

Full Length Article

Synthesis of NiCo₂O₄ nanostructures with different morphologies for the removal of methyl orange



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ABSTRACT

Aiming to investigate the adsorption removal performance of NiCo₂O₄ as water purification adsorbents, magnetic materials NiCo₂O₄ with six different morphologies were successfully synthesized by a facile method. NiCo₂O₄ with six different morphologies were characterized by scanning electron microscope, Fourier transform infrared spectroscopy, X-ray diffraction, N₂ adsorption-desorption, vibrating sample magnetometry and X-ray energy dispersive spectrometry. In this study, we mainly explored the effect of specific surface area, pore volume and pore size on the performance for the removal of methyl orange, and the adsorption capacity followed an order of (b) NiCo₂O₄ nanorods > (e) balsam-like NiCo₂O₄ > (f) rose-like NiCo₂O₄ > (d) NiCo₂O₄ nanoribbons > (a) NiCo₂O₄ flowerlike nanostructures > (c) dandelion-like NiCo₂O₄ spheres. The results indicated that NiCo₂O₄ nanorods exhibited better adsorption performance. The reasons for the excellent adsorption capacity of NiCo₂O₄ nanorods were also discussed in depth by analyzing scale and surface characteristics. Besides, NiCo₂O₄ could be easily recovered from solution, which may avoid potential secondary pollution. Moreover, adsorption kinetics, the influence of pH and adsorption mechanism were comprehensively investigated. This finding indicated that NiCo₂O₄ were promising adsorbents for water purification.

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1. Introduction

In recent years, water pollution raises much concern due to the fast development of industry [1–8]. Organic dye containments play a major role in the pollutants because they have complex aromatic molecular structures, which make them stable and resistant to degrade [9–13]. Therefore, the removal of organic dyes before discharge is necessary. Various methods, such as chemical oxidation, photochemical degradation, electrochemical process, membrane separation and adsorption, have been applied for the removal of organic dyes [14–18]. Among these techniques, adsorption is considered as the most popular method owing to its advantages of simplicity, low cost, high efficiency and no other additional reagents and equipment [19–22].

Many researchers have developed many adsorbents, such as active carbon, carbon nanotubes, polyaniline, manganese oxides and noble metal/metal oxide nanocomposites, for the removal of organic dyes [23–32]. However, it is notable that there are secondary pollution problems for adsorbents left in solution. Although some nanostructured Fe-based magnetic materials are widely used

in adsorption, the synthesis process of these materials may be relatively complicated and costly. Therefore, it remains a daunting challenge for searching a low-cost, easy separation and high efficiency adsorbent.

Cobalt-nickel oxides (NiCo₂O₄) have been a topic of interest because of their prominent advantages of low cost, environmental friendliness and natural abundance. To date, many researchers have made significant efforts to improve NiCo₂O₄ performance. Cui et al. synthesized core-ring structured NiCo₂O₄ nanoplatelets as electrocatalysts for oxygen reduction reaction [33]. Yuan et al. prepared NiCo₂O₄ nanosheets as high-performance electrodes for supercapacitors [34]. Li et al. synthesized NiCo₂O₄ microspheres as anode materials for Li-ion batteries [35]. Besides, NiCo₂O₄ was proved to be the most effective adsorbent in the family of MCo₂O₄ (M = Zn, Mn, Cu, Ni) [36]. Although NiCo₂O₄ has been widely applied, the main emphasis of these reported work mainly focuses on improving the adsorption capacities by modifying materials with NiCo₂O₄. To the best of our knowledge, limited information is available on investigating on the effect of specific surface area, pore volume and pore size of NiCo₂O₄ on adsorption capacity.

Inspired by the aforementioned considerations, we reported herein six different morphologies of NiCo₂O₄ by a simple hydrothermal-calcination method to avoid abovementioned disadvantages. These materials were characterized by scanning electron

