Degradation of industrial dinitrotoluene wastewater by Bi-S-TiO_2/β-CD composites under UV light

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Abstract. The mesoporous Bi-S-TiO_2/β-CD was prepared by an evaporation induced self-assembly (EISA) method and photoinduced self-assembly method, and was characterized by UV-vis diffuse reflectance spectroscopy (UV-vis DRS), X-ray diffraction (XRD), Scanning electron microscopy (SEM), High resolution transmission electron microscopy (HRTEM). Experimental results indicated that β-CD attached on the surface of Bi-S-TiO_2 and Bi-S-TiO_2/β-CD exhibits better photoactivity than Bi-S-TiO_2 under UV light irradiation ($250<\lambda<$ 380 nm), which causes DNT completely mineralized within 5 h.

1. Introduction

TiO_2 as an environmental friendly photocatalyst attracted many attentions, because of its chemical stability, high photocatalytic activity, low cost and nontoxicity. However, TiO_2 can only be used for 4% of the available light due to its large band gap (3.2 eV). Furthermore, the high electron-hole recombination rate also makes it a relatively low efficient photocatalyst [1]. In order to overcome its disadvantages, methods have been applied, such as metal doped and surface modification. Some literatures reported the use of Bi element to improve the photoactivity of TiO_2, which is attributed to the introduction of Bi^{3+x} ions replace some of Ti^{4+}, and enhance the separation efficiency of charge carriers [2-4]. It is also widely reported that sulfated TiO_2 could increase its photoactivity, which may be due to the introduction of S^{2-} ions to replace some of O^{2-}, and inhibits the recombination of the photo electron-hole [5]. In the present study, the use of Bi element doped, sulfate ion impregnation and carbon materials modification were employed to tackle these drawbacks.

β-cyclodextrin (β-CD), a cyclic oligosaccharide, possesses an electronic and hydrophobic interior microenvironment in its cavity structure, which allows hydrophobic molecules to be easily trapped into its cavity by displacing water. Since it has a lot of hydroxyl groups, the exterior of its cavity is hydrophilic. The unique structure makes it easy to from inclusion complexes with a range of organic molecules. In recent years, β-CD immobilized TiO_2 composite has been widely used in wastewater treatment [6,7]. Feng et al. [8] reported that cyclodextrins can be attached to the surface of TiO_2 and form nanowires under continuous UV illumination. Subsequently, a large number of TiO_2-β-CD composite materials were used in wastewater treatment and the dye-sensitized solar cells, such as TiO_2-β-CD -MWCNT (Multi-walled carbon nanotubes) [9], β-CD-TiO_2-RGO(Reduced graphene oxide) [10], TiO_2-C_{60} [11], β-CD-functionalized Fe_3O_4@TiO_2 [12]. Therefore, modified with β-CD or TiO_2 for improving β-CD immobilized TiO_2 composite performance become one of most important research hotspots.

In this contribution, we used two strategies in synergy to improve photocatalytic performance of TiO_2 nanomaterials. Firstly, the sulfated ordered mesoporous Bi-TiO_2 were synthesized by an evaporation induced self-assembly (EISA) process and impregnated with the solution of

$(NH_4)_2S_2O_8$. Secondly, mesoporous Bi-S-TiO_2 composites modified by β-CD were prepared base on UV-induced self-assembly method. β-CD was proved to form 1:1 inclusion complexes with DNT molecules[13], the subject of this study is the photocatalytic removal process of dinitrotoluene wastewater, to elucidate the influence of β-CD on sulfated Bi-doped TiO_2 materials, and to evaluate the enhancement of the photo-degradation rates of dinitrotoluene under UV irradiation.

2. Experimental

2.1. Materials

β-CD was supplied by Sinopharm Chemical Reagent Co., Ltd. 1.5%Bi-S-TiO_2 was made by myself, the initial concentration of total nitrocompound is about 400 mg/L and the chemical oxygen demand (COD) is 3100 mg/L. The DNT wastewater was diluted with 10 times before the process of degradation.

2.2. Catalyst preparation

0.8 g of 1.5%Bi-S-TiO_2 and 4 g of β-CD were dissolved in 400 mL deionized water under ultrasonic treatment (sonicated) for 1 h. The suspension was irradiated under a 15 W UV lamp for 24 h with stirring. After a week, the supernatant liquid was removed and the solid phase was washed with an excess of deionized water. The sulfated 1.5%Bi-S-TiO_2/β-CD nanoparticles were dried under dynamic vacuum for 24 h at 60 °C.

2.3. Characterization

The UV-vis DRS spectra of powdered samples were recorded on a Shimadzu 365 UV-vis spectrophotometer between 200-800 nm. XRD patterns of powdered samples were performed on a high resolution powder X-ray diffractometer model Netherlands PANalytical X'Pert PRO MPD diffractometer with Cu Kα radiation as the X-ray source (40 kV, 40 mA, λ = 0.15406 nm). SEM images of powdered samples were obtained on FEI, QUANTA-250 microscope with an acceleration voltage of 5 kV.

