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Magnetic and optical properties of zinc chromite nanostructures prepared by microwave method

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Abstract: The nanostructures of zinc chromite ($ZnCr_2O_4$) were fabricated by the microwave method. It was shown that the well-crystallized spinel structure is formed after annealing at 700 °C. The influence of reaction time and irradiation power of oven on the size and shape of the as-prepared $ZnCr_2O_4$ samples was studied. The synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), photoluminescence (PL) spectroscopy, Fourier transform infrared (FTIR) spectra and vibrating sample magnetometry (VSM), respectively. The optical band gap calculated using DRS was found to be 3.50 eV for $ZnCr_2O_4$ nanostructures. Photoluminescence measurements also confirmed this result.

Key words: zinc chromite; nanostructures; superhydrophilicty; magnetic property; optical property

1 Introduction

Zinc chromite ($ZnCr_2O_4$) is a mixed oxide which crystallizes in the cubic system and has a normal spinel structure. Non-magnetic Zn^{2+} and magnetic Cr^{3+} ions have strong preference for the tetrahedral A- and the octahedral B-sites, respectively. $ZnCr_2O_4$ is very attractive as air depollution catalytic material, for a variety of reactions like oxidative dehydrogenation of hydrocarbons, oxidation of hydrocarbons, synthesis of methanol [1], gas sensing [2], as photocatalyst [3,4] and humidity sensing [5]. Photocatalytic degradation processes have been widely applied as techniques of destruction of organic pollutants in wastewater and effluents [6]. $ZnCr_2O_4$ was synthesized previously by multifarious methods including mechanical activation [7], high-temperature solid-state reaction [8], micro-emulsion method [2], solution method [9] and spray pyrolysis [10]. The most general method for preparing spinels involves solid state reaction of the parent metal oxides that are mechanically mixed in the form of finely divided powders [7]. However, for completion of the reaction, a temperature of about 1100 °C for several days is needed [5]. The damages of solid-state routes such as inhomogeneity, larger particle size and lack of stoichiometry control are avoided when the material is synthesized using a solution-based method. It is very important to recognize that proper choice of the synthesis route and precursor and the knowledge of its composition and structure are crucial to tailor-make a pure product. For this reason, in order to obtain spinel zinc chromite nanoparticles, we selected a synthesis method belonging to wet chemistry. Using microwave energy to synthesize the materials in a convenient and simple way has been recognized, since the method is faster, more economical and cleaner [11]. A variety of inorganic materials such as chalcogenides [12], nitrides [13], complex oxides [14], silicides [15] and zeolites [16], were synthesized using the microwave approach. Because microwave irradiation is easily generated, various Zn-related nanostructures were synthesized using this method [17−23].

In this work, we reported a novel and rapid microwave method for the preparation of $ZnCr_2O_4$ nanostructures. The nanostructures were synthesized from reaction between $Zn(NO_3)_2{\cdot}6H_2O$ and $CrCl_3{\cdot}6H_2O$ in the presence of sodium dodecyl-benzene-sulfonate (SDBS) as surfactant. The effects of different parameters such as power of oven and time of irradiation were also studied.

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2 Experimental

2.1 Materials and physical measurements

All the chemical reagents used in our experiments were of analytical grade, were purchased from Merck and used as received without further purification. The XRD patterns of the products were recorded by a Rigaku D-max C III XRD using Ni-filtered Cu K_α radiation. SEM images were obtained on Philips XL−30 ESEM equipped with an energy dispersive X-ray spectroscopy. The EDX analysis with an accelerating voltage of 20 kV was done. Room temperature photoluminescence (PL) was studied on a Perkin Elmer (LS 55) fluorescence spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu Varian 4300 spectrophotometer in KBr pellets. UV–Vis absorption spectra of the samples were obtained with a UV–Vis DRS spectrophotometer (Shimadzu, model UV−3101) with a scan rate of 5 nm/s. TEM image was obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV.

2.2 Synthesis of $ZnCr_2O_4$ nanostructures

In a general procedure, 0.2 g $Zn(NO_3)_2{\cdot}6H_2O$ precursor and 0.1 g SDBS as surfactant were dissolved in 20 mL of distilled water under vigorous stirring. By adding 0.35 g $CrCl_3{\cdot}6H_2O$ and raising the pH to 11 with NaOH, a compound was precipitated. Afterward, the solution was exposed to microwave irradiation with different powers and time. The microwave oven followed a working cycle of 30 s on and 60 s off (30% power). After heating under microwave irradiation, the nanoparticles were cooled to room temperature naturally. Precipitates were flittered, washed with deionized water and ethanol, and then dried at room temperature. Finally, dried precipitates were annealed in air at 700 °C for 3 h. Table 1 shows the conditions of reactions in detail.

