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Urchin-like NiO Superstructures Prepared by Simple Thermal Decomposition Process

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Abstract: Urchin-like NiO superstructures have been prepared via a thermal decomposition reaction of NiC_2O_4 at 400℃ for 1 h. The morphology and structure of the synthesized urchin-like superstructures have been characterized by X-ray diffraction, field emission scanning electron microscopy and transmission electron microscopy. The results show that urchin-like NiO superstructures were a polycrystal with cubic structure and typical diameters of 200 to 500 nm and the self-assembly nanoparticles average diameter is 14 nm. The as-prepared NiO superstructures have a high Brunauer-Emmett-Teller surface area of about 60.32 m^2/g. The UV-vis spectrum of urchin-like NiO consists of one peak at 357 nm (3.47 eV).

Keywords: NiO superstructures; Thermal decomposition; Ultraviolet analysis

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Introduction

As a p-type wide-bandgap semiconductor, NiO is a very promising functional material which has attracted increasing attention due to its extensive important applications such as battery electrodes [1], catalysts [2], and gas sensors [3-5]. To date, many NiO nanostructures have been prepared, such as nanoplates [6], nanorings [7], nanobelts [8], nanowires [9], nanotubes [10], mesoporous NiO [11], hollow octahedral [12], polyhedrons [13] and NiO hollow nanospheres [14-17]. The previous works, NiO 3D superstructures (hollow tubes or spheres) often were prepared by template assistant. Therefore, developing simple, high-yield, and environmentally benign methods for synthesizing NiO complex 3D superstructures is still an on-going process. However, to the best of our knowledge, few reports have been concerned the synthesis of NiO nanocrystals as nanoscale building blocks for the construction of urchin-like 3D superstructures.

Herein, urchin-like NiO 3D superstructures were prepared via a simple thermal decomposition method without any template or free surfactant. Urchin-like NiO superstructures were assembled from nanocrystals building blocks.

Experimental

Experimental materials

All the chemical reagents in the experiments were analytical grade (AR) and they were used without further purification. Nickel sulfate ($NiSO_4{\cdot}7H_2O$, AR, Tianjin Zhiyuan Chemical Reagent Co., Ltd), oxalic acid ($C_2H_2O_4{\cdot}2H_2O$, AR, Xi'an Reagent Factory).

Syntheses of urchin-like NiO superstructures

In the typical experiment, 2.84 g of $NiSO_4{\cdot}7H_2O$ (0.01 mol) was dissolved into 30 ml ethylene glycol with continuously stirring about 90 min. Then, 20 ml 0.5 mol/l of $H_2C_2O_4$ (0.02 mol) were added into the solution to form light green precipitate. The precipitate was collected by centrifugation and washed with deionized water and absolute ethanol for several times. After that the precipitate was placed in oven and maintained at 400℃ for 1 h with a heating rate of 10℃/min before

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being naturally cooled to room temperature.

Characterization of Products

X-ray powder diffraction (XRD) patterns of the products were obtained on a Japan Rigaku D/Max-IIIC diffractometer at a voltage of 60 kV and a current of 80 mA with Cu Kα radiation (λ=1.5406 Å), employing a scanning rate of 8°/min in the 2θ ranging from 20° to 80°. Field emission scanning electron microscopy (FESEM) images were explored on a JEOL JSM-6700F microscope. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-3010 transmission electron microscope at an accelerating voltage of 200 kV. Thermogravimetry (TG) and Differential thermal analysis (DTA) measurements were simultaneously measured up to 500℃ at a heating rate of 10℃/min using a Shanghai ZRY-2P. UV-vis absorption spectrum was taken on a UV, Lambda 950 spectrophotometer. N_2 adsorption was determined by BET measurements using a Beijing JW-BK surface area analyzer.