2.4. Photocatalytic activity

The photodegradation of the DNT was under UV light irradiation at room temperature. A certain amount of photocatalysts were dispersed in 50 mL of 40 mg/L DNT aqueous solution in a 150 mL self-designed quartz photochemical reactor. Then the solutions were irradiated with a xenon lamp ($250 < \lambda < 380$ nm). Before irradiation, the suspension was continuously stirred in dark for 30 min to reach adsorption-desorption equilibrium. During irradiation, 2 mL of solution was taken out in a given time interval. The absorbance of DNT were measured by a 752 UV-spectrophotometer. The experiments were carried out according to Chinese national standard GB/4918-85.The degradation efficiency (D (%)) of DNT was measured by (Eq. (1)).

$$D\ (\%) = (A_0 - A) / A_0 \times 100 \quad (1)$$

Where A_0 is absorbency before irradiation; and A is absorbency after irradiation.

3. Results and discussion

3.1. UV-vis DRS Spectra

Fig.1. shows the UV-vis DRS spectra of the S-TiO_2, 1.5%Bi-S-TiO_2 and 1.5%Bi-S-TiO_2 samples. The absorption thresholds for the photocatalysts were obtained from the UV-vis DRS curves by extrapolating the tangent lines of the spectra. The band gap energy (E_{bg}) has been calculated using following equation:

$$E_{bg} = 1240/\lambda \quad (2)$$

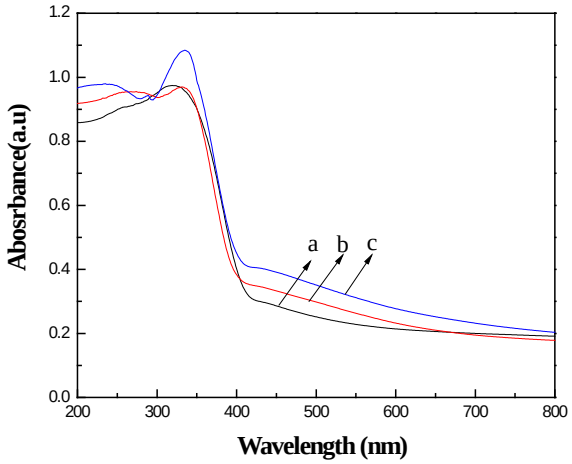

Fig.1. UV-vis DRS Spectra of a) S-TiO_2; b) 1.5%Bi-S-TiO_2; c) 1.5%Bi-S-TiO_2/β-CD

The band gaps calculated for S-TiO_2, 1.5%Bi-S-TiO_2 and 1.5%Bi-S-TiO_2/β-CD were found to be 2.81 eV, 2.74 eV and 2.67 eV. The band gap of 1.5%Bi-S-TiO_2/β-CD is smaller than the 1.5%Bi-S-TiO_2, which is attributed to the ligand to metal charge transfer (LMCT) between β-CD and Ti^{4+} located in an octahedral coordination environment. It is clear that the absorption ability of the photocatalyst is enhanced in the UV region, and the absorption edge shifts to the visible-light region (400~800 nm).

3.2. X-ray diffraction

The XRD patterns of β-CD, 1.5%Bi-S-TiO_2 and 1.5%Bi-S-TiO_2/β-CD are shown in Fig.2. The peaks close to $2\theta°$ of 25.3, 38.0, 47.9, 53.9, 55.1, 62.8, 68.9, 70.4, and 75.2 displayed by the XRD experiment demonstrated that the anatase TiO_2 in the TiO_2-detrxin wires conserve their anatase crystal features. No change in the phase of 1.5%Bi-S-TiO_2/β-CD from 1.5%Bi-S-TiO_2, which is due to no temperature involved in the preparation. The XRD results show that the 1.5%Bi-S-TiO_2/β-CD nanoparticles are highly crystalline.

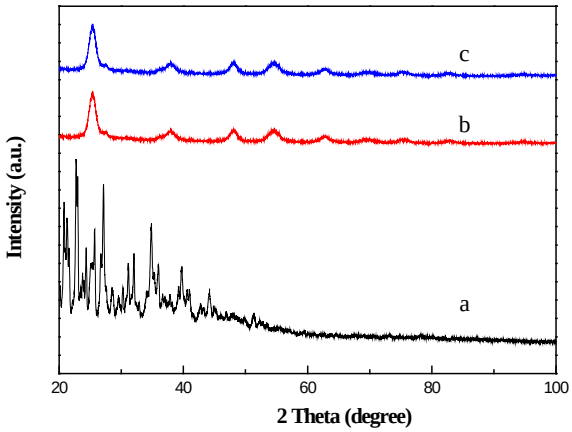

Fig.2. XRD images of a) β-CD; b) 1.5%Bi-S-TiO_2; c) 1.5%Bi-S-TiO_2/β-CD.

3.3. SEM

Fig.3. shows the SEM image of 1.5%Bi-S-TiO_2/β-CD. From the picture, it can be seen clearly that the particles are small, and the particles are independent.

