Construction of TiO$_2$/ZnO Heterostructure for Photocatalytic Application

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Abstract. The double hierarchical nanostructure of TiO$_2$/ZnO were prepared by an effective way of combining electrospinning and the RF Magnetron Sputtering technique. In this work, the anatase TiO$_2$ nanofibers were prepared by electrospinning polyvinylpyrrolidone (PVP)/tetrabutyl titanate (Ti(OBu)$_4$) solutions on glass substrates followed by calcination at 500$^\circ$C, and then dense secondary ZnO nanorods were grown by magnetron sputtering technique. It shows that ZnO nanocrystals distributed on the TiO$_2$ nanofibers could serve as favorable hole channels and receptors for efficient separation of photoexcited charge carriers, which results in significantly enhanced photocatalytic performance of ZnO/TiO$_2$ heterostructure compared with TiO$_2$ nanofibers, and ZnO film. The presented approach is hoped to be applied to the construction of other photocatalytic systems.

1. Introduction

As a wide bandgap semiconductor, titania, exists in three different phases: anatase, rutile and brookite. As shown in previous literature the anatase titania is also found to have high photocatalytic detoxification and is extremely effective in the degradation of organic pollutants[1]. Its low cost and nontoxicity also makes it ideal for use in photocatalytic applications. Especially TiO$_2$ nanofibers exhibited greater photocatalytic activity for the decomposition of various dyes compared to bulk TiO$_2$ because of the small and uniform diameters, large specific surface areas and a high degree of structural order[2]. Typically, the electrospinning process is considered as an ideal way to prepare the nanomaterials with its low cost and convenience. The electrospinning process uses electrostatic attraction generated by the high voltage between a charged polymer and a grounded collector to produce Nano-fibers[3]. For TiO$_2$ nanofibers, the following calcination process at high temperatures is very important for obtaining uniform dimensions and high crystallinity nanofibers[4].

As known, the separation is an very important factor for the photocatalysis[5]. Thus, there is a formidable challenge leaves us for reducing quick recombination rate of photogenerated electron–hole pairs of TiO$_2$. As known, ZnO is an excellent n-type semiconductor exhibiting comparable efficiency for various photocatalytic reactions, which is also have been studied by lots of literatures[6]. But on the other hand, ZnO suffers from intrinsic drawback of photocorrosion, which greatly reduces its photoactivity and photostability[7]. As a meaningful
attempt, the research activities have been proliferated to construct the ZnO/TiO$_2$ nanocomposites to solve these problems[8]. Currently, research interests have centered around designing and synthesis of the ZnO/TiO$_2$ nanocomposites. The resultant hybrids usually exhibit much better catalytic performance than bare catalysts. Most ZnO/TiO$_2$ hybrids are in the form of nanoparticles due to their unique geometries. However, the catalytic performances of nanofibres are superior to those of spherical nanoparticles due to the relatively high specific area and unique nanoparticle alignment[9], which could cause efficient charge separation through interparticle charge transfer along the nanofibre framework, though those are hardly reported for constructing the ZnO/TiO$_2$ composites by (rf) magnetron sputtering.

In our work, the TiO$_2$ NF were prepared via electrospinning and high-quality zinc oxide films on TiO$_2$ NF are prepared by reactive radiofrequency(RF) magnetron sputtering. The structural and photocatalytic properties of TiO$_2$/ZnO heterostructure are examined through EDS, SEM, TEM, and UV–vis absorption spectra. What’s more, the mechanism of this heterojunction is studied.

2. Experimental

2.1 Chemicals and Materials

Polyvinylpyrrolidone(PVP)(MW=1,300,000), etrabutyl titanate Ti(OBu)$_4$, ethanol, glacial acetic acid, ZnO target with 99.95% purity.

2.2 Preparation of TiO$_2$ Nanofibers Via Electrospinning

The TiO$_2$-NF were electrospun from a solution of PVP/Ti(OBu)$_4$ solutions. Briefly, 0.75 g of PVP was added to 7.5 mL of ethanol and kept stirring for 2 hours[10]. Separately, 1.5 g tetrabutyl titanate was mixed with a 6 mL 1:1 by volume solution of acetic acid and ethanol, stirred 2h, and then mixed with the first solution. Then the solution was stirred for about 4 h followed by its immediate loading into a 10 mL plastic syringe having a stainless steel needle (20 gauges). The needle was connected to a high-voltage power supply that could generate DC voltages up to 15 kV[12]. The solution feed rate was maintained 1.0ml/h. The electrospun fibers were collected for several hours (~10 h) to make a thick mat on a rotating drum electrode which was wrapped with aluminium foil and placed ~15 cm away from the tip of the needle horizontally.