Results and Discussion

TG/DTA

In order to study the thermal decomposition characteristics of nickel oxalate precursor, the thermogravimetry-differential thermal analysis (TG-DTA) curves of the as-prepared precursor were shown in Fig. 1. The TG curve showed that a major step weight loss was about 48.73%, closed to the theoretical value (48.98%), which was corresponded to the decomposition of the precursor started at about 360. It is indicated that the decomposition temperature of the precursor was at about 360℃. Moreover, when the temperature was above 360℃, TG/DTA curves were maintained on a level, indicating that the precursor decomposed completely. In addition, the results were also used to determine the temperature of the thermal treatment of the precursors. Finally, 400℃ was selected as the decomposition temperature.

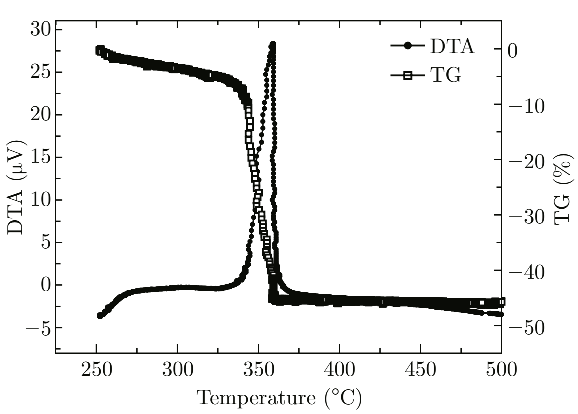

Fig. 1 TG/DTA curve of the obtained NiO precursor.

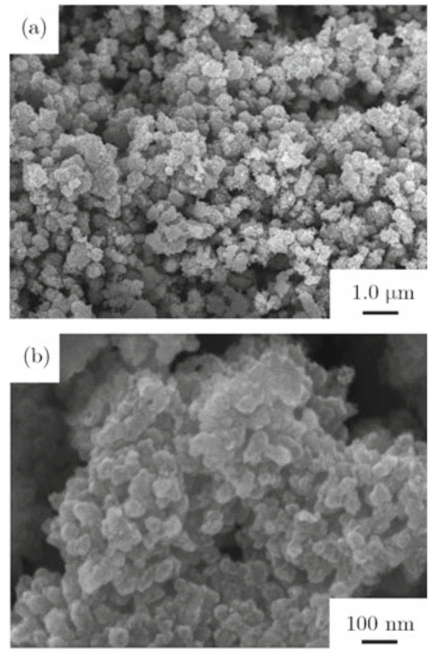

Fig. 2 FESEM image of samples obtained at 400℃ for 1 h.

FESEM

Typical FESEM images of the NiO were shown in Fig. 2. Figure 2(a) is an overview of the samples with the uniform urchin-like superstructures with a length from 200 to 500 nm. A high multiple FESEM image is shown in Fig. 2(b). The urchin-like NiO superstructures might derive from a mount of nanocrystals by self-assembly under Vander Waals forces. Meanwhile, several particles together formed soft agglomerates.

XRD

XRD pattern of NiO sample obtained at 400℃ for 1 h is shown in Fig. 3, which agreed well with the reported data (JCPDS No. 47-1049). NiO possessed a cubic structure and the average grain size of the NiO nanocrystals self-assembling superstructures was 14 nm calculated from Scherrer's equation. No other peaks for the impurities were observed.

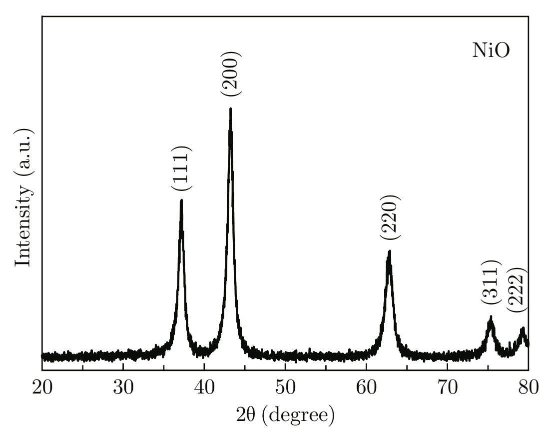

Fig. 3 XRD image of samples obtained at 400℃ for 1 h.

