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Facile preparation of Ti^{3+} self-doped TiO_2 microspheres with lichi-like surface through selective etching

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ABSTRACT

A novel composite $Al(acac)_3$/Al-TiO_2 is synthesized via facile flame thermal method and Ti^{3+} self-doped TiO_2 microspheres with lichi-like surface is prepared by selective etching the composite with HCl. The samples are investigated by scanning electron microscopy (SEM), inductively coupled plasma-atomic emission spectrometry (ICP), X-ray diffraction (XRD), electron paramagnetic resonance (EPR) and X-ray photoelectron spectra (XPS), respectively. SEM shows that microspherical TiO_2 with lichi-like surface is obtained and the rough surface is resulted by etching $Al(acac)_3$ in the composite, which is further confirmed by ICP and iodoform reaction from the characterizations to the etching solution. EPR and XPS indicate the presence of Ti^{3+} on the surface of the microspheres after HCl etching. The XPS results also imply that Ti^{3+} may be formed by removing the partly doped Al in the resulted samples. No reducer or reducing condition are needed through the whole synthesis procedures and it would be a new strategy for the preparation of nanostructured TiO_2.

1. Introduction

TiO_2 is a promising semiconductor since its extensive applications such as producing H_2 from water, electricity production and environment purification. Recently, Ti^{3+} self-doped TiO_2 has been a new and hot point in element doped TiO_2 due to its ability being excited by visible light as well as good electronic conductivity [1,2–4]. The common approaches to prepare Ti^{3+} self-doped TiO_2 contain reducing Ti^{4+} with strong reducers, such as $NaBH_4$ [2] and Zn [3] or by CO and NO at 500–600 °C [4]. These techniques involve long reaction time, complex equipment or strong reducers. Moreover, it is reported that the Ti^{3+} produced by reduction on the surface can be easily oxidized in air and water [5]. Methods have also been proposed in order to keep the stability of Ti^{3+} in TiO_2 [1,6]. Wang et al. [1] used H_2O_2 to oxidize TiH_2 from Ti^{2+} to Ti^{3+}, extending the lifetime of Ti^{3+} by maintaining some Ti^{2+} left while Morra et al. [6] depicted that Ti^{3+} is stable if the system has a similar component to Ziegler–Natta Catalyst.

In this work, we proposed an environmentally friendly two-step approach to prepare Ti^{3+} self-doped TiO_2 microspheres with lichi-like surface through reduction-free route. Firstly, the composite $Al(acac)_3$/Al-TiO_2 microspheres were prepared by facile flame thermal approach and then the doped Al and composited $Al(acac)_3$ in the samples are removed by selective etching with HCl.

2. Materials and methods

Tetrabutyl orthotitanate (98%, TBOT), absolute ethanol(AR) and aluminium acetyllacetonate (98%, $Al(acac)_3$) all from Sinopharm Chemical Reagent Co. Ltd were used as received. $Al(acac)_3$/Al-TiO_2 powders were prepared via a facile thermal method. Briefly, a mixture of 35 ml of ethanol, 5 ml of TBOT and desired amount of $Al(acac)_3$ were stirred and formed a stable and clear solution. A match was used to ignite the solution and gray powders were obtained after burning. Then, 6 ml of HCl solution (0.1 mol/L) was added to the each sample and maintained for 24 hours. The powders were washed by water for eight times and $AgNO_3$ solution was used to make sure no Cl^- was remained in the samples. Finally, the samples were dried in oven at 60 °C for 48 h. The sample are labeled as X-BH and X-AH, X represents molar ratio of Al to Ti in the sample, BH and AH mean before and after HCl etching treatment, respectively.

