CARBON NANOFIBERS LOADED WITH Sm-DOPED TiO_2 FROM ELECTROSPUN POLYACRYLONITRILE/ TITANIUM OXOACETATE AS PHOTOCATALYSTS

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Introduction

Adsorption capacity and separation efficiency of electron-hole pairs are key factors affecting the photocatalytic property of TiO_2 and thus inhibiting its practical applications [1]. Dispersing TiO_2 nanoparticulates onto carbon nanofibers (CNFs) with large specific surface area and good adsorption ability [2,3] and doping with nonmetal [4,5] or metal elements [6,7] are considered as effective means to improve the photocatalytic property of TiO_2.

In this work, we choose the rare earth element of samarium (Sm) as a dopant and CNFs as supports to fabricate the Sm-doped TiO_2 nanoparticles dispersed onto CNFs (Sm-TiO_2/CNFs) from polyacrylonitrile/titanium oxoacetate composite nanofibers by using electrospinning technique and thermal processes.

Experimental

Two grams of PAN fibrils was dissolved into 18ml DMF with ultrasonic stirring to form a PAN solution. $Ti(OC_4H_9)_4$ (2ml) were mixed with a solution containing 2ml DMF, 2ml acetic acid and the $Sm(NO_3)_3$ with a mole percents of 1.5 relative to TiO_2. Then the mixed solution was slowly dripped into the pre-prepared PAN solution under magnetic stirring to obtain a homogeneous electrospinning solution, which was then electrospun at an electrostatic potential of 10 kV and a feed rate of 0.3-0.6ml/h. The as-spun nanofibers were stabilized in air at 250°C for 30min, hydrolyzed in deionized water for 2h, and finally calcined at 600°C in N_2 for 2h to fabricate CNFs loaded with Sm-doped TiO_2 nanoparticles as photocatalysts.

The morphology of samples was observed by field emission scanning electron microscope (FESEM, Hitachi S-4700). Energy dispersive X-ray (EDX) analysis was performed on an EDAX system attached to the same FESEM. X-ray diffractometer (XRD, Rigaku D/max 2500 VB2+/PC, Cu Kα) was used to study the crystal phases. X-ray photoelectron spectroscopy (XPS) spectra were obtained by a system (Thermo VG ESCALAB 250) with Mg Kα (1253.6eV) X-ray radiation source.

The photocatalytic activity of Sm-TiO_2/CNFs samples was investigated by the degradation of the methyl orange aqueous solution under UV light irradiation as described in our previous paper [8].

Results and Discussion

SEM and TEM images of Sm-TiO_2/CNFs (Fig.1) show that the CNFs with an average diameter of the order of 400nm are uniformly decorated with the Sm-doped TiO_2 nanoparticles (about 10nm), which can be determined by the XRD (Fig.2) and EDX results (Table. 1).

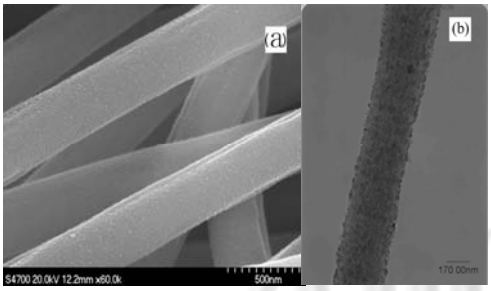

Fig.1 SEM (a) and TEM (b) images of Sm-TiO_2/CNFs

Table1. EDX Atom Percentage of TiO_2/CNFs and Sm-TiO_2/CNFs

Element (At%)	TiO_2/CNFs	Sm-TiO_2/CNFs
C	80.87	81.12
N	2.66	1.07
O	10.78	10.92
Ti	5.69	6.78
Sm	0.00	0.11

Compared the XRD pattern of Sm-TiO_2/CNFs with that of TiO_2/CNFs, we can find that the two samples both show diffraction peaks at 25.3°, 37.8°, 48.05°, 55.08°, 62.5°, which are ascribed to the (101)、(004)、(200)、(211) and (204) planes of anatase TiO_2, indicating that Sm-doping does little effect on the crystal phases but has slight effect on the sizes of TiO_2. The average grain sizes of TiO_2 calculated by Debye-Scherrer equation were about 13nm and 10nm for TiO_2/CNFs and Sm-TiO_2/CNFs, respectively, indicating that Sm-doping could hinder the increase of crystallite size during calcinations [7,8].

Fig. 3 shows the XPS spectra of O_{1S} in Sm-TiO_2/CNFs. There are at least two kinds of chemical states of O_{1S}, including crystal lattice oxygen (O_L) and adsorbed oxygen (O_H) with the binding energies at 530.4eV and 533.2eV, respectively. O_L is mainly attributed to the contribution of Ti-O in TiO_2 crystal lattice, and the O_H is related to adsorbed oxygen mainly induced by oxygen cavity resulting from the

chemisorbed water. It can be found that the proportion of O_H in Sm-TiO_2/CNFs increased comparing with that of TiO_2/CNFs, indicating that Sm-doping could increase oxygen cavity on TiO_2 surface, which can bring about improvement in the photoactivity by capturing photo-induced electrons and inhibiting the recombination of electrons-holes pairs effectively [7,8].

Fig.4 illustrates the photodegradation of methyl orange in the presence of Sm-TiO_2/CNFs under UV irradiation. It is clear that the photoactivity of Sm-TiO_2/CNFs improves remarkably in comparison with that of TiO_2/CNFs due to Sm-doping.

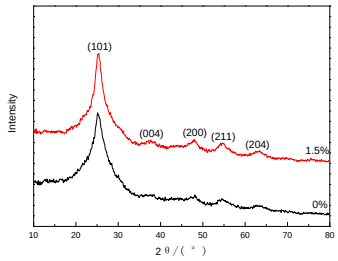

Fig.2 X-ray patterns of TiO_2/CNFs and Sm-TiO_2/CNFs

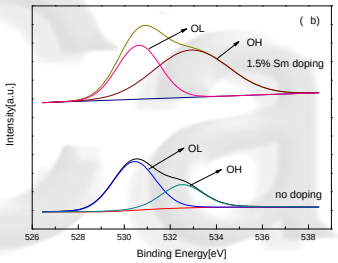

Fig.3 XPS patterns of O_{1s} of TiO_2/CNFs (no doping) and Sm-TiO_2/CNFs

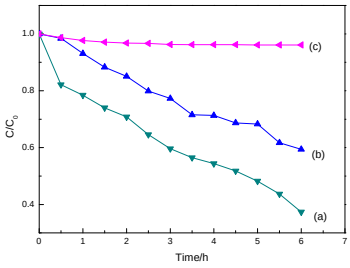

Fig.4 Photodegradation of methyl orange in the presence of Sm-TiO_2/CNFs (a), TiO_2/CNFs (b) and control (c) under UV irradiation

Conclusions

A heterostructured Sm-TiO_2/CNFs photocatalyst, with about 10nm of Sm-TiO_2 nanoparticles interspersed onto CNFs uniformly, can be prepared from electrospun Sm-doped $Ti(OC_4H_9)_4$/PAN nanofibers using stabilization at 523K in air, hydrolysis and subsequent carbonization at 873 K in N_2. The Sm-TiO_2/CNFs shows remarkable higher photocatalytic efficiency than TiO_2/CNFs as a result of Sm-doping, which can hinder the increase of crystallite size during carbonization.

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