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Hydrothermal synthesis of coral-like palladium-doped $BiFeO_3$ nanocomposites with enhanced photocatalytic and magnetic properties

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A B S T R A C T

Coral-like palladium-doped $BiFeO_3$ (Pd/BFO) nanocomposite was synthesized via a simple two-step hydrothermal route. X-ray diffraction, UV–visible diffuse reflectance spectroscopy, field emission scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray and vibrating sample magnetometer were used to investigate the crystallinity, morphology, optical and magnetic features of the samples. The synthesized samples exhibited enhanced visible light photoactivity for the degradation of malachite green dye as compared to those of pure BFO and commercial TiO_2. The enhancement in the photoactivity was attributed to the formation of heterojunction between the Pd and BFO, which was beneficial for yield of highly reactive hydroxyl radicals as confirmed by photoluminescence-terephthalic acid test. Owing to the magnetic behavior of coral-like Pd/BFO, this nanocomposite can also be easily recovered by a magnetic field along with good reusability.

1. Introduction

Photocatalysis using solar irradiation offered green and energy saving technology for the destruction of hazardous pollutants. As one of catalyst materials, perovskite BFO has been garnered significant attention because of its visible light response (E_g = ~2.2 eV), low cost, chemical stability and ferroelectric as well as ferromagnetic properties [1–3]. Nevertheless, the narrow photo-response range and high recombination rate of photogenerated charge carrier limited its practical applications. Loading noble metal nanoparticles onto BFO surface is a good approach to circumvent the lapses. Such nanocomposites are expected to display enhanced photocatalytic performance due to the effective transfer of interfacial electron via the reduction of charge carrier recombination [4–6]. So far, noble metal doped-BFO nanocomposites including Ag/BFO [5], Pt/BFO [6] and Au/BFO [7] have been synthesized and they displayed improved activities. Various techniques such as sol-gel, co-precipitation, hydrothermal and ultrasonication have been utilized to fabricate the noble metal doped-BFO nanocomposites [4–6]. Among them, the hydrothermal method is widely applied in semiconductor nanostructures production due to its merits such as low energy requirement, high reactivity, relatively non-polluting set-up and ease of controlling of the aqueous solution [7–13].

In this work, a simple two-step process based on hydrothermal reaction was used to synthesize coral-like Pd/BFO nanocomposites. The coral-like structure formed by the hydrothermal technique can provide more active sites for photocatalytic reaction. To our knowledge, the Pd/BFO nanocomposites were not reported in early reports. Additionally, Pd has been chosen as active noble metal and it is relatively cheaper than platinum and gold [14,15]. The visible light photodegradation of malachite green (MG) based on the nanocomposites was evaluated and compared with those of pure BFO and commercial TiO_2. Furthermore, the magnetic behaviour of the nanocomposites can facilitate the separation of the catalysts from the aqueous solution.

2. Experimental

Details about the pure BFO and Pd/BFO nanocomposites preparation, catalyst characterization, photocatalytic measurement can be found in Supplementary Information.

3. Results and discussion

Fig. 1a depicts the XRD patterns of pure BFO and Pd/BFO nanocomposites. As for pattern of pure BFO, all diffraction peaks were well crystallized and agreed well with a rhombohedral phase (JCPDS 20–0169) [4,9], indicating that single crystalline BFO phase

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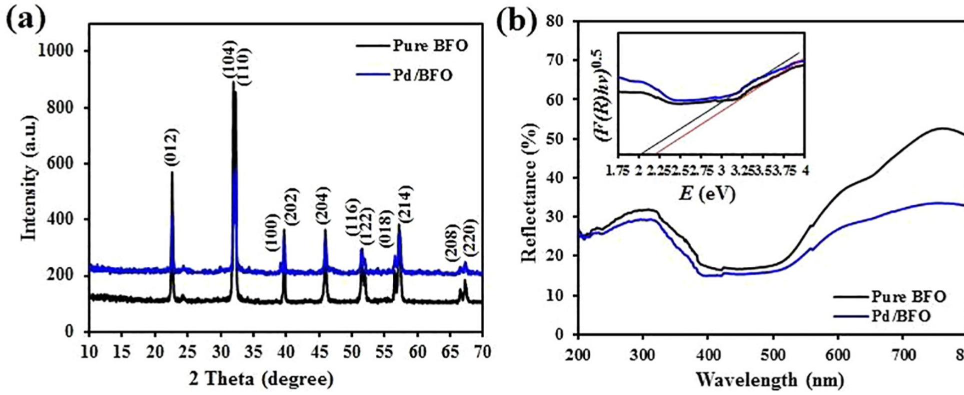

Fig. 1. (a) XRD pattern and (b) UV–vis DRS spectra of pure BFO and Pd/BFO nanocomposites. Insert of (b) is the plot of $(F(R)hv)^{0.5}$ vs $E(hv)$.

can be obtained by the hydrothermal process. Pattern for Pd/BFO exhibited negligible differences with that of pure BFO, most likely due to the small quantity of these dopants [6,10]. UV–vis DRS of the as-synthesized samples is displayed in Fig. 1b. In comparison to the pure BFO, Pd/BFO exhibited significantly enhanced absorption in visible light region ranging from 450 to 800 nm. This can be explained by Pd served as visible light absorbing sensitizer and center of charge carrier separation, which will benefit the photocatalytic activity of nanocomposites [14,15]. The band gap values were acquired from the Tauc plot obtained via transformation based on Kubelka–Munk (*K–M*) function ($F(R) = (1-R)^2/2R$), where *F(R)* is the *K–M* function and *R* is the reflectancy (%). The band gap values were determined by intercept of the $(F(R)hv)^{1/2}$ versus energy of light (E) as shown in inset of Fig. 1b. The measured band gap values were 2.23 eV and 2.03 eV for pure BFO and Pd/BFO, respectively. These values were consistent with the previous reports [16,17].

