MOF-derived Co$_3$O$_4$/NiCo$_2$O$_4$ double-shelled nanocages with excellent gas sensing properties

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Abstract

Co$_3$O$_4$/NiCo$_2$O$_4$ double-shelled nanocages (DSNCs) were successfully prepared through a metal-organic frameworks (MOFs) route. The strategy includes the synthesis of zeolite imidazolate framework-67 (ZIF-67)/Ni-Co layer doubled hydroxides precursor and subsequent transformation to Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs by thermal annealing of the as-prepared precursor in air. Various techniques such as XRD, SEM, EDS, BET and TEM were employed for the characterization of microstructure and morphology of the as-prepared Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs. The use of as-prepared Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs as a gas sensing material in a gas sensor gave an enhanced sensitivity to acetone compared with result obtained in Co$_3$O$_4$ nanocages (NCs). In addition, excellent reversibility and selectivity of the sensor were observed. These properties make the Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs a good candidate for acetone detection.

1. Introduction

Core-shell hollow structure functional materials have attracted a multitude of attentions in recent years on account of their potential applications in gas sensing, catalysts, drug delivery and so on [1–3]. Many novel approaches have been reported for the synthesis of core-shell hollow structures, such as Kirkendall effect [4,5], template-assisted method [6,7]. Notwithstanding, template-assisted method has been regarded as one of the most effective and forthright ways to prepare hollow structures, but it needs a tedious procedure to remove various templates and also has quite a variety of difficulties to manage the incompatibility issue between the desired materials and the template surfaces [8].

As it was stated above, template is not only important for controlling the final shape of materials, but also vital for the compositions of the products. In our research work, ZIF-67 ([Co(MeIm)$_2$]$_n$, MeIm = 2-methylimidazole) has been chosen as an ideal template because of its large surface area (BET $= 1232$ m$^2$·g$^{-1}$), and pore volumes. Also, its well-defined morphology, high chemical and thermal stabilities of normal Zeolites making it a good template [9]. In addition, ZIF-67 can easily be removed from acidic solution through an ingenious co-precipitation methods [10]. Co-ions which were dissolved from ZIF-67, co-precipitated with Ni$^{2+}$ in the nickel nitrite ethanol solution to form Ni-Co layers of doubled hydroxides (ZIF-67/Ni-Co LDH) and subsequent annealed in air to give Co$_3$O$_4$/NiCo$_2$O$_4$ double-shelled nanocages (DSNCs). This research work could provide a feasible and ingenious ways to prepare non-spherical multi-shelled hollow structures with different shell materials.

2. Experiment section

In a typical synthesis, 291 mg of Co(NO$_3$)$_2$·6H$_2$O and 328 mg of 2-methylimidazolate were separately dissolved in 25 ml of methanol. The solution of 2-methylimidazolate in methanol was added to solution of Co(NO$_3$)$_2$·6H$_2$O in methanol under continuous stirring for a period of 30 min. The mixture was then aged for 24 h at room temperature and purple precipitate was obtained. The precipitate was collected by centrifuging. The collected sample was then washed with methanol and dried to obtain ZIF-67. The ZIF-67/Ni–Co LDH was formed by dispersing ZIF-67 into Ni(NO$_3$)$_2$·6H$_2$O in ethanol solution and kept for a period of 30 min. Co$_3$O$_4$ NCs and Co$_3$O$_4$/NiCo$_2$O$_4$DSNCs were obtained by annealing the as-obtained ZIF-67 and yolk-shelled particles in air at 450 °C for 2 h with a ramp rate of 1 °C min$^{-1}$ respectively.

The obtained samples were examined by Rigaku MiniFlex 600 Powder X-ray diffractometer with Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å). The morphology and microstructure of the products were characterized using Transmission Electron Microscope (TEM, JEM-2100, Japan) and a Field Emission-Scanning Electron Microscope (FESEM, JSM-7800F, Japan). Surface area measurements were performed by

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Results of the sensor fabrication were similar to our previous works [11,12]. Gas sensing properties were measured in a home-designed sensor testing system under laboratory conditions (25 °C, 40 RH%).

