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Controlled synthesis of bismuth sulfide nanorods by hydrothermal method and their photocatalytic activity

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ABSTRACT

Bi_2S_3 nanorods with orthorhombic structure were successfully synthesized through hydrothermal method. Systematic experiments were accomplished to study the variable factors such as the Bi/S molar ratio, reaction time and reaction temperature, which have great impact on the structural morphologies of Bi_2S_3 and the photocatalytic performance. TEM and FE-SEM images reveal that the prepared Bi_2S_3 is flower-like built up from many nanorods with average 30–50 nm in diameter and 0.5–1 μm length. The optimal conditions for the preparation of Bi_2S_3 nanorods were Bi/S molar ratio 1/2 for 20 h at 180 °C to obtain the highest photocatalytic activity of ~98% towards methylene blue (MB) degradation. It is also found that the determined *k* values for Bi_2S_3 nanorods prepared at Bi/S molar ratio 1/2 was higher 40 and 5.5 times than that the samples prepared at either low or high Bi/S molar ratios 1/0.5 and 1/5, respectively.

1. Introduction

Metal sulfides are confirmed to be highly efficient photocatalysts because they have a broad light absorption and high charge, since photogenerated electrons and holes can speedily transfer to catalysts surface for oxidizing organic pollutants [1–4]. Metal sulfides have huge potential application such as photovoltaic cells, photodetectors, and photodegradation of organic pollutants under visible light and UV illumination [1–4]. Bi_2S_3 is a favorable semiconductor not only because of its chemical constancy and nontoxic components but also because of its large absorption coefficient about 105 cm^{-1} [5]. In addition, Bi_2S_3 has *n*-type semiconductor and large electron mobility for different applications [6]. It has been largely employed in photovoltaic cells, [7,8] medicine contrast agent, [9,10] biomolecule detector, [11] and photocatalyst [12–16]. The bandgap energy and separation and efficient transport of charge carriers of the semiconductors are the main factors for successful utilization of semiconductor nanoparticles in photoelectron transmutation devices. The Bi_2S_3 band edges are valuable for separation of charge carriers, and generation a defect-free interface [17–19]. In photocatalysis application under visible light and UV illumination, when the semiconductors subjected to light with the energy > the bandgap energy, electrons in the valence band of the semiconductor materials are excited to the conduction band, leaving holes behind the valence band. The photogenerated charge carriers can expeditiously derive photocatalysis by reacting with organic pollutants onto the semiconductors surface [18–22]. The process of photoelectron transmutation to obtain high photonic efficiency is extremely affected by morphology, particle size, phases and crystallinity. In recent years, a lot of efforts to get the ease synthetic routes for Bi_2S_3 nanostructures such as nanodots, nanorods, nanoflowers, and nanowires have been done [14–25]. It can be prepared by microwave-assisted, hydrothermal method, hot injection technique, ionic liquid-assisted, or solvothermal method [14–25]. There are different factors influencing the as-prepared Bi_2S_3 nanocrystals such as the precursor concentration, Bi:S molar ratio, reaction temperature and reaction time, which eventually influence the energy-level structure and optical absorption [24,26–28]. Although, the performance of Bi_2S_3 nanocrystals has been investigated in different applications [24], however, the effect of synthesis parameters on the morphology and phases of Bi_2S_3 nanocrystals and photocatalytic performances needs to be addressed. For this reason, in this contribution, one-step synthesis of Bi_2S_3 nanorods using thiourea as a source of sulfur was employed. The impact of experimental variables, such as the precursor concentration Bi:S molar ratio, reaction temperature and reaction time on the phase structure, morphology and photocatalytic performance of the prepared Bi_2S_3 photocatalyst have been systematically examined. The experimental findings indicated that the prepared Bi_2S_3 nanorods exhibited noteworthy photocatalytic activity for the photodegradation of MB at high concentration [50 ppm] at short time. The optimal conditions for the preparation of Bi_2S_3 nanorods

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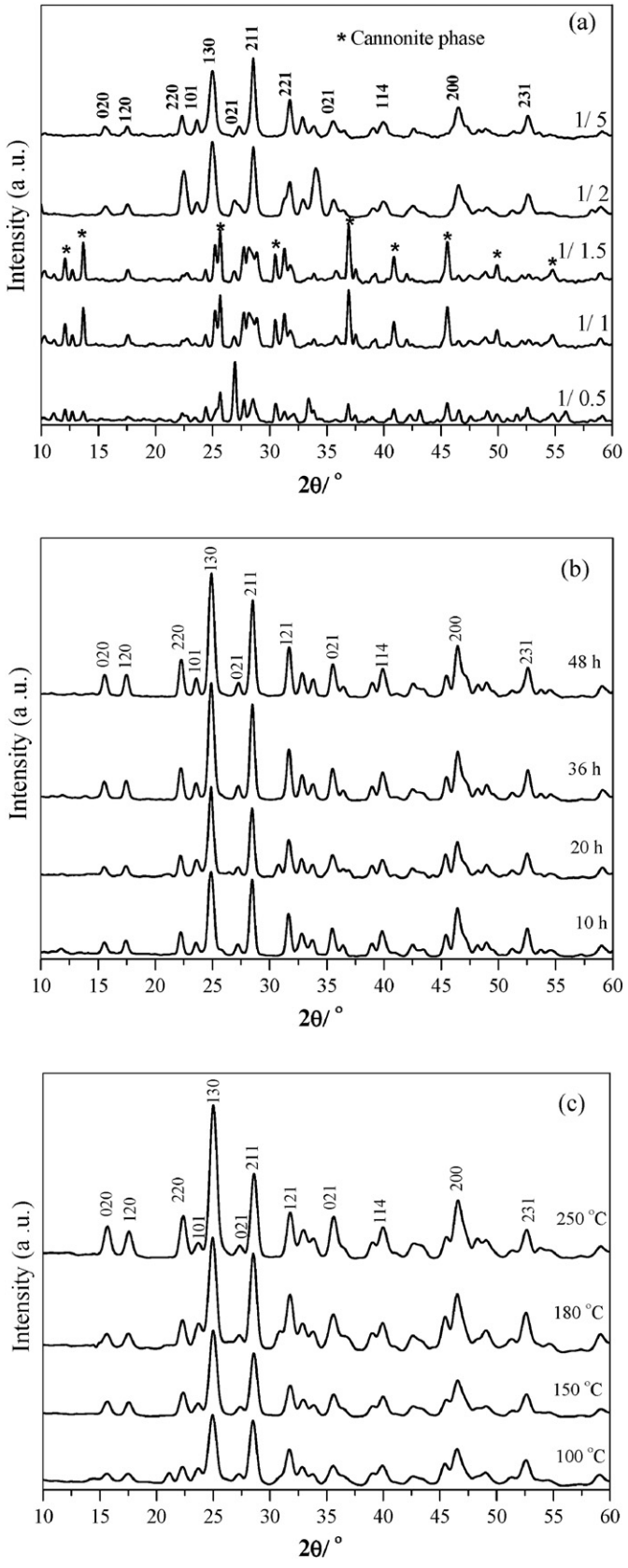