Fig. 2 displays the FESEM images of the samples. As shown in Fig. 2a and b, pure BFO had coral-like structure with diameters ranged from 110 to 130 nm and the addition of Pd did not change the morphology of coral-like BFO. The morphology and microstructure of the Pd/BFO were also characterized by TEM analysis (Fig. 2c). A large number of Pd nanoparticles were quite uniformly distributed on the coral-like BFO surface. The Pd particles showed quasi-spherical-shaped with sizes ranging from 15 to 27 nm. The FESEM and TEM analyses revealed the coral-like structure and tight contact interface of Pd/BFO. The elemental analysis of coral-like Pd/BFO was identified using the EDX (Fig. 2d). The Pd, Bi, Fe and O peaks can be easily observed. Furthermore, the EDX mapping of coral-like Pd/BFO is presented in Fig. 2e–h. The different color images indicated that the Pd, Bi, Fe and O elements enriched areas of the samples respectively, which confirmed the formation of coral-like Pd/BFO nanocomposites.

MG is a cationic triphenylmethane dye which widely used as a medical sterilizer, colouring agent and dye in different industries. The toxicological tests on MG identified its carcinogenic and mutagenic activities on warm-blooded animals [18]. Therefore, MG dye was selected as a model pollutant for the visible light photoactivity of the samples. Fig. 3a displays the absorption spectrum of MG solution in the presence of coral-like Pd/BFO at different durations. The absorption peak at 616 nm corresponded to the MG molecule became weaker with the extended irradiation time, indicating the MG degradation over the coral-like Pd/BFO. Fig. 3b shows that the degradation of MG reached 88.4% by coral-like Pd/BFO nanocom-

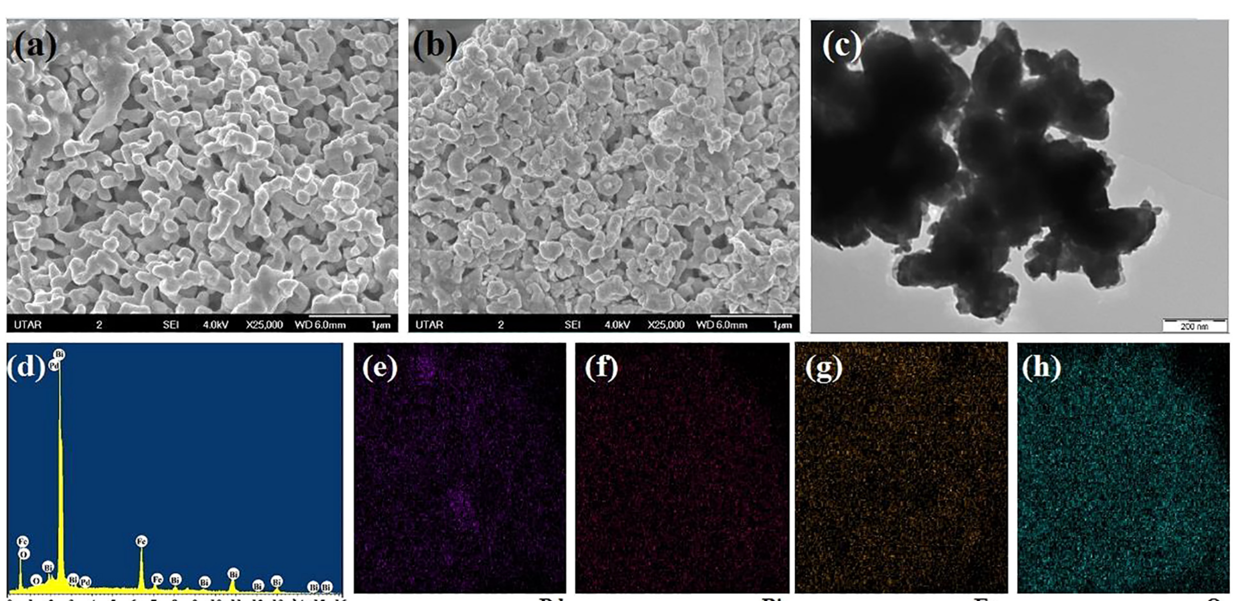

Fig. 2. FESEM images of (a) pure BFO and (b) Pd/BFO; (c) TEM image of Pd/BFO; (d) EDX spectrum of Pd/BFO and (e)–(h) EDX elemental mapping images of Pd/BFO nanocomposites.