemical conversion [24]. A number of researchers have focused on the synthesis of nanomaterials with excellent light absorption properties to improve the photo-thermal conversion efficiency of solar devices. Jin et al. [25] investigated the photo-thermal conversion mechanism of gold NP-based

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solar volumetric receivers. Hogan et al. [26] synthesised gold nanoshells and elucidated a mechanism for photo-thermal conversion which is consistent with the Fourier law of heat conduction. Ni et al. [27] 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. Liu et al. [28] have revealed that the high temperature is favorable for solar energy storage and the heat regenerators are found to be the key to the overall system performance. It is worth mentioning that the photo-thermal conversion can be combined with a simultaneous purification process.

The separation of the TiO_2 NPs is a main bottleneck in spite of photocatalysis by TiO_2 NPs being efficient, which restricts the application of these photocatalysts for the treatment of wastewaters [29]. The NPs used for these applications must be able to be recovered and reused; otherwise, they can cause secondary pollution. These issues severely limit large-scale application of solar technology. Recently, magnetically assisted chemical separation has been shown to be a straightforward approach for removing heavy metals from aqueous solutions. Magnetic separation provides a workable approach for removing magnetic particles by applying external magnetic field appropriately, which can inhibit the agglomeration of nanoscale catalysts during their recovery and increase their stability [30]. For example, Ding et al. [31] have reported the controlled synthesis of $Fe_3O_4@SiO_2$ NPs via a reverse micro-emulsion method, which could be beneficial to biological and environmental applications. Fan et al. [32] have demonstrated that magnetic $Fe_3O_4@SiO_2$ NPs can potentially be used as an adsorbent and have also provided a simple and fast separation method for removing heavy metal ions from aqueous solutions. These studies have provided an approach to not only significantly reduce the material consumption, but also to avoid causing secondary pollution. However, to our best knowledge, there are a few publications to research the recovery speed and efficiency of nanoparticles in the application of solar energy, let alone enhance the recovery speed and efficiency of nanoparticles by control the magnetic field [29–32]. Compared to previous work [15,30], this study put forward a broader applicable method for recyclable photo-thermal conversion and purification, and establishes the relationship between the recovery efficiency of nanoparticles and the magnetic field.

In this work, we report the preparation of $Fe_3O_4@TiO_2$ NPs, which combine the properties of TiO_2 and Fe_3O_4 to provide a material which facilitates recyclable purification and separation. The $Fe_3O_4@TiO_2$ NPs can enhance the temperature of suspension to accelerate photocatalytic disinfection activity under different solar illumination power. Initially, the $Fe_3O_4@TiO_2$ NPs were characterised by Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and magnetic property analysis. Subsequently, the analysis of photo-thermal conversion combined photocatalytic experiments were carried out to study the degradation performance at different solar illumination intensities. We observed the photocatalytic performance of Rhodamine B (RhB) under visible light to investigate the photocatalytic degradation activity of the $Fe_3O_4@TiO_2$ NPs. Finally, we compared the separation of the $Fe_3O_4@TiO_2$ NPs at different magnetic field strengths to study the speed and separation efficiency of their recovery.

2. Materials and methods

2.1. Chemicals

Iron(II) chloride tetrahydrate, Iron(III) chloride hexahydrate, titanium(IV) fluoride, and ammonia solution were purchased from Aladdin Reagent (Shanghai, China). All the reagents were of the analytical reagent grade and used as received. Deionised water was used in all experiments.

2.2. Synthesis of $Fe_3O_4@TiO_2$ NPs

The synthesis of the $Fe_3O_4@TiO_2$ was carried out as follows. Typically, a solution containing $FeCl_2{\cdot}4H_2O$ (0.98 g) and $FeCl_3{\cdot}6H_2O$ (2.4 g), with a mole ratio of 1:2, was stirred vigorously for 10 min and subsequently purged with nitrogen to remove oxygen from the solution. Subsequently, the pH of the suspension was adjusted to 10.0 using a 25 wt.% NH_3H_2O solution. Thereafter the suspension was moved into a 100 mL flask in a water bath at a temperature of 80 °C for 30 min. The black precipitate was then washed with 50% ethanol by magnetic attraction. Subsequently, the Fe_3O_4 NPs were slowly mixed into a 4 mL 0.01 M TiF_4 solution which was stirred vigorously for 10 min. Later, the suspension was transferred into Teflon-sealed autoclave with 50 mL deionised water added. The autoclave was sealed and maintained at 180 °C for 48 h prior to being allowed to cool in ambient air. Finally, the final $Fe_3O_4@TiO_2$ NPs were separated from the reaction product by magnetic separation.

2.3. Characterisation

Scanning electron microscopy analysis was performed using a SUPRA 55 SAPPHIRE SEM (SEM, SUPRA 55 ZEISS, Germany) at an accelerating voltage of 20 kV [19]. Transmission electron microscopy patterns of the $Fe_3O_4@TiO_2$ nanoparticles were obtained using a field emission microscope (TEM, JEM-2010, Japan) [30]. The magnetic property images of the $Fe_3O_4@TiO_2$ NPs and Fe_3O_4 NPs were obtained using a vibrating sample magnetometer (VSM, MPMS SQUID, US) [19,30]. X-ray diffraction images were obtained by an X-ray diffractometer (XRD, D8-Advance Bruker, Germany) with a 2θ angle in the range of 20 to 80° at room temperature [19]. X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra, Japan) was undertaken by ESCA Laboratory MKII instrument with Mg KR radiation as the exciting source [30]. The specific surface area analysis, pore size and volume determination were obtained by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods (Quantachrome Autosorb-1C-VP, US) [33].

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 Au-Light Ltd. Co., China) and an electric scale (Practum313-1CN, Sartorius, Göttingen, Germany). The test chamber consists of an acrylic beaker

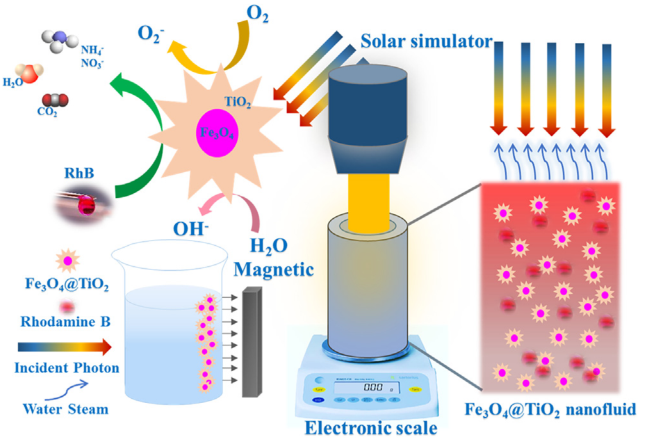

Fig. 1. Schematic of the experimental setup for solar recyclable purification systems.