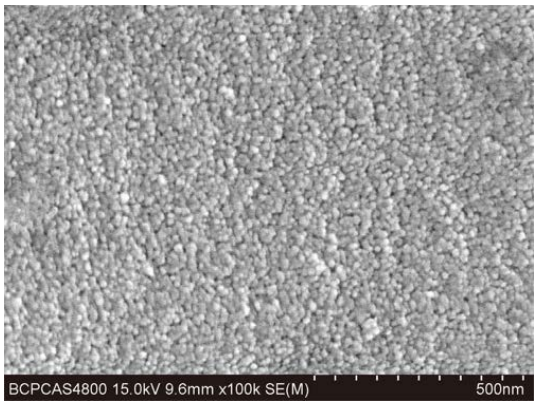

Fig.3. SEM images of 1.5%Bi-S-TiO_2/β-CD.

3.4. TEM

There was no change in the lattice structure of 1.5%Bi-S-TiO_2 after β-CD modification, which is according with the result of XRD patterns. However, the outer boundary of the 1.5%Bi-S-TiO_2/β-CD was distinctly different, and the HRTEM image was showed in Fig.4. The outer boundary of the 1.5%Bi-S-TiO_2/β-CD was coated by an amorphous carbon, which indicated that β-CD attached to the surface of 1.5%Bi-S-TiO_2 during the assembly process. The HRTEM image showed a highly crystalline anatase with the crystalline lattice of 0.36 nm. The average particle sizes of TiO_2 estimated from HRTEM image were around 10 nm.

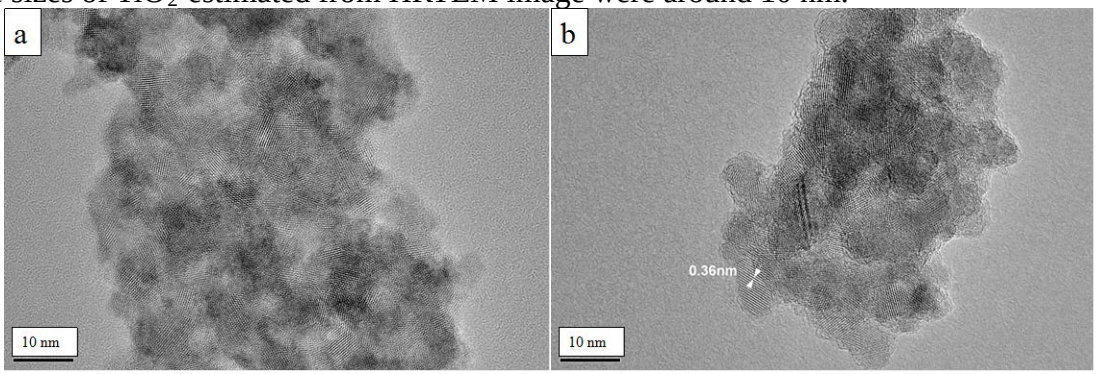

Fig.4. HRTEM images of composites.a) 1.5%Bi-S-TiO_2; b) 1.5%Bi-S-TiO_2/β-CD

3.5. Photocatalytic Activity Tests

As seen in Fig.5, The degradation efficiency followed the order by 1.5%Bi-S-TiO_2/β-CD > 1.5%Bi-S-TiO_2 > S-TiO_2 > blank. The optimum photocatalytic efficiency was observed in 1.5%Bi-S-TiO_2/β-CD, which caused 95.6% DNT degraded under UV irradiation. The enhanced photocatalytic activity could be attributed to β-CD could from 1:1 inclusion complexes with DNT molecules.

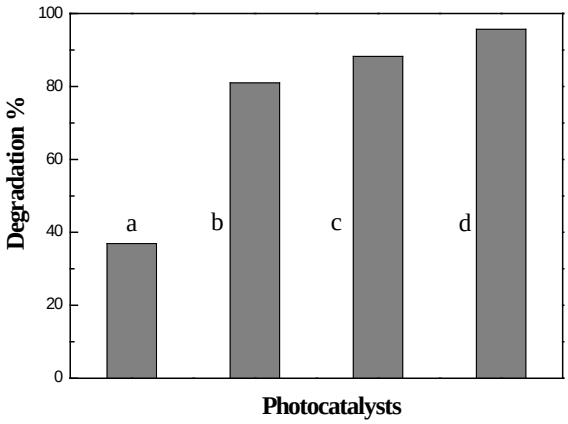

Fig. 5. Photodegradation of DNT using the different photocatalysts under UV light for 5 h. a) blank; b) S-TiO_2; c) 1.5%Bi-S-TiO_2; d) 1.5%Bi-S-TiO_2/β-CD.

4. Conclusions

1.5%Bi-S-TiO_2/β-CD nano composite was synthesized by EISA and photoinduced self-assembly method. The photocatalysts with anatase single-phase exhibit highly photoactive. It due to that the introduction of the Bi and S species in the TiO_2 lattice, which trap the electrons and facilitated the separation of the electron-hole pairs. β-CD could facilitate electron transfer from the excited DNT to TiO_2 conduction band. Their collaborative effects lead to the enhancement of photocatalysts light absorption. Further investigation of this composite material affecting a single type of pollutant is still in progress.

Acknowledgements

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