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Enhanced photocatalytic performance of hierarchical $Bi_2O_2CO_3$ microflowers by Fe(III) modification

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ABSTRACT

Hierarchical $Bi_2O_2CO_3$ microflowers with Fe(III) clusters grafted on the surfaces were synthesized through a simple impregnation technique. The as-prepared samples were characterized by scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and UV–vis diffuse reflectance spectroscopy. The photocatalytic activity was evaluated by the decomposition of methyl orange in an aqueous solution under visible-light ($\lambda > 420$ nm) and simulated sunlight illumination. The results show that the Fe(III) clusters are just deposited on the surfaces rather than doped in the lattices of $Bi_2O_2CO_3$. It is found that the morphologies and crystal structures of $Bi_2O_2CO_3$ microflowers were not changed after modification of Fe(III) clusters. The photocatalytic activities of the Fe(III)-modified $Bi_2O_2CO_3$ were markedly increased by the modification of Fe(III) clusters under visible light and simulated sunlight irradiation. The enhanced photocatalytic performance can be attributed to the direct interfacial charge transfer from the valence band of $Bi_2O_2CO_3$ to the surface Fe(III) clusters, which offer a new channel for the efficient generation of the hole in the valence band of $Bi_2O_2CO_3$ substrate.

1. Introduction

Semiconductor-based photocatalysis, a promising method for solving energy and pollution problems, shows great potentials for solar energy conversion, hydrogen evolution, and degradation of organic pollutants [1–5]. Recently, bismuth-based oxides with Aurivillius-layered structure, such as Bi_2WO_6 [6,7], Bi_2MoO_6 [8,9], $BiVO_4$ [10,11], BiOX (X=Cl, Br, I) [12–14], and so on, have received a great deal of attention among various semiconductor photocatalysts due to their high photocatalytic activity. Bismuth subcarbonate ($Bi_2O_2CO_3$), as a typical member of Aurivillius-related oxide family, is composed of $Bi_2O_2^{2+}$and CO_3^{2-} layers, with the plane of the CO_3^{2-} group orthogonal to the plane of the $Bi_2O_2^{2+}$ layer [15]. Its tortile spatial structure was found to show unique photocatalytic properties under UV–vis light irradiation [16–18]. For instance, Zheng and co-workers first reported the synthesization of different morphologic $Bi_2O_2CO_3$ samples and their photocatalytic performance for degrading the organic pollutants under solar light [16]. Yang et al. synthesized egg-tart shaped $Bi_2O_2CO_3$ hierarchical nanostructures and investigated its photocatalytic properties for the degradation of Rhodamine B under UV light irradiation [17]. Su's group reported the fabrication of hierarchical $Bi_2O_2CO_3$ microspheres with high efficiency for the degradation of organic dyes under visible light irradiation [18]. However, $Bi_2O_2CO_3$ belongs to the wide-band-gap semiconductor and can only be excited by UV light (less than 5% of the solar light), restricting its practical application under solar light. Therefore, it is necessary to develop efficient strategies to increase the sensitivity of $Bi_2O_2CO_3$ to visible light.

To utilize solar energy efficiently, the doping of various anions (N, S, C, etc.) and cations (Fe, Cu, Cr, etc.) into the lattice of photocatalysts have been made to tune the band gap of photocatalysts to enhance the absorbance in visible light region [19–22]. These doped photocatalysts are sensitive to visible light because a localized narrow band above the valence band (VB) that originates from the doped ions was formed. However, these photocatalysts typically exhibit a much lower activity under visible light than under UV light [23]. Recently, It was reported that semiconductor photocatalysts grafted with some transition metal oxide nanoclusters, such as Fe(III) or Cu(II) nanoclusters, can also extend light absorption to visible light region without inducing impurity levels in the band gap and serve as visible-light sensitive photocatalysts [24–33]. When Fe(III) or Cu(II) nanoclusters were grafted onto the surface of photocatalysts, electrons in the valence band (VB) can be directly excited to these clusters via an interfacial charge transfer (IFCT) under visible light irradiation, leaving the holes with strong oxidizing power in the valence band to drive the degradation of organic pollutants. Moreover, these clusters can