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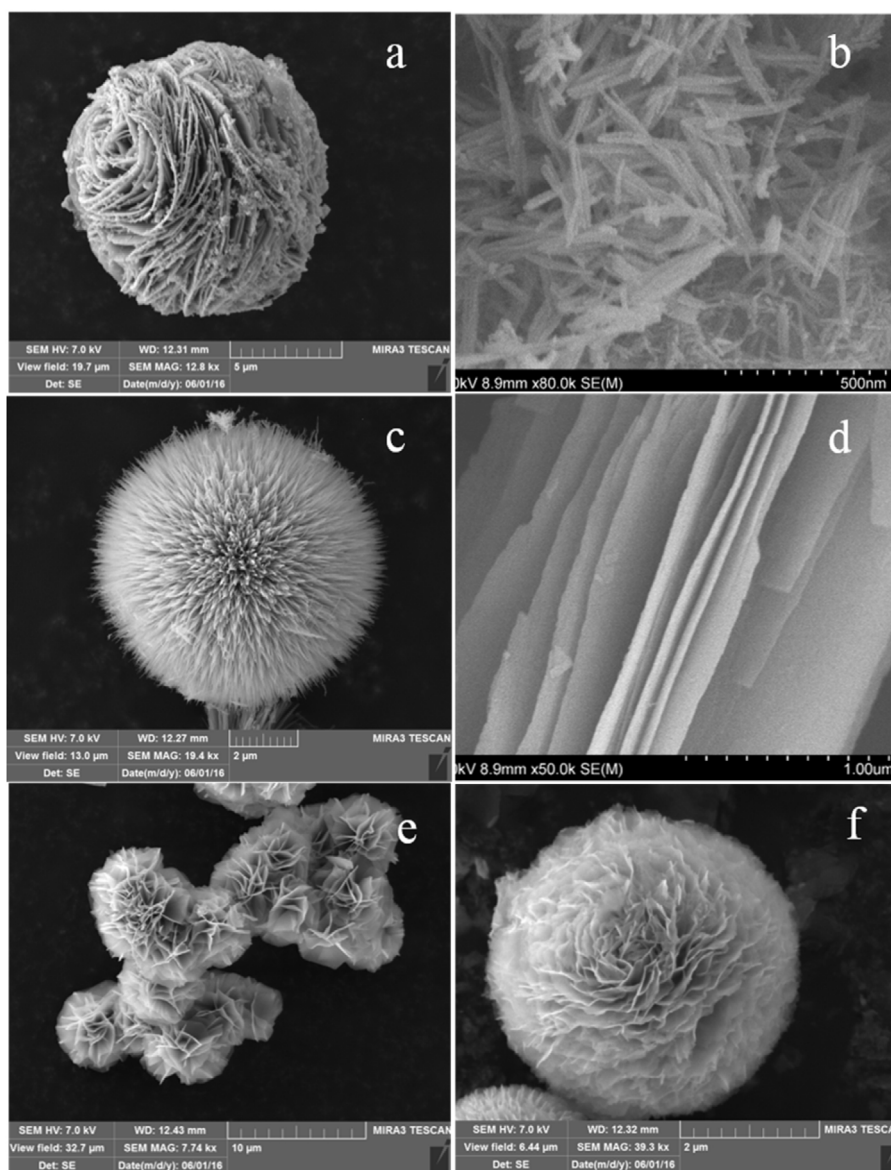


Fig. 1. SEM images of (a) NiCo_2O_4 flowerlike nanostructures, (b) NiCo_2O_4 nanorods (c) dandelion-like NiCo_2O_4 spheres, (d) NiCo_2O_4 nanoribbons, (e) balsam-like NiCo_2O_4 , (f) rose-like NiCo_2O_4 .

Table 1
Surface characteristics of different materials.

Materials	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	Pore size (nm)
NiCo_2O_4 flowerlike nanostructures	63.11	0.127	8.04
NiCo_2O_4 nanorods	119.11	0.231	7.72
dandelion-like NiCo_2O_4 spheres	45.93	0.242	21.05
NiCo_2O_4 nanoribbons	97.84	0.172	7.03
balsam-like NiCo_2O_4	124.01	0.166	5.34
rose-like NiCo_2O_4	70.62	0.282	16.01

microscope (SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), N_2 adsorption-desorption, vibrating sample magnetometry (VSM) and X-ray energy dispersive spectrometry (EDS). Methyl orange (MO) was analyzed as the adsorption model. The adsorption performance of NiCo_2O_4 with different morphologies was investigated. Particularly, the reasons for the enhanced adsorption capacity for NiCo_2O_4 nanorods were

discussed in depth by analyzing scale and surface characteristics. Besides, adsorption kinetics, the influence of pH and the adsorption mechanism were comprehensively investigated to evaluate adsorption behavior. It is believed that this research will provide useful information for the removal of organic pollutants.

2. Experimental section

2.1. Materials

2.1.1. Synthesis of porous NiCo_2O_4 flowerlike nanostructures (a) [37]

In a typical procedure, 2 mmol of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 4 mmol of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 60 mL of ethanol solution (40 mL of ethanol and 20 mL of H_2O). Then the mixture solution was transferred into a Teflon-lined stainless steel autoclave, and the autoclave was heated at 180°C for 6 h. The product was filtered, washed repeatedly with water and ethanol, and dried

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