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Facile synthesis of urchin-like ZnO hollow spheres with enhanced electromagnetic wave absorption properties

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ABSTRACT

Urchin-like ZnO hollow spheres were synthesized by a simple hydrothermal method and their electromagnetic and microwave absorbing properties were investigated. The enlarged SEM image shows that as-prepared ZnO precursor is composed of randomly close-packed porous nanosheets. On the contrary, well-crystallized ZnO spheres are obtained after calcination. The TEM images provide further insight into the detailed structure, showing the typically urchin-like and hollow morphology of ZnO calcined at 500 °C. The SAED pattern clearly demonstrates the single-crystalline feature of urchin-like ZnO hollow spheres. It can be found that the urchin-like ZnO calcined at 500 °C exhibit relatively higher EM wave absorption properties than others. The maximum RL is up to −20 dB at 14.3 GHz and the EM wave absorption shows dual peaks with increasing thickness.

1. Introduction

Along with the increasing use of gigahertz (GHz) electromagnetic (EM) waves in industrial, commercial, and military applications, new EM wave absorbing materials with properties such as wide frequency range, strong absorption, relative lightweight, and high resistivity have aroused growing attention. The nanostructured materials have attracted great interest as microwave absorbing and shielding materials in the high-frequency range due to their many unique chemical and physical properties [1].

Hollow microspheres have been extensively researched and applied in various fields, such as gas sensors, catalysts, and lithium ion batteries [2–4]. Recently, some researchers have been focused on ZnO, which can be used as microwave absorbing materials motivated by their lightweight and semiconductive properties and also by the fact that their large-scale synthesis can be easily realized [5]. ZnO is probably the richest family of nanostructures among all materials, both in structures and in properties; however, the influence of the morphology of ZnO nanostructures on absorption has not been studied, and the mechanism of absorption has still been puzzling researchers so far. Thus, it is necessary to study the novel properties of these unique nanostructures and the intrinsic reasons for microwave absorption of the ZnO nanocomposites.

In this letter, we report that the synthesis of urchin-like ZnO hollow spheres, formed by accumulation of ZnO nanoparticles, combining the merit of micro-porous structure with the high surface area of nanoparticles. Moreover, the effects of urchin-like ZnO hollow spheres on EM wave absorption properties are evaluated by the subsequent dielectric measurement. The enhanced reflection loss (RL) mechanism for the ZnO hollow spheres is also discussed.

2. Experimental

Urchin-like ZnO hollow spheres were prepared by a hydrothermal approach using zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) as a zinc source. In a typical synthesis, glucose monohydrate ($C_6H_{12}O_6 \cdot 6H_2O$, 20 mmol), 40 mmol zinc nitrate and urea ($CO(NH_2)_2$, 40 mmol) were dissolved in 15 ml of deionized water under stirring. The above two solutions were mixed immediately before the experiment and placed in a 50 ml capacity Teflon-lined stainless steel autoclave, which was heated in an oven at 180 °C for 20 h. After hydrothermal treatment, the black precipitates were centrifuged, and then with deionized water and absolute alcohol washed several times. The washed precipitates were dried in a vacuum oven at 60 °C for 12 h. After synthesis, the zinc–carbon composites were

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calcined in air at 500 °C and 600 °C (heating rate of 1 °C/min) for 4 h to remove carbon core, leading to urchin-like ZnO hollow spheres.

X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max 2500 equipment with Cu *K*α radiation operated at 40 kV and 40 mA. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method based on the adsorption data. The particle size and morphology were visualized by using a FEI Quanta 600 FEG scanning electronic microscope (SEM) and a FEI Tecnai G^2 F20 S-TWIN transmission electron microscope (TEM). The chemical states were investigated by X-ray photoelectron spectroscopy (XPS, ESCA PHI5400). Raman spectra were obtained on a Nicolet Almega spectrometer. The EM parameters were measured in a HP 8753D vector network analyzer. The samples were prepared by mixing the samples with paraffin wax at 30% weight fraction. The samples were pressed into a toroidal shape ($\varphi_{out}=7.00$ mm, $\varphi_{in}=3.04$ mm).

