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Short Communication

The enhancement in photocatalytic activity of bismuth modified silica and bismuth silicate nanofibers

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ABSTRACT

We investigated photocatalytic and adsorption properties of silica (SiO_2), bismuth (Bi) modified silica and bismuth silicate ($Bi_4(SiO_4)_3$) nanofibers. Nanofiber average diameter was ~150 nm and length was several micrometers. The bandgap of SiO_2 decreased with increased Bi content and its value was 3.7 eV for $Bi_4(SiO_4)_3$. The Bi-modified photocatalyst (nanofibers) exhibited enhanced degradation efficiency as compared to pure nanofibers. The pseudo first order kinetic model explained the photocatalytic kinetics of the photocatalyst with rate constants of 0.081 min^{-1} and 0.406 min^{-1} for SiO_2 and $Bi_4(SiO_4)_3$ nanofibers, respectively.

1. Introduction

The discharged liquid effluents containing toxic dyes from industries have deleterious effects on aquatic life, human beings and microorganisms [1]. Chemical reaction, oxidation and hydrolysis processes taking place in contaminated water can produce dangerous products which are the source of eutrophication and non-esthetic pollution [2]. These dyes also inhibit the penetration of sunlight into contaminated water thereby affecting the photosynthesis and subsequently the productivity of autotrophs [3]. Therefore, removal of dye pollutant by traditional physical techniques and through the photocatalytic process has received increased attention.

SiO_2 is a low cost, non-toxic and an easily synthesized amorphous material. It has good adsorption performance but its wide bandgap limits its practical application as a photocatalyst. It is reported that the introduction of a small amount of impurities into amorphous materials improved its properties. Moreover, the insulating materials can be changed into electronically active materials by successful doping [4]. Bi is a narrow bandgap material (~2 eV.), which has a high adsorption co-efficient. It is expected that the incorporation of Bi^{+3} ions shift the absorption edge of SiO_2 from the ultraviolet to the visible region. Doping of metal ions [5] can enhance the photocatalytic activity of silica by narrowing its bandgap. The incorporation of Bi ions into SiO_2 acts as an electron donor material, which is beneficial for the oxidation of water to O_2 and the degradation of an organic pollutant to CO_2 under ultraviolet (UV) light [6]. Nanostructures are favorable for environmental remediation applications [7]. Here we report for the first time the effect of Bi on adsorption, the photocatalytic activity of SiO_2 nanofibers and the enhanced photocatalytic activity of $Bi_4(SiO_4)_3$ nanofibers in the degradation of cationic dye.

2. Experimental

Nanofibers were prepared using electrospinning as described in detail elsewhere [8] and were denoted as $xBi:(1-x)SiO_2$, where x is the molar ratio of Bi:Si. To investigate the photocatalytic activity of nanofibers, the photodegradation of MB was studied by using a homemade photo-reactor which was irradiated directly by a high pressure mercury lamp (200 W) (311 mW/cm^2). The experiment was performed at room temperature and the distance between the solution and lamp is 10 cm. With light on, an aliquot of 5 mL reaction solution was drawn after desired time intervals. The solution was centrifuged and filtered through a 0.5 μm filter paper prior to the photodegradation analysis. Tested samples were prepared by adding the 1.5 g catalysts to the 12.5 mmol/L concentrations of MB dye solutions; neutral pH was adjusted by using NaOH or HCl, and was regularly measured. The effectiveness of MB removal by catalysts was recorded for different pHs and contact times. The absorbance of the standard MB solution of different concentrations was determined using UV–visible spectroscopy (wavelength = 665 nm). The absorbance vs. concentration working curve was well fitted by regression equation $A = 3.28\ C + 0.02$. The equilibrium concentration of MB (mmol/L) was calculated using the working curve.

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3. Result and discussion

Transmission electron microscope (TEM) images reveal that SiO_2 and $Bi_4(SiO_4)_3$ nanofibers have a porous structure (Fig. 1(a) and (e)). Fig. 1(b)–(d) gives the rough estimation of the smooth surface of 0.01Bi–0.99SiO_2 nanofibers, 0.05Bi–0.95SiO_2 nanofibers and 0.1Bi–0.9SiO_2 nanofibers, respectively, at the same resolution. The TEM images indicate that the diameter of nanofibers is greater than 150 nm. The inset in Fig. 1(e) shows an SEM image of $Bi_4(SiO_4)_3$ nanofibers. The average diameter of nanofibers is ~150 nm and the average length of the nanofibers is ~150 μm. Fig. 1(f) shows the N_2 adsorption–desorption isotherms for SiO_2 and $Bi_4(SiO_4)_3$ nanofibers. The specific surface area of $Bi_4(SiO_4)_3$ nanofibers is less than that of SiO_2 nanofibers. The shape of the curves indicates that this is due to the decrease in the pore size of the $Bi_4(SiO_4)_3$ nanofibers.