Table 1 Reaction conditions for preparation of $ZnCr_2O_4$ nanostructures

Sample No.	Time/ min	Power/ W	Annealing temperature/°C	Surfactant	Product
1	4	600	700	SDBS	$ZnCr_2O_4$
2	6	600	700	SDBS	$ZnCr_2O_4$
3	8	600	700	SDBS	$ZnCr_2O_4$
4	6	750	700	SDBS	$ZnCr_2O_4$
5	6	900	700	SDBS	$ZnCr_2O_4$
6	8	900	700	SDBS	$ZnCr_2O_4$
7	6	600	700	−	$ZnCr_2O_4$
8	6	600	−	SDBS	$ZnCrO_4$

3 Results and discussion

3.1 XRD analysis

Figure 1(a) shows XRD pattern of the as-prepared $ZnCr_2O_4$, which indicates that this sample is a pure-phase compound. The product has peaks corresponding to the cubic $ZnCr_2O_4$ (space group: *Fd*3*m*) phase with cell constants $a=b=c=8.3275$ Å, which are in agreement with JCPDS No. 22−1107. The intense and sharp diffraction peaks suggest that the obtained product is well crystallized. Figure 1(b) shows the XRD pattern of $ZnCr_2O_4$ nanostructure before calcination. According to this figure, with calcination of the $ZnCr_2O_4$ samples at 700 °C for 3 h, the crystallinity of the products is increased.

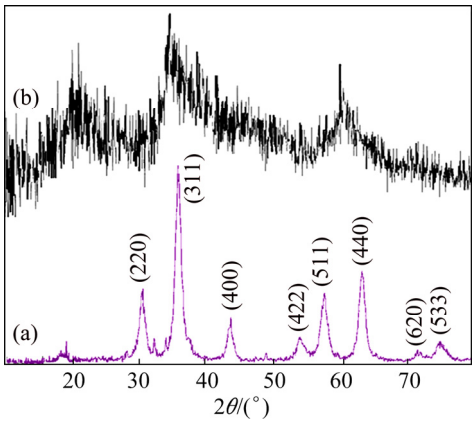

Fig. 1 XRD pattern of Sample 2 (a) and Sample 8 (b)

3.2 Morphology and microstructure analysis

To investigate the effect of irradiation time on the morphology of products, the reaction was performed in 4, 6 and 8 min at 600 W, as shown in Figs. 2(a)−(c), respectively. At first, when the reaction took place for 4 min, which was not enough for the separation of the particles, the agglomerated particles were obtained (Fig. 2(a)). By increasing the time to 6 min, the particles were separated. In addition, uniform particles were formed due to sufficient time for the reaction (Fig. 2(b)). When the reaction occurred for 8 min, the particles were agglomerated. This was due to the fact that after optimum amount of reaction time, further irradiation would increase as the prepared particles' kinetic energy and collision of these particles would increase, which led to the agglomeration of particles (Fig. 2(c)). For investigating the effect of surfactant on the morphology and particle size of the products, one test was carried out in the absence of SDBS for 6 min at 600 W (Fig. 2(d)). This figure shows that the particles coalesced and turned into bulk structures.

SEM images of the as-synthesized products at 6 min and different powers of 750 and 900 W are exhibited in Figs. 3(a) and (b), respectively. When the irradiation

