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A simple and facile route to synthesize anatase/rutile mixed phase TiO_2 nanofibers with superior photocatalytic performance

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Abstract: A combination of one dimensional nanostructure and optimized anatase/rutile mixed phase nanofibers were synthesized by an efficient route of electrospinning method to enhance the performance of photocatalytic activity. The structural properties of the mixed-phase TiO_2 nanofibers (MPTNF) were characterized by XRD and Raman spectroscopy. The morphological studies were investigated by scanning electron microscopy and transmission electron microscopy. The photocatalytic activity was evaluated by degradation of methyl orange (MO), a significant increase in the reaction rate was observed with MPTNFs under UV light irradiation. The results suggest that synergistic effect of anatase/rutile mixed phase with one dimensional nanostructure and the band alignment between the two phases of TiO_2 provided the subsequent improvement of adsorption capacity and the enhancement of catalytic efficiency.
Key words: nanofibers, electrospinning, photodegradation.

Introduction and Experimental

Considering the global scenario, environmental pollution and energy crisis have become serious issues to seek innovative solution to confront in human society. Until now, Titanium dioxide (TiO_2) has been considered one of the most promising photocatalysist semiconductor materials because of its nontoxicity, low cost and excellent oxidizing ability. In particular, 1D TiO_2 nanofibers have been extensively explored for several technological applications such as catalysis, gas sensing, lithium ion batteries and photovoltaic cells [1, 2]. The electrospinning technique is an excellent inexpensive method for producing nanofibers. TiO_2 occurs as two important polymorphs, the stable rutile and metastable anatase. Anatase titania is usually considered to be more photoactive than rutile [3]. Even so, rutile TiO_2 is thermodynamically stable phase and exhibits excellent physical and chemical properties which are better than those of anatase [4]. Despite its merits, the photocatalytic efficiency of the pure TiO_2 is quite limited, mainly due to rapid recombination of photogenerated electron−hole pairs within TiO_2 [5]. In this paper, we report mixed phase (anatase/rutile) TiO_2 nanofibers

(MPTNFs) prepared by an electrospinning technique. It is well demonstrated that the obtained nanofibers showed enhanced photocatalytic activity compare to the pure phase TiO_2 nanofibers.

Initially, 0.5 g of titanium tetraisopropoxide was dissolved in a mixture of 2 ml of ethanol and 2 ml of acetic acid to obtain a transparent yellow solution. One gram of polyvinylpyrolidone (PVP) was dissolved in a mixture of 10 ml of ethanol and 2 ml of N-N dimethylformamide (DMF) to control the viscosity. These two solutions was stirred for 10 min and loaded into a 2-ml syringe. The distance of 15 cm and a DC voltage of 20 kV were maintained between the tip of the needle and the collector. After electrospinning, the obtained fibers were calcined in air at 600 ˚C for 1 hr to form a mixed phase.

Results and Discussion

The phase and structure of the samples were determined by XRD as shown in Fig. 1(A). The diffraction pattern of MPTNFs can be assigned to the (101), (004), (200) and (204) crystal plane of pure anatase phase of TiO2 (JCPDS 21-1272), (110), (101), (111), (210), (211), (220), (002) and (310) planes of the rutile phase (JCPDS 21-1276) respectively indicating the mixed phase of TiO_2 nanofibers. To investigate further the crystalline quality of MPTNFs, Raman spectroscopy was recorded in the range of 100 to 1000 cm^{-1}, as shown in Figure 1 (B). The spectra shows four bands at 151, 425, 510 and 614 cm^{-1} corresponding to the E1g (anatase), Eg (rutile), A1g (anatase) and A1g (rutile) modes respectively and additionally, a broad band at 248 cm^{-1} due to second-order scattering feature [6]. Figure 1 (C) and (D) shows the morphology of as-spun nanofibers and calcined nanofibers investigated by FESEM. It can be seen that the surface of as spun nanofibers are very smooth with the average diameter of 150 nm and non-porous (Figure 1C). After sintering at 600ºC, (Figure 1D) the nanofibers surface became much rougher than the as-spun fibers and the average diameter of these MPTNFs shrank to 125 nm.

