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Monodispersed 3D $MnWO_4$–TiO_2 composite nanoflowers photocatalysts for environmental remediation

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ABSTRACT

Pollutants from textile industries into water-bodies have caused huge environmental hazards. The semiconductor mediated photocatalytic purification of polluted water is a promising environmental remediation technology. In the present study $MnWO_4$–TiO_2 composite nanoflowers endowed with efficient photocatalytic activity have been successfully synthesized by facile hydrothermal approach. XRD, SEM, TEM, EDX spectroscopy and UV-DRS were used to characterize the as-synthesized samples. The average size of composite nanoflower is ~2 μm while the nanorods constructing the nanoflowers had the average diameters of 90 nm. The photocatalytic activity of the $MnWO_4$–TiO_2 nanoflowers for the degradation of methyl orange (MO) in visible light was much higher than of pristine TiO_2 nanorods and $MnWO_4$ nanoflowers respectively. The superior photocatalytic activity could be attributed to the formation of a $MnWO_4$–TiO_2 heterojunction in the $MnWO_4$–TiO_2 nanoflowers.

1. Introduction

Synthetic dyes are widely used in many industries like textile, leather tanning, paper production, food technology, hair colorings etc. Azo dyes constitute the largest class of dyes used in industry. In the past few decades, the environmental problem due to the textile effluent has increased with the development of industries. It is estimated that approximately 10–15% of the dye is lost during the dyeing process. Due to large-scale production and extensive applications, synthetic dyes can cause considerable environmental pollution and are serious health-risk factors. These synthetic dyes not only impose a threat to microorganisms and aquatic life but also to human beings. The removal of such toxic contaminants is a major issue for the researchers and scientists [1]. Photocatalysis has emerged as most promising green technology for environmental remediation [2]. Over the past few decades TiO_2 has been regarded as an efficient photocatalyst for its high activity, chemical stability, non-toxicity and low cost. Therefore TiO_2, as photocatalyst have attracted much attention and has been extensively utilized for environmental remediation as well as in solar cells [3]. However, due to its large band gap (3.2 eV) and high photo-induced charge recombination its practical application and efficient solar energy utilization is restricted. Strategies have been developed to overcome the above mentioned limitations. Recently, the formation of heterojunction by coupling of two semiconductors with narrow band gap has attracted special attention to improve the efficiencies of photocatalysts owing to the synergistic effects. These heterogeneous/hybrid systems not only utilize more visible light, but also suppress the recombination of photogenerated electron–hole pairs. $MnWO_4$ is a narrow band gap semiconductor, which possess electronic and magnetic properties. Moreover, $MnWO_4$ has been reported as an active photocatalyst under visible light [4,5]. The heterostructural composite of two semiconductors can promote efficient electron–hole separation and thus improve the photoelectrochemical activity [6–12]. For instance, Kong et al. have

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synthesized the BiOBr–$ZnFe_2O_4$ heterostructures which were found to exhibit higher photocatalytic activity for the degradation of Rhodamine B than pristine BiOBr and $ZnFe_2O_4$ [13]. Theoretically, the photocatalytic reaction is considered to occur on the surface of photocatalysts [14], therefore the morphology and surface properties of the photocatalyst greatly influence the photocatalytic activity. In this article, we have described a facile and rapid hydrothermal approach without the use of any surfactant or/template for the synthesis of pristine TiO_2, $MnWO_4$ and $MnWO_4$–TiO_2 composite nanoflowers respectively. The photocatalytic degradation of MO dye has been studied over the surfaces of the as-synthesized TiO_2, $MnWO_4$ and $MnWO_4$–TiO_2 composite under visible light illumination. Experimental results clearly indicated that $MnWO_4$–TiO_2 nanocomposites exhibit efficient photocatalytic activity for the degradation of MO dye as compared to pure $MnWO_4$ and TiO_2. $MnWO_4$ have the advantages of good stability, high magnetic properties and suitability [15,16]. A magnetic photocatalyst allows easy recovery of the photocatalyst from the treated water by magnetic force without the need for further downstream treatment process. To the best of our knowledge, so far no work has been reported on the photocatalytic degradation of MO dye over the surface of $MnWO_4$–TiO_2 photocatalyst. Herein, we report the facile preparation of a semiconductor $MnWO_4$–TiO_2 composite and a plausible mechanistic degradation pathway was proposed for the complete mineralization of MO. The improved efficiency of as-synthesized nanohybrid $MnWO_4$–TiO_2 photocatalyst consisted of $MnWO_4$ and TiO_2 semiconductors is a splendid alternative for the elimination of toxic dyes from wastewater and simultaneously improve the quality of water.