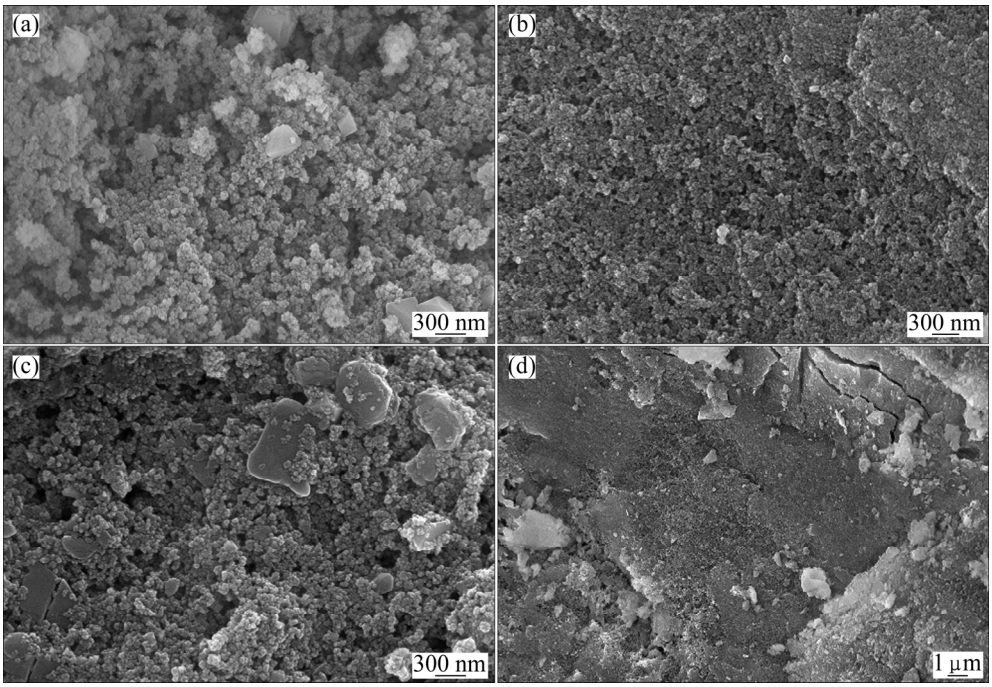

Fig. 2 SEM images of different samples: (a) Sample 1; (b) Sample 2; (c) Sample 3; (d) Sample 7

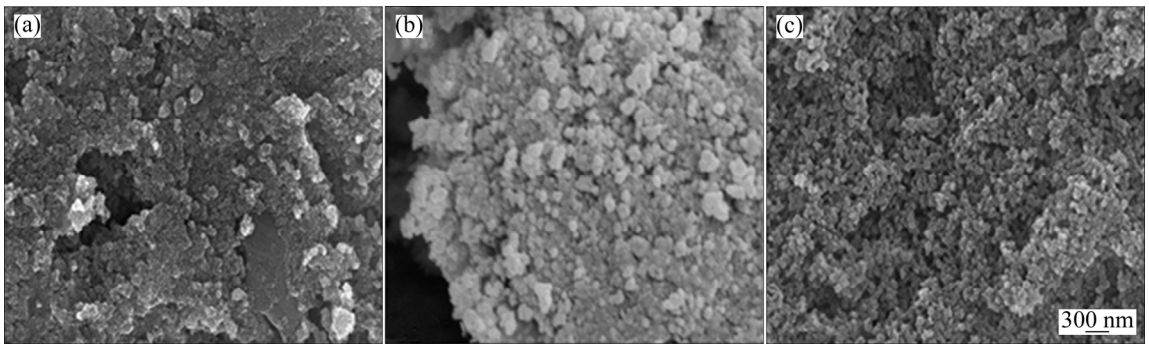

Fig. 3 SEM images of as-prepared nanostructures: (a) Sample 4; (b) Sample 5; (c) Sample 6

power was 600 W, small particles were obtained (Fig. 2(b)). Based on Figs. 3(a) and (b), it can be confirmed that by increasing the irradiation power to 750 and then 900 W, the agglomerated particles were produced. This is due to the fact that the particles have higher kinetic energy when the irradiation power is increased, and particles can fuse together again. By increasing the reaction time to 8 min at 900 W (Fig. 3(c)), the chances of collision between nanoparticles increase and the average diameter of nanoparticles decreases.

The morphological and structural features of $ZnCr_2O_4$ products, shown in Fig. 4, were characterized with transmission electron microscope (TEM), which show the shape of semi-sphere. The diameter of these nanoparticles is in the range of 10−15 nm.

3.3 FTIR analysis

FTIR spectroscopy has been widely applied in solid state chemistry because it can provide information on structural characteristics of inorganic solids in crystalline and amorphous states. Figure 5 demonstrates the FTIR spectrum of Sample 2 obtained after annealing up to 700 °C. Two high frequency modes corresponding to peaks at 515.13 and 627.44 cm^{-1} mainly involve the displacement of oxide anions relative to the chromium cations along the direction of the octahedral chains, and tentatively assigned to Cr—O stretching [7].