3. Results and discussion

XRD patterns of urchin-like ZnO calcined at 500 °C and 600 °C are shown in Fig. 1a. As can be seen, the diffraction peaks of calcined ZnO located at 31.750°, 34.439°, 36.251°, etc. are corresponding to (100), (002), (101), etc. planes of ZnO (JCPDS card no. 05-0664). The diffraction peaks of as-prepared ZnO precursor appear at 13.057°, 24.227°, 28.309°, etc., which correspond to the (200), (310), (020), etc. planes of $Zn_5(OH)_6(CO_3)_2$ (JCPDS card no. 72-1100). Its relatively weak intensity demonstrates that $Zn_5(OH)_6(CO_3)_2$ phase is not well crystallized. Besides, no peaks for other phases are observed, indicating its high purity. Fig. 1b shows the Raman spectra of ZnO. The Raman peak of calcined ZnO at $\sim 1502\ cm^{-1}$ (G band) originates from in-plane vibration of sp^2 carbon atoms, and the D band ($\sim 1119\ cm^{-1}$) indicates the defects due to extensive oxidation [6]. The peaks in the spectra of calcined ZnO are observed at $331\ cm^{-1}$, $438\ cm^{-1}$, $464\ cm^{-1}$ and $579\ cm^{-1}$, corresponding to the spectra of ZnO nanocrystals [7]. The spectrum of as-prepared ZnO precursor exhibits no obvious G and D bands, indicating its low degree of graphitization compared to others. XPS spectra (Fig. 1c–e) indicate the presence of Zn, O and C elements in the samples. O 1s XPS spectra (Fig. 1d) of the samples can be deconvoluted into two peaks, the peaks at 533.5 eV, 531.9 eV and 530.0 eV are attributed to the oxygen vacancies and original lattice oxygen species in ZnO [8]. Under an alternating EM field, the charge carriers arising from the defects in ZnO crystal will response to the relaxation polarization and loss, contributing to the increase in ε' of the sample [9]. The porous feature of ZnO was further characterized by BET analysis. Fig. 1f presents the N_2 adsorption–desorption isotherms and BJH pore size distribution curves (inset) of ZnO. According to the IUPAC classification, the loop observed would be ascribed as type H3 hysteresis loops, indicating the existence of abundant pores [10]. The average pore diameters are around 7.99, 4.03 and 3.13 nm. The BET surface area of the samples is 36.1, 20.7 and 17.1 m^2/g.

The morphology of the samples is shown in Fig. 2. As shown in Fig. 2a, b, and d, dispersed microspheres with a diameter 5–6 μm can be observed. High-resolution SEM images in Fig. 2a(inset), c, and e reveal very different morphologies for all samples. For as-prepared ZnO precursor (Fig. 2a(inset)) homogeneous ZnO structures, consisting of a combination of plates and spheres were formed. The enlarged SEM image of one single sphere shows that it is composed of randomly close-packed porous nanosheets. On the contrary, well-crystallized ZnO spheres are obtained (Fig. 2c and e). Enlarged SEM images clearly show that calcined ZnO are in fact an assembly of nanosheets that grow radically from the center outward, and the entire structure resembles a sea urchin. The calcined ZnO show highly crystallized nanosheets and nanoparticles (Fig. 2c and e), in opposition to the compact structure shown by the as-prepared ZnO precursor. This is also reflected in the high specific surface area that is 53% larger for as-prepared ZnO precursor (36.1 m^2/g) than that of ZnO calcined at 600 °C (17.1 m^2/g). The analysis of EDS patterns in Fig. 2f confirms the existence of Zn, O, and C elements in the samples, which is consistent