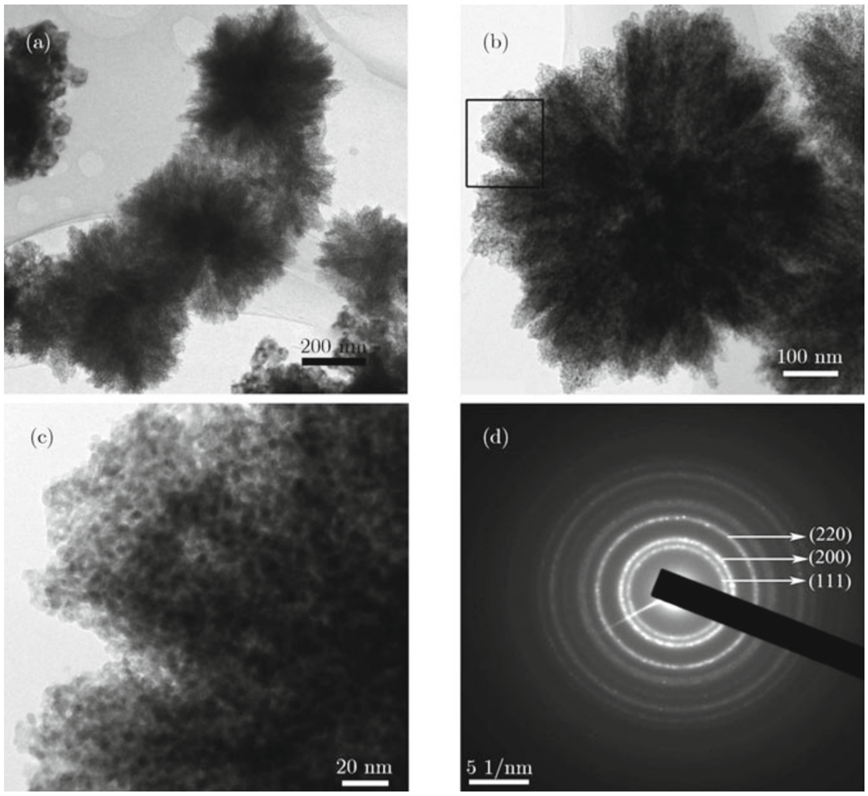

Fig. 4 TEM and SAED images of samples obtained at 400℃ for 1 h. (a∼c) TEM; (d) SAED.

TEM

Further characterization of the NiO superstructures was performed by TEM and selected area electron diffraction (SEAD), as shown in Fig. 4. Figure 4(a) showed amount of the as-prepared urchin-like NiO superstructures. The average size of superstructures was about 400 nm. A typical TEM image of single urchin-like NiO superstructures was shown in Fig. 4(b) with the size of 400 nm. The superstructures assembled from the nanocrystals can be observed in the high multiple TEM image (see Fig. 4(c)), which is according to rectangular frame of Fig. 4(b). Meanwhile, SAED pattern is presented in Fig. 4(d) according to Fig. 4(c), indicated the polycrystalline cubic phase of NiO (111), (200), (220) crystal plane diffraction. The TEM and SAED analyses revealed that urchin-like NiO superstructures were polycrystalline cubic structure.

UV/vis absorption spectra

The UV/vis absorption spectra of the as-synthesized urchin-like NiO superstructures were illustrated in Fig. 5. It can be seen that the morphological changes of the NiO semiconductor were accompanied by remarkable changes in the UV-vis spectra because of the significant difference in crystal size associated with NiO [18]. In this case, a peak of 357 nm was observed with the NiO average grain size of 14 nm composing the superstructures. The bandgap energy of urchin-like NiO superstructures is about 3.47 eV, which is smaller than the value (3.55 eV) reported by Yu Lin et al. [19], and also smaller than the normal NiO value (3.6∼4.0 eV). The optical band edge exhibited obvious red shift.

