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Novel nanosized anatase TiO_2 hexagonal prism filled with nanoporous structure

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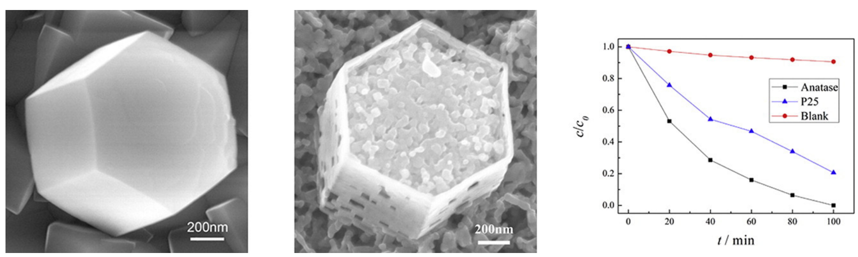
HIGHLIGHTS

- Novel nanosized hexagonal TiO_2 filled with nanoporous structure is synthesized.
- The hexagonal TiO_2 exhibits better photocatalytic property than commercial P25.
- Well-ordered geometry is facilitating rapid and long-distance charge transfer.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, we demonstrate the synthesis of a novel nanosized TiO_2 with the potential photocatalytic applications. Firstly, the hexagonal prisms were synthesized by dealloying TiCu amorphous alloy in HNO_3 solution containing F^- ions. These hexagonal prisms were composed of $(NH_4)_{0.3}TiO_{1.1}F_{2.1}$ wrapped with anatase TiO_2 shell. After calcination at 550 °C, the hexagonal anatase TiO_2 prisms filled with nanoporous structure were formed. The as-formed materials were characterized by field emission scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and UV–visible diffuse reflectance spectra (DRS). The formation procedure and mechanism were discussed. The as-formed hexagonal TiO_2 combines the advantages of well-ordered hexagonal prism and nanoporous structure, and then exhibits good photocatalytic properties. The unique nanostructure of hexagonal TiO_2 is expected to benefit as an advanced photocatalyst.

1. Introduction

In recent years, nanosized TiO_2 was regarded as one of the most promising materials because of its importance for environmental and energy-related applications [1–3]. The properties of TiO_2 are affected by their intrinsic electronic structure, crystalline phase, grain size and morphology [4–6]. Various kinds of TiO_2 with different morphologies have been reported, such as nanoflower, nanorod, nanowire and nanotube [7–9]. In our previous works, nanoporous TiO_2 was obtained by dealloying Ti-Cu amorphous alloys [10–12]. The dealloying method has the advantage of producing bicontinuous open nanoporosity extending in three dimensions. In comparison with crystalline alloys, amorphous alloys are considered as good starting alloy for dealloying due to their monolithic phase with a homogeneous composition and structure down to subnanoscale.

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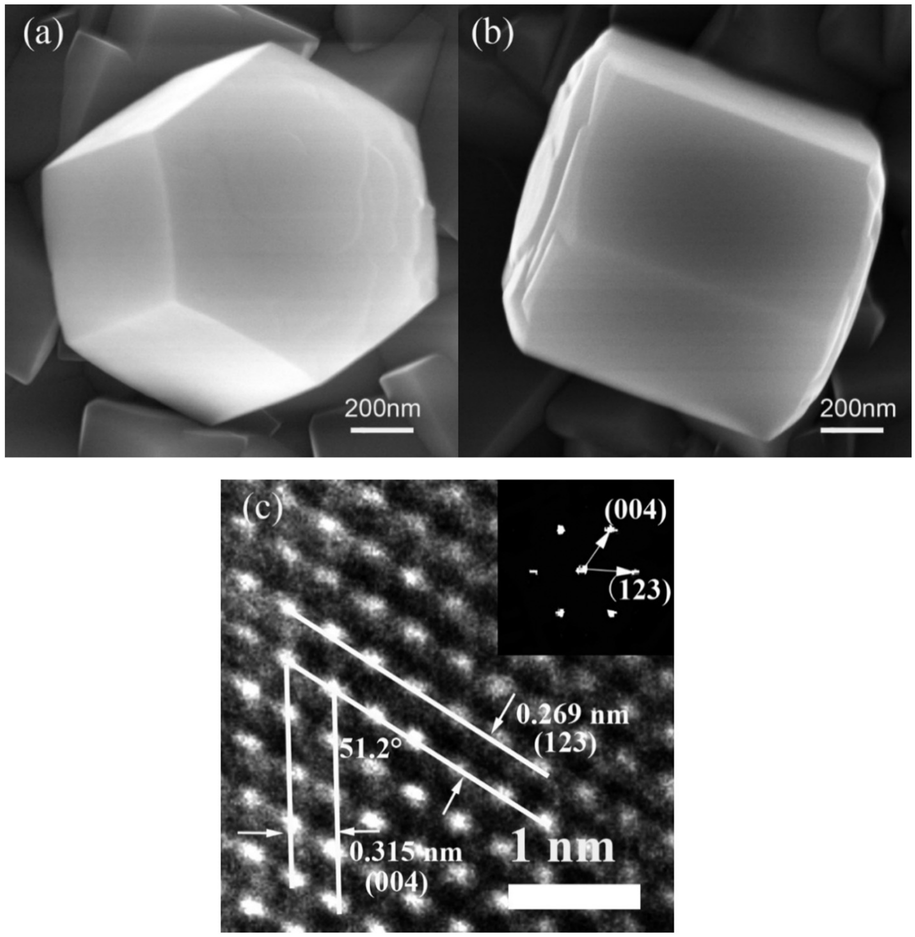