Fig. 1. (a) XRD patterns obtained from Bi_2S_3 nanorods prepared at different Bi/S molar ratios (1/0.5), (1/1), (1/1.5), (1/2) and (1/5) for 20 h. Reaction time at 180 °C reaction temperature, (b) effect of reaction time 10 h, 20 h, 36 h and 48 h on Bi_2S_3 prepared at Bi/S molar ratio (1/2) and 180 °C reaction temperature; (c) effect of reaction temperature of Bi_2S_3 nanorods prepared at 100 °C, 150 °C, 180 °C and 250 °C on its structure phase at Bi/S molar ratio (1/2) for 20 h reaction time.

Table 1
The relationship of reaction time-crystallinity and temperature-crystallinity of the prepared Bi_2S_3 nanorods on their photocatalytic activity.

Reaction time, h	Crystallinity, %	Photocatalytic activity, %
10	67.0	72.3
20	80.6	97.9
36	91.2	68.9
48	100	63.3
Reaction temperature		
100 °C	46	32
150 °C	73.0	87.4
180 °C	80.6	97.9
250 °C	98.8	90.9

were Bi/S molar ratio 1/2 for 20 h at 180 °C to obtain the highest photocatalytic activity of ~98% towards methylene blue (MB) degradation. The photocatalytic activity of the Bi_2S_3 nanorods prepared at Bi/S molar ratio 1/2 was superior to that of all synthesized samples and it exhibited high photocatalytic performance.

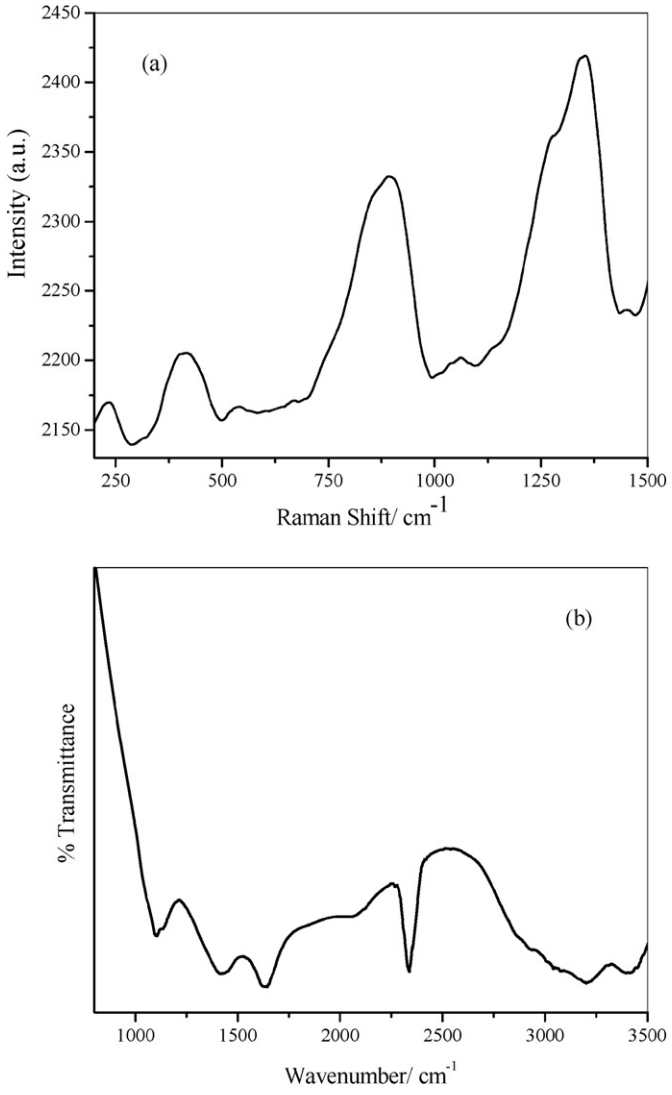

Fig. 2. (a) Raman spectroscopy of the optimized Bi_2S_3 sample obtained at Bi/S molar ratio (1/2) at 180 °C for 20 h; (b) FT-IR of the optimized Bi_2S_3 sample obtained at Bi/S molar ratio (1/2) at 180 °C for 20 h.