3.4 EDS and PL analyses

X-ray energy dispersive spectroscopy (EDS) analysis measurements were used to characterize the chemical composition of the products (Fig. 6(a)). The results for $ZnCr_2O_4$ in the presence of SDBS at 600 W for 6 min (Sample 2) show that only elements Zn, Cr and O exist. In addition, neither N nor C signals were detected in the EDS spectrum, which means that no

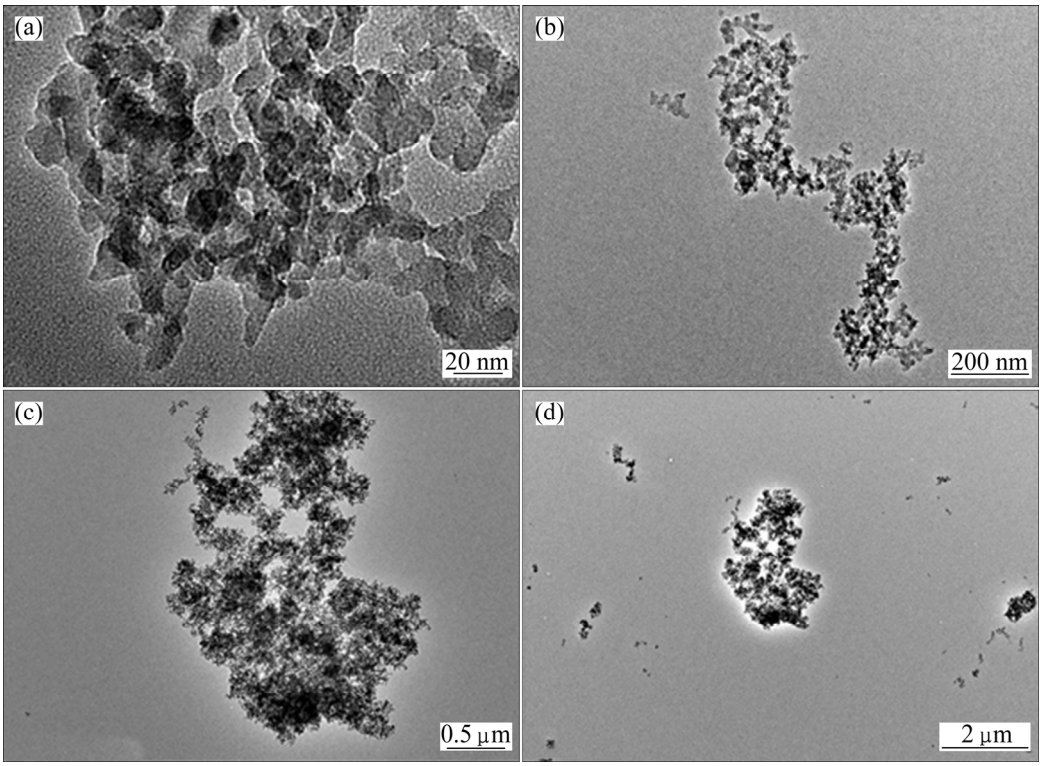

Fig. 4 TEM images of Sample 2

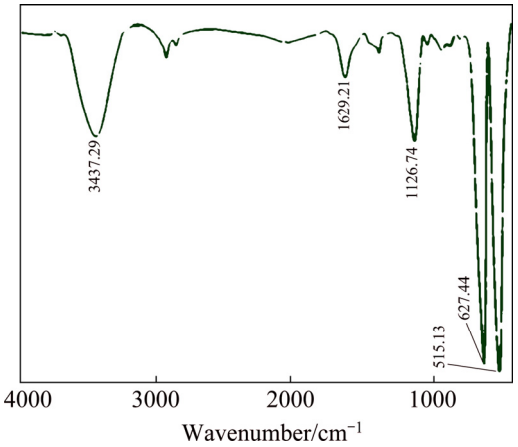

Fig. 5 FTIR spectrum of as-synthesized $ZnCr_2O_4$ nanostructures (Sample 2)

solvent or capping agent exists in the sample. Figure 6(b) shows the PL spectrum of $ZnCr_2O_4$ prepared by the microwave method. A sharp peak at 365 nm was observed and band gap of sample was calculated about 3.39 eV.