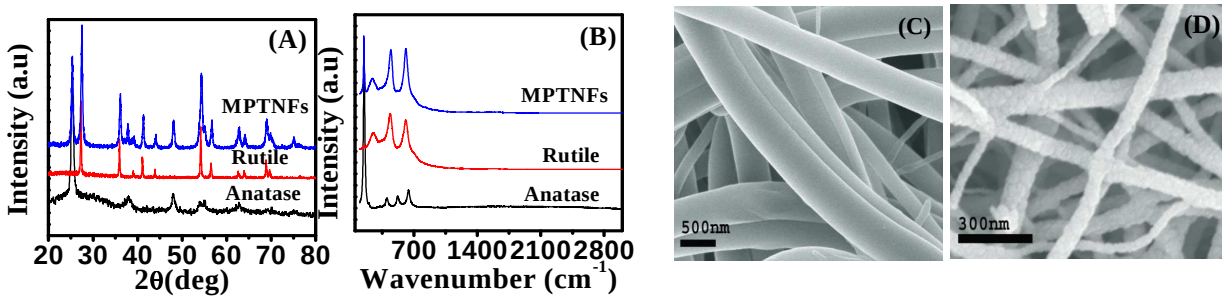

Fig. 1 (A) XRD pattern of anatase , rutile and MPTNFs. (B) Raman spectra of anatase, rutile and MPTNFs. (C) and (D) SEM images of the as-spun nanofibers and MPTNFs respectively.

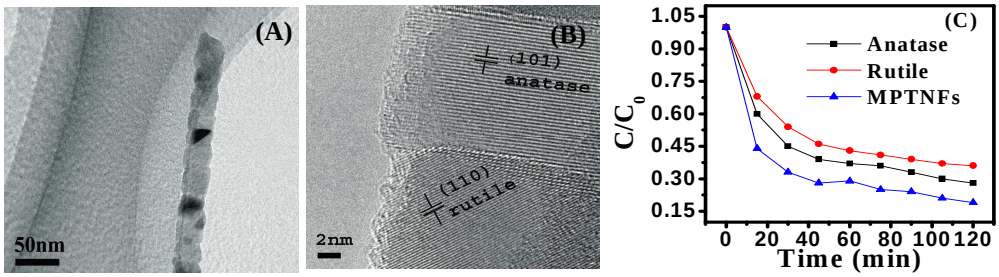

Fig. 2. (A) TEM and (B) HRTEM images of MPTNFs. (C) Photodegradation of MO, (C/C_0) as a function of irradiation time

To get more detailed information about the crystalline structure of MPTNFs, TEM and HRTEM observations were carried out and as shown in Figure 2 (A and B). Presence of lattice interplanar spacing of 0.35 nm corresponding to the (101) plane of anatase phase together with the interplanar spacing of 0.32 nm corresponding to rutile (110) plane of TiO_2 revealed the mixed phase nature of the nanofibers (Figure 2 B). The enhanced Photocatalytic performance of the samples was deduced from the degradation of methyl orange under irradiation of UV light as shown in the Figure 2 (C). The MO solution was found to be quite stable in the absence of a catalyst. The concentration of MO remaining after irradiation was 81 % in the presence of

MPTNFs. Energetically, the morphology and nature of the interface could promote electron transfer from rutile to lower energy anatase trapping sites. The trapping site of anatase has been shown to be 0.8 eV lower in energy than the anatase conduction band, which is below the conduction band of rutile [7]. In these case, recombination rate of photogenerated electron and hole pairs was delayed. As a result, more electrons are available on the surface to take part in the reaction process which results in the significantly higher photocatalytic capability of MPTNFs over anatase or rutile TNFs alone.

Conclusion

MPTNFs were synthesized by using simple electrospinning method. The mixed phase formation was confirmed by XRD and Raman investigation. Fibrous morphology and mixed phase was clearly evident from SEM and TEM analysis with HRTEM respectively. We achieved 81% photocatalytic degradation of MO by the MPTNF due to electron transfer in the rutile/anatase phase junction that migrated photoexcited charges between the two phases which lead to the efficient charge separation and as a result increase the photodegradation rate for potential use.

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