2.3 Synthesis of the ZnO/TiO$_2$ Hybrid Nanofibres

ZnO NPs were prepared on TiO$_2$ NRAs using a reactive RF magnetron sputtering system. High-purity ZnO target (99.999%) of 60 mm diameter and 5 mm thick was used as the sputtering target with a substrate -target distance of 4 cm. Magnetron sputtering was carried out in an argon(99.999%) gas atmosphere. The flow rates of Ar were maintained at 40sccm during the process of depositing[13]. In order to clean the target surface prior to ZnO deposition, the target was pre-sputtered for 30 min. During deposition, the working pressure was maintained at 1.0 Pa. The sputtering power was 150 W during deposition.

2.4 Characterization Methods

The microstructures of the samples were evaluated use EDS. The morphology was determined by SEM, TEM. The absorption spectra of the samples were obtained by using an UV–vis–NIR spectrometer.
2.5. Photocatalytic Activity

Photocatalytic activity of ZnO/TiO₂ nanocomposite fibers was evaluated by monitoring the photodegradation of methylene blue aqueous solution under UV light irradiation[9]. For the photodegradation experiments, 20 mg of ZnO/TiO₂ nanocomposite fibers was put in 50 mL of a 5 ppm MB aqueous solution[14]. The solution was stirred in the dark for 30 min to obtain good dispersion and reach adsorption–desorption equilibrium between the organic dye and the catalyst surface. Then under magnetic stirring, the mixed solution was irradiated UV light. The relative concentration of methyl blue in the solution was determined by comparing the UV–vis absorption intensity with that of the initial methyl orange solution at 464 nm.

3. Results and Discussion

![SEM images of the TiO₂, ZnO/TiO₂ nanocomposite fibers, TEM images of the ZnO/TiO₂ NF.](image)

Figure 1. a,b is the SEM images of the TiO₂, ZnO/TiO₂ nanocomposite fibers, TEM images of the ZnO/TiO₂ NF.

These TiO₂ nanofibers are smooth, bead-free and continuous which can be seen in Fig. 1a. ZnO nanoparticles were grown onto the surface of TiO₂ nanofiber after RF Magnetron Sputtering as secondary structure which can be seen in Fig.1b. ZnO nanoparticles are uniformly and strongly attached onto TiO₂ nanofiber surface. Fig. 1c indicates that ZnO nanocrystals were intimately distributed on the TiO₂ nanofiber to constitute a single composite in the fabrication process. Composition elements of the ZnO/TiO₂ heterostructure were demonstrated in the EDS pattern (Fig. 2), consisting of Ti, Zn, and O from hybrid nanocomposites.
Figure 2. EDS spectrum of the ZnO/TiO$_2$NF.

Figure 3. UV–vis absorption spectra of the TiO$_2$, ZnO, ZnO/TiO$_2$ NF.

UV–vis DRS are utilized to determine the optical properties of the samples. Fig3 shows that both TiO$_2$ and ZnO/TiO$_2$ hybrid nanostructure exhibit a pronounced adsorption band in the region spanning from 200 to 400 nm, which is ascribed to that the band gap of the TiO$_2$ is similar to ZnO.
As is shown in Fig. 4. The photocatalytic reaction was quick and the MB concentration became almost zero within 25min while the pure TiO$_2$-NF need 30min. It is found that ZnO/TiO$_2$ heterostructure exhibits remarkably superior photocatalytic activity. The enhancement of the photocatalytic performances may because the form of heterojunction, which could separate the photon-generated carrier to increase the photocatalysis. The high surface to volume ratio of electrospun TiO$_2$-NF is also an important reason. In this structure, the ZnO nanocrystals may increase surface area of the composite nanofibers and maintain a large interfacial contact area to favor a heterojunction effect.

Based on the above reason, the ZnO/TiO$_2$ heterojunction could exhibits an excellent photocatalysis.

4. Conclusions

In this study, we have demonstrated the combination of electrospinning and RF Magnetron Sputtering technique for preparing hierarchical metal-oxide nanoheterostructures. More significantly, the ZnO/TiO$_2$ hybrid system possesses excellent photostability and photocatalytic performances[15]. Consequently, it is hoped that the electrospinning combined RF Magnetron Sputtering technique in our work may open up a new avenue for exploring novel hierarchical photocatalysts for environmental remediation.

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References