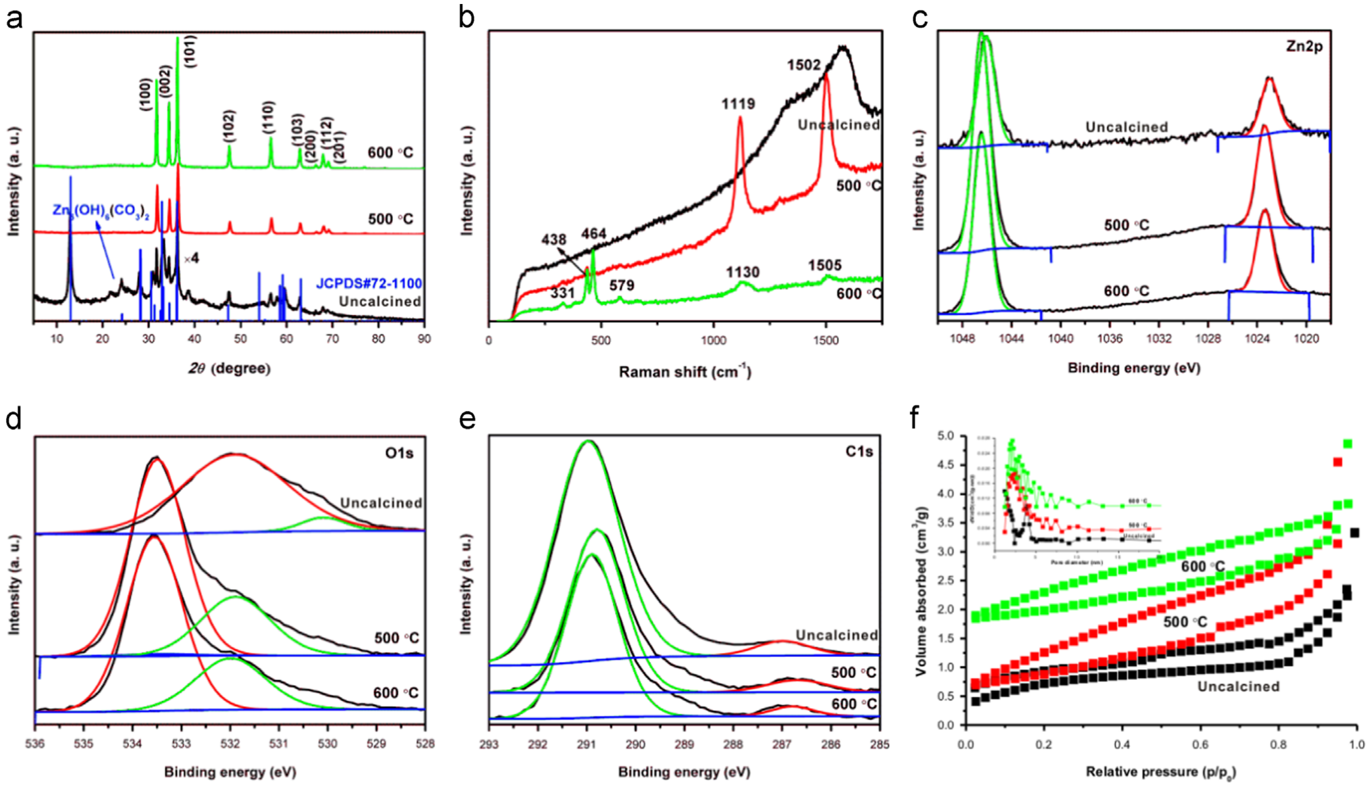

Fig. 1. (a) XRD patterns, (b) Raman spectra, XPS spectra (c) Zn 2p, (d) O 1s, (e) C 1s, and (f) N_2 adsorption–desorption isotherm (Inset of BJH pore size distribution) of urchin-like ZnO precursors calcined at 500 °C and 600 °C.