BET isotherm of urchin-like NiO superstructures

As the product expected to have a high surface area, Brunauer-Emmett-Teller (BET) measurements were performed. The surface area of the urchin-like NiO superstructures obtained at 400℃ calculated from the BET plot was 60.32 m^2/g (Fig. 6), which was lower than that ordered mesoporous NiO (81.8 m^2/g) [20], NiO

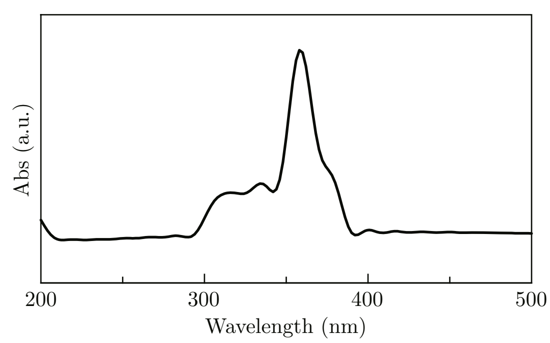

Fig. 5 UV/vis absorption spectra of urchin-like NiO superstructures.

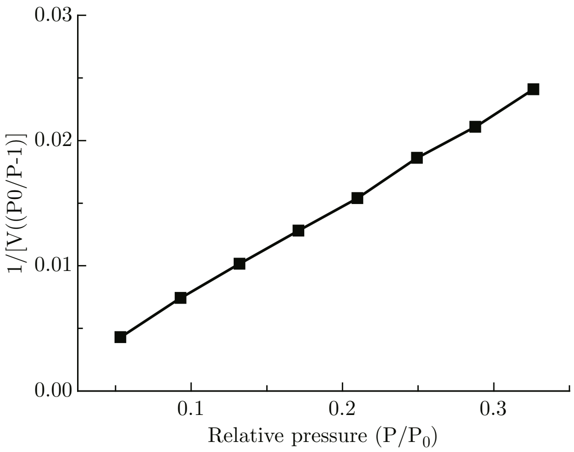

Fig. 6 the plot of BET isotherm for N_2 adsorption-desorption.

microspheres ($81\,m^2/g$) and higher than that NiO nanorods ($13\,m^2/g$) [18]. This result suggests that each of urchin-like NiO structure grows from the cores of the urchin-like NiO superstructures.

The reaction mechanism

In this work, a facile route, namely direct thermal decomposition reaction of NiC_2O_4 in an oven, has been developed to synthesize novel 3D urchin-like NiO superstructures. The chemical reaction for syntheses of 3D urchin-like NiO superstructures can be expressed as:

$$NiSO_4 \cdot 7H_2O \xrightarrow{C_2H_6O_2} Ni^{2+} + SO_4^{2-} + 7H_2O \quad (1)$$

$$C_2H_2O_4 \cdot 2H_2O + Ni^{2+} + SO_4^{2-} \xrightarrow{C_2H_6O_2} NiC_2O_4 \downarrow + 2H^+ + SO_4^{2-} + 2H_2O \quad (2)$$

$$NiC_2O_4 \xrightarrow{\triangle} NiO \downarrow + CO \uparrow + CO_2 \uparrow \quad (3)$$

At the beginning, the $C_2O_4^{2-}$ was added into Ni^{2+} ethylene glycol solution and NiC_2O_4 precipitation formed (see Eq. (1∼2)). Second, NiO superstructures can be obtained as the decomposition reaction of NiC_2O_4 precipitation occurred (see Eq. (3)).

Conclusions

In summary, the work presented here constitutes a simple thermal decomposition method for the fabrication of urchin-like NiO superstructures. The simplicity is that the aging procedure results in the growth of NiO nanocrystals as well as their assembly into urchin-like structures. It has been found that synthesis of precursor was a key to obtain urchin-like morphology. The urchin-like NiO superstructures would open up the possibility of finding their new applications or improving existing performance, for example, as candidates for studying the nanoarchitecture-dependent performance as cathodes in micro-rechargeable lithium batteries. To this purpose, the structures of urchin-like NiO are to be investigated in more detail, as well as on the effect of incorporation of functional additives into the shells.

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