Fig. 1. Morphologies of sample subjected to dealloying for 10 h. (a) and (b) SEM images; (c) HRTEM image coupled with SAED pattern.

In general, fine structure could provide a large specific surface area. Well-ordered geometry of TiO_2 is facilitating rapid and long-distance charge transfer, furthermore improve the catalytic activity [13]. Hexagonal structure is a kind of well-ordered structure which was widely investigated for the ZnO catalytic materials [14,15]. Y. Alivov et al. reported a method for fabrication of pyramid-shaped TiO_2 using TiO_2 nanotube as the starting material [13]. Zhang et al. synthesized the TiO_2 hexagonal prism via a self-template route [16]. In the present work we report a novel nanosized hexagonal TiO_2 filled with nanoporous structure by dealloying TiCu amorphous alloy. This material combines the advantages of well-ordered hexagonal prism and nanoporous structure and exhibits good photocatalytic property.

2. Experimental methods

The TiCu amorphous alloy ribbons were used as starting materials. According to our previous experiments, too high Ti content, such as higher than 70 at.%, in the alloy would result in the dense passive film and depress the further reaction. After many attempts, $Ti_{40}Cu_{60}$ is considered as the appropriate composition to product good microstructure of the catalyst. The preparation of $Ti_{40}Cu_{60}$ amorphous alloy ribbons had been described in Ref [12]. $Ti_{40}Cu_{60}$ amorphous alloy ribbons were immersed in 14.3 M HNO_3 solution with F^- concentration of 0.1 M (by adding NaF) in a Teflon-lined stainless steel autoclave. The reaction was carried out at 70 °C for 10 h. Original $Ti_{40}Cu_{60}$ amorphous ribbon

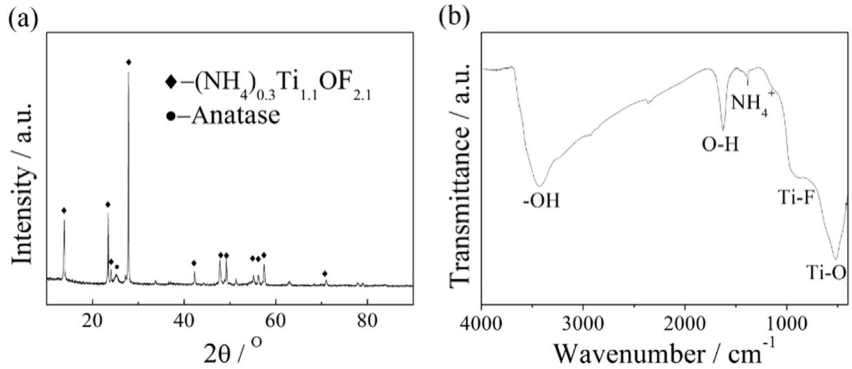

Fig. 2. XRD pattern (d) and FTIR pattern (e) of sample subjected to dealloying for 10 h.