2. Experimental

2.1. Photocatalysts preparation

Titania nanorods were prepared by sol–gel electrospinning method as described elsewhere [17]. Polyvinyl acetate (PVAc, Mw = 500,000 Aldrich, USA) solution (18 wt%) was prepared by dissolving PVAc in *N, N*-dimethylformamide (DMF, 99.5 assay, Showa Co. Japan) under magnetic stirring for 8 h at room temperature. 5 g of titanium isopropoxide (TIPP, 98.0 assay, Junsei Co. Ltd., Japan) was taken in a separate bottle and a few drops of acetic acid were added till the solution turn out to be transparent. Then 6 g of PVAc solution was mixed slowly into the solution under vigorous stirring. The final resulting solution was put in a 10 ml syringe and a voltage of 20 kV was applied to this solution. The as-synthesized nanofiber mat was initially dried at 80 °C for 24 h under vacuum and after that calcined at 600 °C for 2 h in air with a heating rate of 2 °C/min.

$MnWO_4$–TiO_2 composite nanoflowers were prepared by hydrothermal method using $Na_2WO_4.2H_2O$ and $Mn(NO_3)_2$ (Samchun Chemical Ltd.) as precursors. In brief, 1.65 g of $Na_2WO_4.2H_2O$ and 1.44 g of $Mn(NO_3)_2$ were dissolved separately in 50 ml of deionized water. Then both aqueous solutions were mixed slowly and the pH of resulting solution was maintained (~9.0) by adding liquid ammonia. Subsequently as-synthesized titania nanorods (25 wt%) were mixed in the final solution. The composite solutions were subsequently transferred into a Teflon-lined stainless steel autoclave (120 ml capacity), sealed and maintained at 180 °C for 24 h. The reaction mixture was cooled to room temperature. The obtained precipitate was washed with distilled water, separated by filtration and dried in an oven at 80 °C overnight. $MnWO_4$–TiO_2 composite nanoflowers were obtained as final product. Pristine $MnWO_4$ nanoflowers were also prepared using the same experimental procedure as described above for $MnWO_4$–TiO_2 without the supplementation of TiO_2 nanorods.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku/Max-3A X-ray diffractometer. Field emission scanning electron microscope (FESEM, JEOL JSM6700) was used to observe morphology of the pristine and composite samples. Energy dispersive X-ray (EDX) spectroscopy being attached to scanning electron microscopy (SEM) was used to analyze the composition of samples. The transmission electron microscopy (TEM) images were acquired using a JEOL JEM-2010 microscope. The photoluminescence (PL) spectra of the samples were measured at room temperature using the 325 nm line of a He–Cd laser at a power of 25 mW for excitation (Kimmon Koha, JP/IK 3302 R). The light absorbance of the samples was measured using UV–Vis diffused reflectance spectrum (UV-DRS, 525 Shimadzu).

2.3. Photocatalytic test

The photocatalytic degradation of MO was carried out using catalysts (100 mg) suspended in 100 ml of (10 ppm) MO aqueous solution under visible light irradiation. The stirred mixture was irradiated by a 150 W halogen lamp with a 400 cutoff filter. Prior to photocatalytic reactions, the suspension was magnetically stirred in the dark for 15 min to obtain a good dispersion and reach adsorption–desorption equilibrium between the organic molecules and catalyst surface. Aliquots were withdrawn from the suspension at specific time intervals and centrifuged immediately at 12,000 rpm. The variations in the concentration of the MO solution under illumination were monitored by UV–Vis spectrophotometer.

3. Results and discussion

Besides a number of advantages; the rapid developments of industrialization have resulted in certain hazardous effects on environment and human beings as well. Azo dyes have widely being employed for coloring and printing [18]. During the extensive production and use of dyes, the concentrated dye wastewater is drained into aquatic systems without being effectively treated. In recent years, semiconductor photocatalytic process has shown a great potential as economic, environmental friendly and sustainable treatment for wastewater [2]. Herein, well-designed high aspect ratio monodispersed 3D nanoflower clusters of $MnWO_4$–TiO_2 composite were synthesized by facile hydrothermal approach in the present study. The reaction parameters such as temperature, duration and suitable pH feasible to get consistent flower-like morphology were found to be 180 °C, 24 h and 9 respectively. The XRD spectra of the pristine $MnWO_4$, TiO_2 and $MnWO_4$–TiO_2 composite photocatalysts were shown in Fig. 1. The XRD pattern in Fig. 1a and b could be perfectly indexed as pure anatase structure for TiO_2 (JCPDS 89–4921) and the monoclinic structure for $MnWO_4$ (JCPDS 74–1497), respectively. The diffraction peaks of the $MnWO_4$–TiO_2 composite were sharp and intense, indicating the highly crystalline character of the nanoflowers (Fig. 1c). The characteristic peak of TiO_2 observed in Fig. 1c corresponds to the diffraction from (101) plan whereas all the other diffraction peaks correspond to the monoclinic $MnWO_4$. No impurity peak was found in $MnWO_4$–TiO_2 composites, suggesting that the composites have only two-phase composition: $MnWO_4$ and TiO_2.

Fig. 2 shows the SEM micrographs of the synthesized TiO_2 nanorods, $MnWO_4$ and $MnWO_4$–TiO_2 composite nanoflowers respectively at different magnifications. It can be clearly seen that the TiO_2 nanorods have uniform diameter size (Fig. 2a, b) and the diameter of nanorods was found in the range of 200–300 nm. Fig. 2c, d shows the SEM image of $MnWO_4$ uniform clusters of