3.5 Contact angle analysis

The contact angle (CA) of the $ZnCr_2O_4$ nanoparticles (Sample 2) is shown in Fig. 7. Contact angle is a quantitative measure of the wettability of a surface. Hydrophilicity basically refers to hydrogen bonding with water molecules [24]. The $ZnCr_2O_4$ showed a hydrophilic surface at a contact angle of 5.3°.

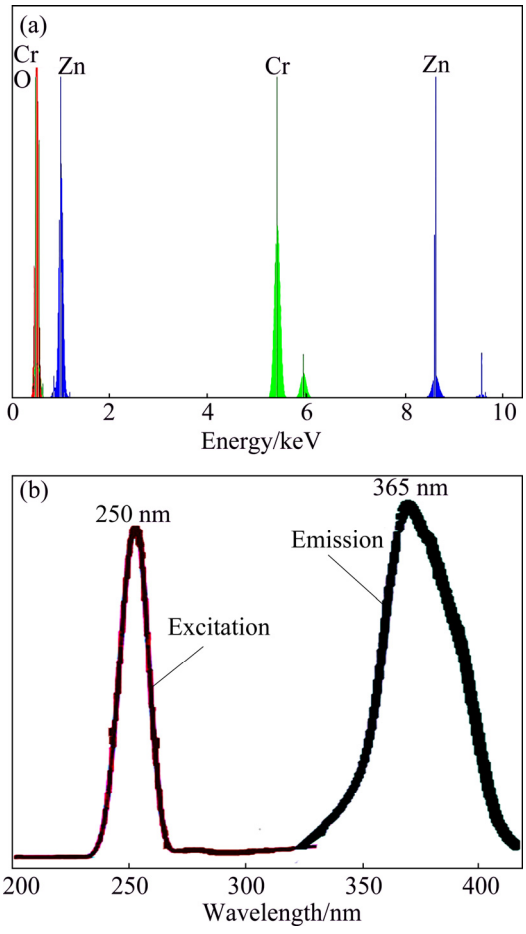

Fig. 6 EDS pattern (a) and PL spectrum (b) of Sample 2

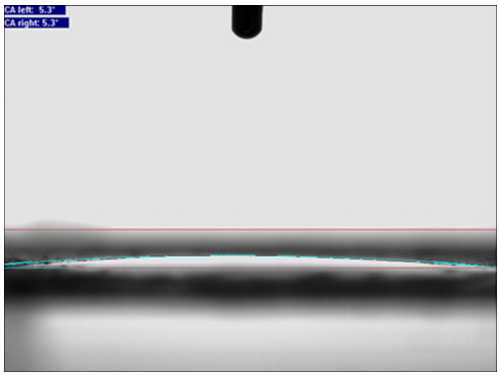

Fig. 7 Photograph of measured contact angle on rough surface of $ZnCr_2O_4$ materials (Sample 2)

3.6 DRS and VSM analyses

The optical properties of $ZnCr_2O_4$ nanostructures were studied by UV–Vis DRS spectra. The spectra were recorded in wavelength region between 200 and 800 nm at room temperature. The estimated values of the band gap energy (E_g) of $ZnCr_2O_4$ nanoparticles are shown in Fig. 8(a). The optical gap was calculated using Tauc relation by plotting $(\alpha hv)^2$ against hv, where α and hv denote the absorption coefficient and photon energy, respectively. The direct band gap energy of $ZnCr_2O_4$ is found to be 3.50 eV, which is in a good agreement with the value reported in Ref. [25].