The morphology and microstructure were characterized by PHILIPS-XL30FEG SEM. X-ray diffraction (XRD) analysis carried on a Bruker D/8 advanced diffractometer which used Cu Kα radiation was analyzed to identify the phase composition of the resulted samples. The presence of Ti^{3+} was proved by X-ray photoelectron spectroscopy (XPS) on RBD upgrated PHI-5000C ESCA system and EPR on Bruker EMX-8/2.7 at X-bond microwave. To confirm the component of the composite, 100 ml HCl (0.1 mol/L) mixed with Sample 5-BH was stirred for 24 h and the etching solution by centrifugation was reserved for ICP measurement and iodoform reaction. The amount of Al is measured by ICP on HITACHI P4010

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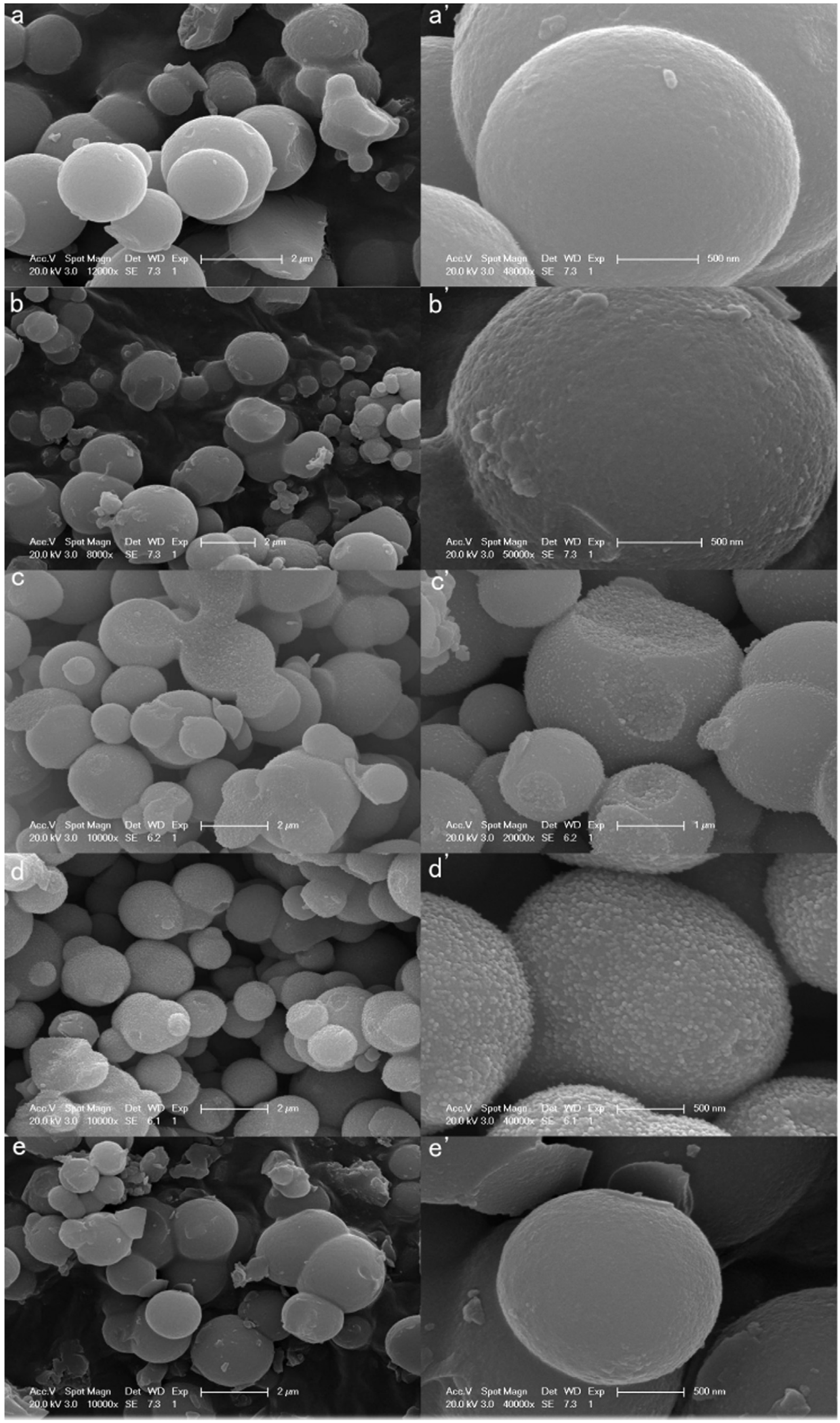

Fig. 1. SEM images of TiO_2 samples with different Al-Ti molar ratio after HCl etching treatment (a) 0-AH (b) 0.5-AH, (c) 1-AH, (d) 5-AH, and before HCl etching treatment (e) 5-BH as well as (a' b' c' d' e') are their corresponding enlarged view.