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Facile synthesis, photoluminescence properties and microwave absorption enhancement of porous and hollow ZnO spheres

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ABSTRACT

Three-dimensional (3D) porous ZnO nanostructures were synthesized via one-pot solvothermal treatment. The structural, morphological and spectral properties were investigated using X-ray diffraction (XRD), N_2 sorption measurement, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Raman spectroscopy, and photoluminescence (PL) spectroscopy. It was found that the minimum reflection loss value of ZnO calcined at 500 °C reached −5.62 dB at 16.24 GHz with the thickness of 2.5 mm, which had a superior performance of microwave absorption than those uncalcined and calcined at 600 °C. The possible mechanism for the formation of porous ZnO hollow spheres was proposed. The relationship of the ZnO microstructure and the microwave absorption properties was revealed via studying the dielectric loss and interference multi-reflection absorption in this paper as well. In addition, the photoluminescence results show that the uncalcined ZnO and porous hollow ZnO calcined at 500 °C and 600 °C show a narrow and sharp UV emission at 355.8 nm and a relatively broad visible spectra emission at around 423 nm.

1. Introduction

With the modern technology developing rapidly, the electromagnetic (EM) wave interference has become a serious problem and curious concern. In recent years, EM wave absorbing materials have attracted considerable attention because of their promising application in military and commercial markets. For example, the microwave absorbing materials can reduce radar reflection of target to achieve a better shielding defense system. Similarly, microwave absorber employed in daily lives can prevent human beings from harmful EM radiation [1]. Therefore, a great deal of microwave absorbents has caused enormous focus by many researchers including ferrite, carbon fibers and conductive polymers. The nanostructured ZnO materials, as an important *n*-type semiconductor, have been extensively applied in various fields such as ultraviolet (UV) lasers, solar cells, gas sensors, photocatalysis [2–5] and so forth due to their special physical and chemical properties. Recently, many studies demonstrate that ZnO can be also used as a microwave absorption material. Complex morphology and different dimensionalities have attracted great research interest due to the fact that their advanced geometric structure and atom arrangement on the specific facets of these nanostructures can provide novel properties. Controlled synthetic method is of vital importance for advanced functional materials because it not only helps to explore material fabrication techniques, but also provides opportunities to reveal the relationship between material structure and property [6]. To fabricate efficient shielding materials, various microscopic morphologies and structures of ZnO have been studied for their microwave absorption characteristics. Chen et al. [7] showed that pure ZnO nanowire is a low-loss material, and strong microwave absorption in the X band is enhanced with the concentration of nanowire increasing in the composites. Zhuo [8] has reported that ZnO nanostructures (nanowire and nanotrees) with paraffin composites have been investigated in the frequency of 0.1–18 GHz. Excellent microwave absorption performances have been observed in ZnO nanotree composite compared to ZnO nanowire composite. The value of minimum reflection loss for the composites with 60 vol.% ZnO nanotrees is −58 dB at 4.2 GHz with a thickness of 4.0 mm. Such strong absorption is attributed to the unique isotropic antenna morphology of the ZnO nanotrees in the composite. Li et al. [9] showed that the reflection loss for composite with 50 vol.% ZnO net-like structures is −37 dB at 6.2 GHz with a thickness of 4.0 mm. Further investigation by Cao et al. [10] demonstrated that cagelike ZnO/SiO_2 (weight ratio 1:5) nanocomposites exhibit a relatively strong attenuation of −10.68 dB at the frequency of 12.79 GHz to EM waves. The special morphology and distribution configuration of cagelike ZnO nanostructures resulted in enhanced absorption for EM waves. The microwave absorption of porous hollow ZnO by CO_2 soft-template was also reported [11]. And a minimum reflection loss value of wax

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Table 1
Microwave absorption properties of the reported ZnO samples.

Samples	Thickness (mm)	f_m (GHz) (optimal RL)	Minimum RL (dB)	Percentage	Refs.
ZnO nanowire	1.0	10.75	-12.28	7% (vol.%)	[7]
ZnO nanotree	4.0	4.2	-58	60% (vol.%)	[8]
Netlike ZnO	4.0	6.2	-37	50% (vol.%)	[9]
Cagelike ZnO/SiO$_2$	3.0	12.79	-10.68	20% (wt.%)	[10]
Porous hollow ZnO	4.0	12.8	-36.3	25% (wt.%)	[11]
Tetra-needle ZnO whisker	1.0	4.0	-2.3	50% (wt.%)	[26]
Porous ZnO	2.5	16.24	-5.62	30% (wt.%)	This work

composite with 25 wt.% porous hollow ZnO is −36.3 dB at 12.8 GHz with a thickness of 4.0 mm. Table 1 lists corresponding microwave absorption indexes of related ZnO with different structures and morphologies. Previous reports have demonstrated that ZnO can become a strong EM absorbing material. Therefore, we try to prepare porous ZnO of much thinner thickness with better microwave absorption property.