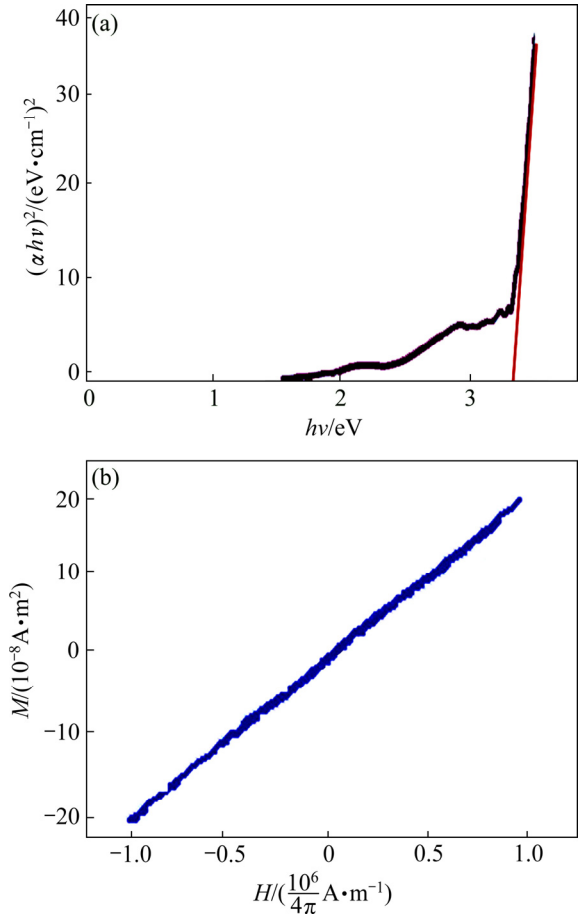

Fig. 8 Diffuse reflectance spectrum (a) and M–H curve of $ZnCr_2O_4$ nanostructures (Sample 2) (b)

Figure 8(b) shows the dependence of magnetization with the applied magnetic field (M–H curve). $ZnCr_2O_4$ is a cubic spinel at room temperature with magnetic ions (Cr^{3+}, s=3/2) at the B sites and is a typical example of the geometrically frustrated system. Temperature variation of magnetic susceptibility measurement confirms that the ceramic material is paramagnetic at above −173 °C. Below this temperature, anti-ferromagnetic interaction develops. However, the geometry of the cubic lattice results in a frustrated spin system [16].

In comparison with other similar works illustrated in Table 2, our method is simpler and more commodious. We used microwave method for the preparation of products. Microwave synthesis of inorganic materials gains importance due to less complex synthesis procedure and shorter reaction time.

Table 2 Characterization comparison of $ZnCr_2O_4$ nanostructures with other similar works

Method	Precursor	Ref.
Spray pyrolysis method	$Zn(NO_3)_2$, $Cr(NO_3)_2$	[10]
Sol–gel method	$Zn(NO_3)_2{\cdot}4H_2O$, $Cr(NO_3)_2{\cdot}9H_2O$	[26]
Thermal decomposition	$Cr(NO_3)_3{\cdot}9H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$	[27]
Hydrothermal route	$Zn(NO_3)_2{\cdot}6H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$	[4]

Oxides with spinel structure are some of the most studied compounds in solid-state sciences due to interesting physico-chemical properties and are found to be useful in many technological applications such as magnetic materials [28], super hard materials [29], and high-temperature ceramics [30]. In particular, zinc chromite ($ZnCr_2O_4$) ceramic spinels are commonly used as humidity sensors, magnetic material and catalytic materials in lots of heterogeneous chemical processes such as CO oxidation, catalytic combustion of hydrocarbons, reduction of several organic molecules and sensing properties [1−5].

4 Conclusions

The present study demonstrates successful synthesis of zinc chromite nanostructures via microwave method. The XRD patterns reveal that the $ZnCr_2O_4$ nanostructures prepared by annealing the precursor at 700 °C for 3 h have good crystallinity with fine cubic structure. The nanostructures exhibit a regular morphology with homogeneous particle size distribution. The FTIR spectrum also confirms nanostructure of

prepared products. According to the magnetic measurement, $ZnCr_2O_4$ nanostructure exhibits the room temperature paramagnetic behaviour. In addition, it is believed that this simple process can also be applied to synthesizing other functional materials.

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微波法制备纳米结构铬酸锌的磁学和光学性能

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摘　要：采用微波法制备纳米结构铬酸锌($ZnCr_2O_4$)。结果表明，经 700 °C 退火后 $ZnCr_2O_4$ 为晶型良好的尖晶石结构。研究反应时间和微波照射功率对 $ZnCr_2O_4$ 晶粒尺寸和形貌的影响。分别采用 X 射线衍射(XRD)、扫描电镜(SEM)、能量分散 X 射线(EDX)、透射电镜(TEM)、漫反射光谱(DRS)、光致发光(PL)光谱、傅里叶红外光谱(FTIR)等技术及振动样品磁强计对所合成的 $ZnCr_2O_4$ 样品进行表征。由漫反射光谱(DRS)计算得到 $ZnCr_2O_4$ 纳米结构的光带能隙为 3.50 eV，光致发光光谱分析也证实了该结果。

关键词：铬酸锌；纳米结构；超亲水性；磁学性能；光学性能

(Edited by Wei-ping CHEN)