Fig. 2(a) shows the XRD pattern of pure SiO_2 nanofibers and xBi–$(1-x)SiO_2$ nanofibers, where $x = 0.01$, 0.05, 0.1 and 0.5 were calcined at 600 °C. For pure SiO_2 one broader peak is observed indicating the amorphous nature of SiO_2 nanofibers. For xBi–$(1-x)SiO_2$ with $x = 0.01$ and 0.05 the SiO_2 crystalline structure is starting to become visible with the peak corresponding to (101) reflections at $2\theta = 25.5°$. The incorporation of Bi into SiO_2 causes a chemical disorder and causes a deviation from the short range structure in crystalline SiO_2 (0.01 and 0.05 Bi contents), which is also known as α-quartz (silicate). This may be due to the point defects from the localized state in the bandgap. This hypothesis can be confirmed by the reduction in bandgap energy with an increase in Bi contents (Fig. 2(b)). The occurrence of physical disorder in SiO_2 nanofibers is correlated with the replacement of the Si – O – Si bond with Si – O – Bi; this phenomenon is further analyzed by FTIR analysis in Fig. S1 [9,10]. Therefore, it can be concluded that the Bi ions can be incorporated into the SiO_2 lattice. With further increase in bismuth content, evident structural changes are observed in calcined nanofibers. A crystalline phase of Bi_2SiO_5 starts appearing when a Bi content of 0.1 is reached with the peaks corresponding to (011), (110), (102) and (111) at $2\theta = 25.16°$, 34.78°, 36.94° and 38.18°. But, at 25.46°, a peak that corresponds to the vestigial silicate SiO_2 also appeared (JCPDS; Card No. 00-036-0287). However, when the Bi content is 0.5, a well crystalline structure of $Bi_4(SiO_4)_3$ is achieved while the other phases of Bi_2SiO_5 decrease gradually. For $Bi_4(SiO_4)_3$, nanofibers with quite obvious peaks at 21.16°, 24.48°, 27.4°, 32.57°,34.89°, 43°, 44.9°, 51.79°, 55.03°, 56.60°,58.12°, 61.10°, 62.56°, 64.0°, 66.76° and 68.16° corresponding to the (211), (220), (310), (321), (400), (420), (422), (431), (530), (532), (620), (541), (631), (444), (543), (552) and (642) planes are observed, respectively. The structure can be considered as the reciprocal linkage of [SiO_4] tetrahedron and [BiO_6] octahedron in the space [11]. The XRD pattern of $Bi_4(SiO_4)_3$ is consistent with the JCPDS, Card No. 01-080-1596 of the crystalline cubic phase of $Bi_4(SiO_4)_3$.

Fig. 2(b) shows the UV–visible absorption spectrum of SiO_2 and xBi–$(1-x)SiO_2$ nanofibers, where $x = 0.01$, 0.05, 0.1 and 0.5. The inset represents the $(\alpha h\upsilon)^{1/2}$ versus hυ plots to measure the bandgap of nanofibers [12]. Where hυ is the photon energy and α is the absorption coefficient. The values of bandgaps are extracted from the inset by extrapolating the linear portion of the graphs. The indirect bandgap of SiO_2 nanofibers is 5.69 eV. It can be seen that as Bi content increases,

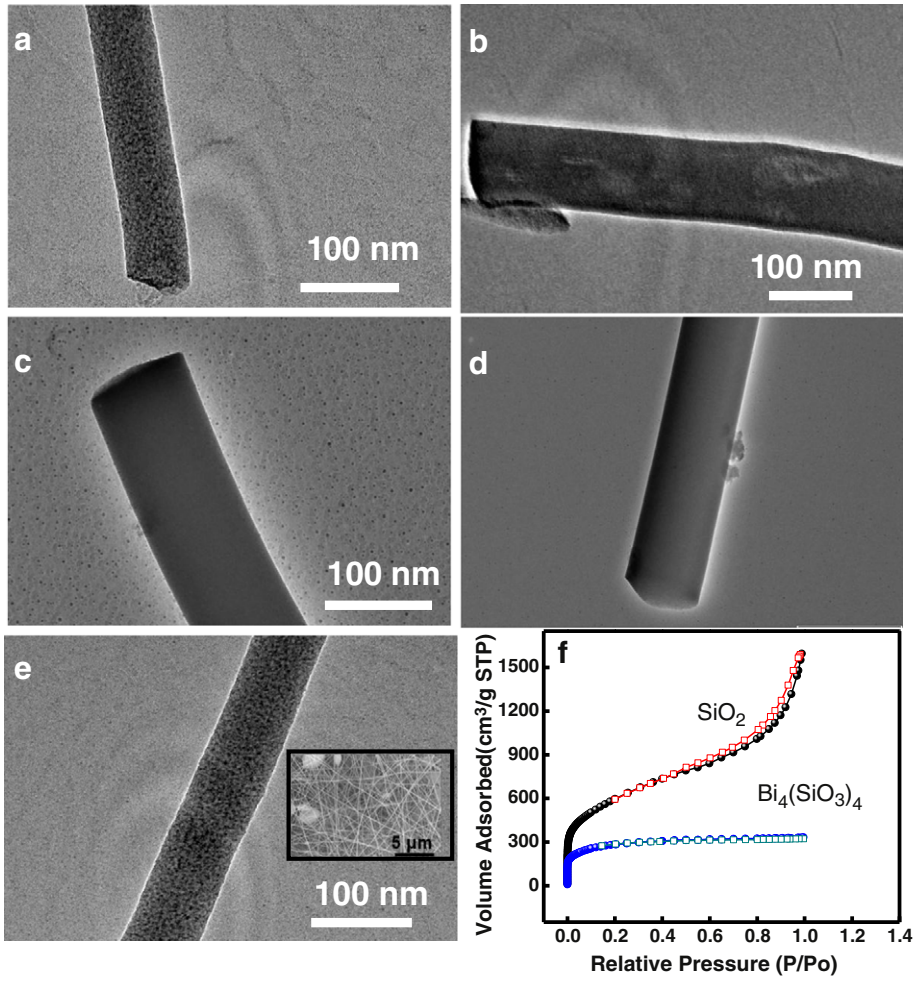

Fig. 1. TEM images of (a) SiO_2 nanofibers, (b) 0.01Bi–SiO_2 nanofibers, (c) 0.05Bi–SiO_2 nanofibers, (d) 0.1Bi–SiO_2 nanofibers, (e) $Bi_4(SiO_4)_3$ nanofibers and (f) N_2 adsorption–desorption isotherms. Inset shows SEM image of $Bi_4(SiO_4)_3$ nanofibers.