ZnO with lightweight, semiconductive features and large scale synthesis has been a desiring highly efficiency material for microwave absorption. Furthermore, the novel properties of special ZnO nanostructure have attracted increasing interests. Despite lots of researches on ZnO absorbent, until now there have been only few reports on the microwave absorbing property with porous ZnO nanostructure. In this paper, we have successfully synthesized 3D porous ZnO spheres by one-pot simple solvothermal approach. Compared with the synthetic method using a hard-template followed by subsequent removal of the template, the template-sacrificial approach with low cost and environmentally friendly route is much more convenient for its facile and controllable synthesis process [12]. What's more, we believe that the hollow and open porous structures are desirable for the application in the shielding absorbing materials, since the 3D porous ZnO architectures can not only provide the high surface accessibility and more free space to form the multi-interface reflection but also offer point defects to cause another additional pathway for the highly-efficient steady absorption of EM waves. Importantly, the present paper also reveals the intrinsic reasons why porous nanostructured shielding materials have excellent microwave absorption performances.

2. Experimental

In this contribution, we develop a facile solvothermal method using zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) as a zinc source and glucose as carbonaceous source. Typically, D-glucose monohydrate ($C_6H_{12}O_6 \cdot 6H_2O$, 40 mmol), 20 mmol zinc nitrate and urea ($CO(NH_2)_2$, 40 mmol) were mixed and dissolved in 50 ml of ethylene and distilled water with 2:1 volume ratio under vigorous stirring for 30 min until the solutions were completely dissolved. And then the above solutions were placed in 100 ml capacity Teflon-lined stainless steel autoclave, which was heated in a chamber oven to 180 °C for 20 h. After reaction for cooling down to room temperature, the black precipitates were filtered, and then washed several times with distilled water and absolute alcohol. The washed precipitates were dried in a vacuum oven at 80 °C for several hours. The precursor was calcined in air at 500 °C and 600 °C, respectively, for 3 h with a heating rate of 2 °C/min to achieve final white 3D porous hollow ZnO products [13].

X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max 2500 equipment with Cu $K\alpha$ 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 electron microscope (SEM) and a FEI Tecnai G^2 F20 S-TWIN transmission electron microscope (TEM). Raman spectra were obtained on a Nicolet Almega spectrometer. Room temperature photoluminescence (PL) spectroscopy with the He–Cd (325 nm) laser line as the exciting source was used to know the optical properties of the as-synthesized and calcined ZnO in detail. 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

The crystalline structure of the prepared porous ZnO spheres calcined at 500 °C and 600 °C was investigated by X-ray diffraction (XRD) compared with the structure of as-synthesized ZnO solid sphere precursor (Fig. 1). All diffraction peaks are indexed to a relatively pure phase of zincite ZnO with no additional characteristic peaks observed for other impurities. In addition, it can be found that several diffraction peaks are sharp and strong, which confirms ZnO is highly crystallized rather than amorphous. Further structural information can be acquired from Raman spectra of the prepared samples as shown in Fig. 2. ZnO in the wurtzite structure as one of the simplest uniaxial crystals belongs to the $C_{6v}^4(P6_3mc)$ space group [14]. The peaks at about 1360 cm^{-1} and 1574 cm^{-1} are well related to the D and G bands for carbon [15,16], which has demonstrated that ZnO precursor contains carbon component. For the perfect ZnO, only the optical phonons at Γ point of Brillouin zone are involved first-order Raman Scattering, the theory of group predicts the following optical modes: $\Gamma_{opt} = A_1 + 2B_1 + E_1 + E_2$ [14,17], where both the A_1 and E_1 are infrared active and split into transverse optical (A_1TO and E_1TO) and longitudinal optical (A_1LO and E_1LO) components. E_2 mode includes low and high frequency phonons (E_2 low and E_2 high), which associated with the vibration of Zn lattice and oxygen atoms, respectively. In addition, the silent B_1 bond from low and high frequency modes (B_1 low and B_1 high) has been calculated as 260 cm^{-1} and 540 cm^{-1} respectively. Each active vibration mode corresponds to a band in Raman spectrum and the intensity of them is related with the scattering cross section of modes. The spectra of ZnO calcined at 500 °C and 600 °C have a main peak at 438 cm^{-1}, which are the characteristic of wurtzite phase with E_2 vibration mode and

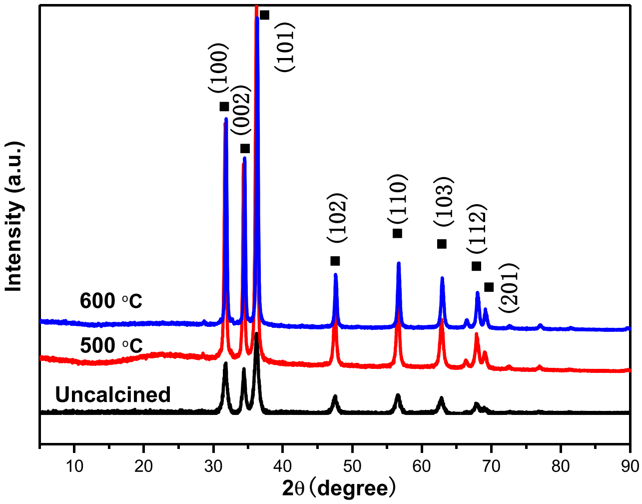

Fig. 1. XRD patterns of uncalcined and calcined ZnO at 500 °C and 600 °C.