3. Results and discussion

The MOFs-derived strategy used in the synthesis of Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs is outlined in Fig. 1. In the first step, the ZIF-67 was synthesized using procedures described by Lou with little modification [13]. The as-synthesized ZIF-67, as expected, exhibited a rhombo-dodecahedron shape with an average size of about 500 nm (Fig. 2b). XRD patterns revealed that the as-synthesized samples matched well with that of the simulated patterns of ZIF-67 (Fig. 2a), which indicated that the as-synthesized templates were phase-pure [14]. In the second step, the ZIF-67 was dispersed in ethanol solution containing Ni(NO$_3$)$_2$ for 30 min to obtain ZIF-67/Ni-Co layered double hydroxides (LDH). The morphology and microstructures of the as-prepared ZIF-67/Ni-Co LDH could be evident from the SEM and TEM images (Fig. 2e, f). Finally, thermal treatments at 450 °C in ambient atmosphere converted the
ZIF-67/Ni-Co LDH to Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs. The morphology and microstructures of Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs were checked utilizing SEM and TEM examined using SEM and TEM respectively. And obtained images were shown in Fig. 2(g, h). It can be observed from the SEM images that the surfaces of Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs became rougher than that of ZIF-67/Ni-Co LDH. The TEM images confirmed the double-shelled structure of Co$_3$O$_4$/NiCo$_2$O$_4$. Besides, the thermal annealing of ZIF-67 produced Co$_3$O$_4$ nanocages (Fig. 2b). The XRD patterns (Fig. 2d) of Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs and Co$_3$O$_4$ NCs were taken to characterize the phase composition and purity. The diffraction peaks of Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs and Co$_3$O$_4$ NCs appeared at the same positions, which made it difficult to confirm the existence of NiCo$_2$O$_4$ in the Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs. The phenomenon might be attributed to the lattice replacement of Co$^{2+}$ of Co$_3$O$_4$ with Ni$^{2+}$ to generate NiCo$_2$O$_4$. Thus, in order to confirm the existence of NiCo$_2$O$_4$, we conducted Energy Dispersive X-ray Spectroscopic analysis (EDS) of Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs (Fig. 2i). The EDS analysis revealed that DSNCs consisted of Co, Ni and O elements, which confirmed the existence of NiCo$_2$O$_4$. The Si, Cu and C elements were attributed to the TEM grid used to support the sample.

To evaluate the specific surface areas and porosity of the Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs and Co$_3$O$_4$ NCs, the N$_2$ adsorption-desorption isotherms and BJH pore size distributions analysis were further conducted (Fig. 3a). The specific surface area of Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs and Co$_3$O$_4$ NCs were calculated by the BET method to be 71.4 and 32.1 m$^2$/g, respectively. Remarkably, the specific surface area of Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs was far higher than Co$_3$O$_4$ nanocages. Both samples displayed a typical type IV adsorption isotherm with a H3-type hysteresis loop, which indicated the presence of the mesoporous structure [15]. This could further be substantiated by the results of pore size distribution measurements (the inset of Fig. 3a).

Typically, the response of a semiconductor gas sensor was highly influenced by the operating temperature. Thus, the responses of the sensors based on Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs and Co$_3$O$_4$ NCs to 10 ppm acetone were tested as function of operating temperatures to determine the optimum temperature, which was shown in Fig. 3b. It is obvious that the response of the two samples sensors gradually increases to the maximum values and then decreases with the increasing of operating temperature. The optimum operating temperature of the sensors based on Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs and Co$_3$O$_4$ NCs were shown to be 238.9 and 261.0 °C, respectively. This “increase-maximum-decrease” phenomenon could be explained as follows: too low operating temperature means small chemical activation of samples which results in a very low response. But too high operating temperature will lead to some adsorbed gas molecules escaping from the sensor surface before reacting with the active oxygen molecules, which means the response will decrease correspondingly. Response and recovery times are important factors of gas sensors. Besides, the Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs sensor displayed enhancement in response to acetone compared to Co$_3$O$_4$ NCs. The enhancement of Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs-based gas sensor properties could be understood in relation to the morphology and microstructures of Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs.
to the synergetic effect exerted by Co$_3$O$_4$ and NiCo$_2$O$_4$ as well as the change of hetero-junction barrier at the different gas atmosphere.

Fast response and recovery can allow a real-time detection. Fig. 3c showed the dynamic response–recovery curves of the sensors based on Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs and Co$_3$O$_4$ NCs to 100 ppm acetone at 238.9 and 261.0 °C, respectively. The response time of the sensors are 8 and 6 s, respectively, and the recovery time were 20 and 28 s, respectively. In realistic applications, gas sensors should have ability to discriminate target gas in different ambient environments and situations. The response of the sensor based on the Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs was measured on exposure to various gases at 238.9 °C, and the result was shown in Fig. 3d. These results implied that Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs sensor exhibited an obvious response for acetone and ethanol, and lesser effects for others at 238.9 °C, indicating the excellent selectivity to acetone as well as ethanol.

4. Conclusions

In summary, highly porous Co$_3$O$_4$/NiCo$_2$O$_4$ double-shelled nanocages with high specific surface area ($71.4 \text{ m}^2\text{g}^{-1}$) has been successfully synthesized via a simple ZIF-67 template chemical transformation with co-precipitated procedure as well as subsequent thermal treatment. As proof-of-concept demonstration of the function, such Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs were used as the sensing material of a gas sensor. The synthesized Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs sensor exhibited enhanced sensitivity and excellent selectivity to acetone when compared with the Co$_3$O$_4$ nanocages, which endowed its great potential in gas sensor application. Our findings may supply rationale for novel design of complex hollow core-shell structure with tunable structure through metal organic frameworks route and enhanced functionalities in various applications.

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References