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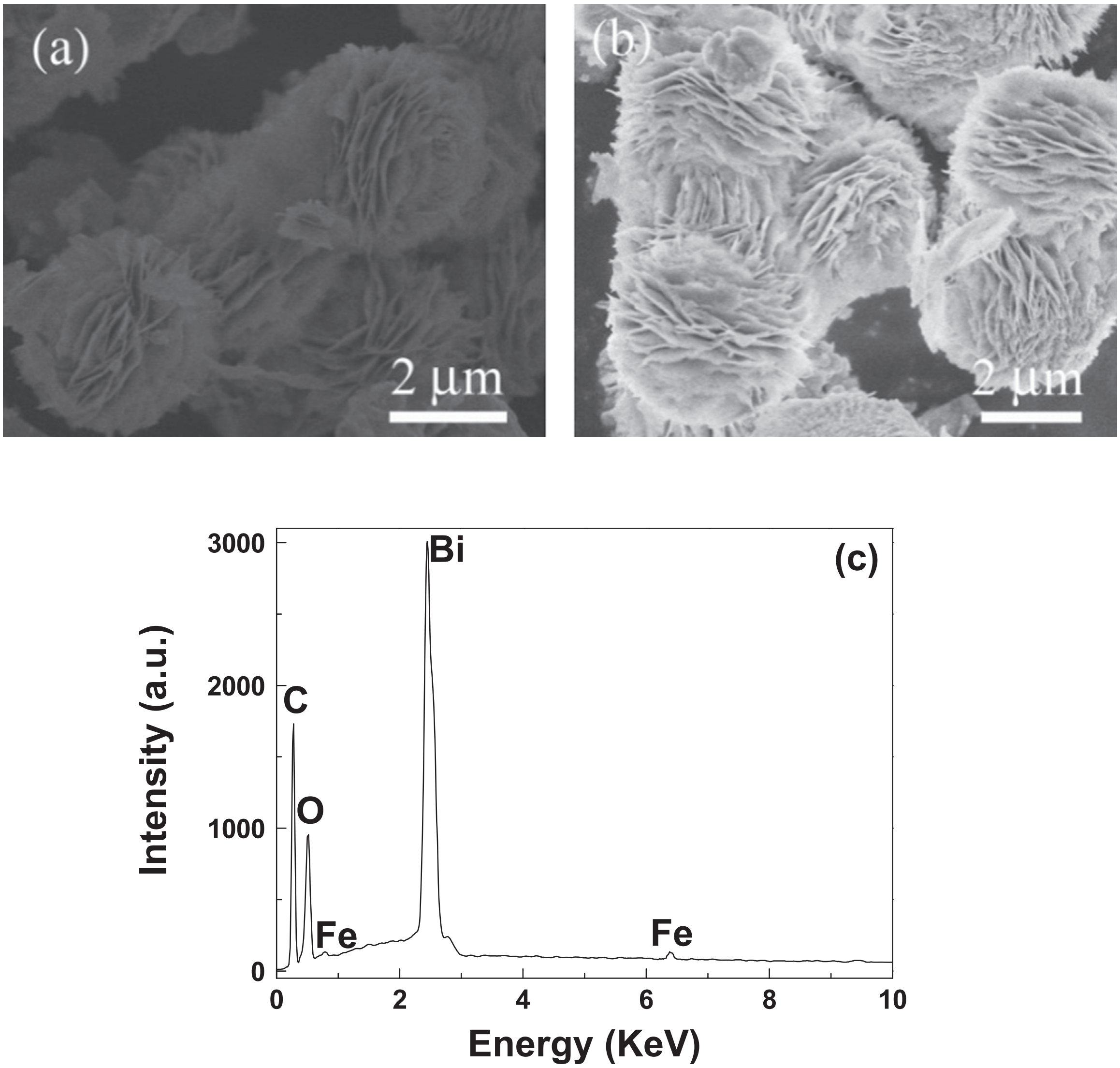

Fig. 1. SEM images of (a) pure $Bi_2O_2CO_3$ and (b) Fe(III)/$Bi_2O_2CO_3$ samples; and (c) corresponding EDX pattern of Fe(III)/$Bi_2O_2CO_3$ sample.

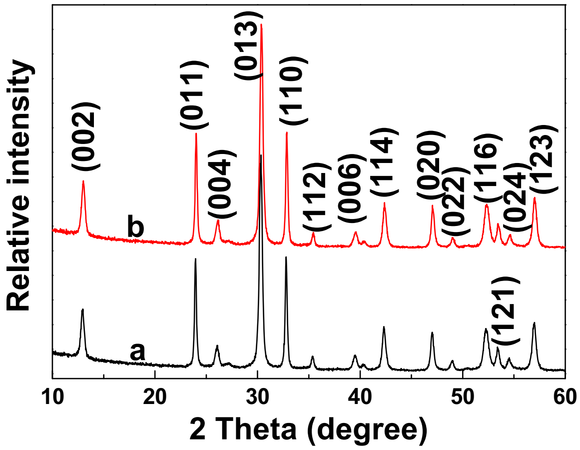

Fig. 2. X-ray diffraction patterns of (a) pure $Bi_2O_2CO_3$ and (b) Fe(III)/$Bi_2O_2CO_3$ samples.

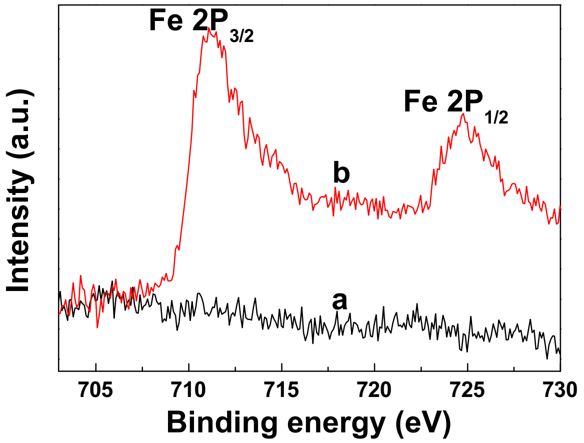

Fig. 3. The high-resolution XPS spectra of Fe 2p for (a) pure $Bi_2O_2CO_3$ and (b) Fe (III)/$Bi_2O_2CO_3$ samples.

mediate the multielectron reduction of oxygen molecules. Therefore, Cu(II) or Fe(III) nanocluster-grafted photocatalysts exhibits a high quantum efficiency under visible light.

In the present study, we, for the first time, investigated the surface grafting of Fe(III) clusters on the wide-band-gap $Bi_2O_2CO_3$. Fe(III)-grafted $Bi_2O_2CO_3$ exhibits an enhancement of photocatalytic activity under visible-light and simulated sunlight irradiation.