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Synthesis and magnetic properties of Fe_3C doped with Mn or Ni for applications as adsorbents

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ABSTRACT

Fe_3C NPs doped with Mn or Ni were prepared via a sol-gel method at the heating rates of 10 and 15 °C min^{-1}. During the experiments, the melamine and the cetyltrimethyl ammonium bromide (CTAB) are used as carbon source for the generation of the materials. Their structure, morphology and magnetic properties are researched and compared. Results show that the particle sizes and magnetic properties of the materials are affected by the dopants. By comparing, we know how the transition metal elements affect the structure and magnetic properties of Fe_3C.

1. Introduction

Iron carbides can find applications in various fields include magnetic, catalysis, medicine and electrochemistry [1–10]. The reasons why these kinds of materials demonstrate so many amazing properties are due to iron carbides consist of carbon atoms occupying the interstices between close-packed iron atoms [11]. The presence of carbon atoms provides iron carbides with excellent properties [12–18], such as elevated saturation magnetization (M_s), air-stability and low toxicity et al. By this, many methods have been created to prepare iron carbides [17,19–23]. For instance, Li and co-workers prepared nitrogen-doped Fe/Fe_3C@graphitic layer/carbon nanotube hybrid from MOFs [24]. Barman et al. fabricated Fe/Fe_3C encapsulated N-doped graphitic nanostructures use Prussian blue as a single precursor [25]. Zhou et al. prepared N-Fe/Fe_3C@C nanomeshes using the polypyrrole–Fe (PPy–Fe) coordination complex as a precursor [26]. Liu et al. prepared nanosized Fe_3C encapsulated within mesoporous nitrogen-doped carbon nanospheres through a colloidal amphiphile-templating approach [27]. However, the accompanying complicated procedures in current synthetic routes produce iron carbide NPs without control over the size and morphology, which is highly necessary for practical applications. Furthermore, at present there is lacking of experimental studies of transition metal doped Fe_3C NPs.

In our previous paper [4,28–30], we have been reported the simple and economic ways to prepare Fe_3C, Mn doped Fe_3C ($(Fe_{1-x}Mn_x)_3C$) and Ni doped Fe_3C ($(Fe_{1-x}Ni_x)_3C$) NPs). All of these materials demonstrate soft magnetic properties, and their M_s values are remained at a high level. The morphology of Fe_3C and $(Fe_{1-x}Ni_x)_3C$ NPs are spherical with core shell structures, however the $(Fe_{1-x}Mn_x)_3C$ NPs shows cubic structures. This may be due to that the Mn-dopant atoms access into the Fe_3C lattice and result in a distorted lattice of Fe_3C as well as the effects on the morphology of Fe_3C NPs.

In this paper, we compared the structure and morphology of these three kinds of materials, and prepared Fe_3C, $(Fe_{0.9}Mn_{0.1})_3C$ and $(Fe_{0.9}Ni_{0.1})_3C$ NPs at different heating rates to get the changing rule of their magnetic properties. Lastly, we explained the reason of the variation of the morphology and magnetic properties of Mn and Ni doped Fe_3C.

2. Experimental

2.1. Precursor

2.1.1. Fe_3C

According to our previous report, melamine (2.52 g) and CTAB (2.92 g) were dissolved in a solution of deionized water (40 mL) and

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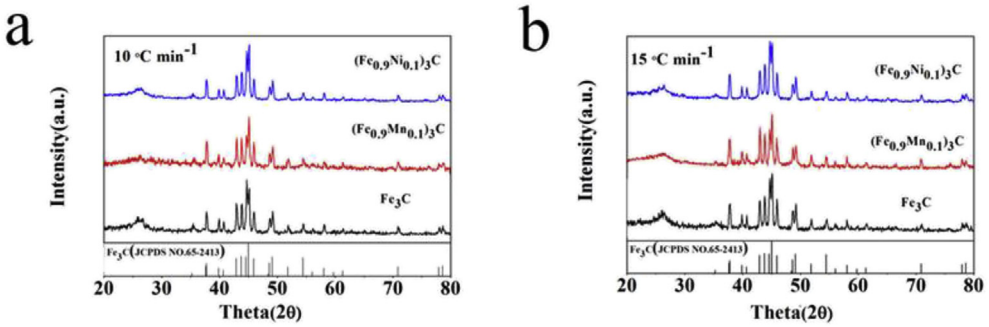

Fig. 1. XRD patterns of Fe_3C, $(Fe_{0.9}Mn_{0.1})_3C$ and $(Fe_{0.9}Ni_{0.1})_3C$ NPs which are prepared at the heating rates of 10 (a) and 15 °C min^{-1}(b).

ethanol (40 mL). Stirring was needed and $FeCl_3 \cdot 6H_2O$ (2.7 g) was added in this process. Then, the solution was transferred to an 80 °C water bath for 3 h (h) a to evaporate the solvent. Finally, the solution was transferred to an oven to dry for 12 h under an air atmosphere.

2.1.2. $(Fe_{0.9}Mn_{0.1})_3C$ and $(Fe_{0.9}Ni_{0.1})_3C$

According to our previous report, a certain amount of $MnCl_2 \cdot 4H_2O$ or $C_4H_6O_4Ni \cdot 4H_2O$ was dissolved in 10 mL of ethanol, denoted as A. Then, 2.52 g of melamine and 2.92 g of CTAB were dissolved in ethanol (30 mL) and deionized water (40 mL) solution, denoted as B. Solution A was then slowly added to B, stirring was needed during this process. Finally, B was transferred to an 80 °C water bath to evaporate the solvent. 3 h later, B was transferred to an oven to dry for 12 h under an air atmosphere.

2.2. Calcinations process

1 g of precursor was placed into the central of tube furnace. Then the tube furnace was heated at the rates of 10 and 15 °C min^{-1} to 680 °C (from room temperature) and held at this temperature for 3 h, then cooled to room temperature naturally. The black powder was the product.

2.3. Characterization

X-ray diffraction measurements (XRD) using Cu Kα radiation (λ = 0.15405 nm) was used to check the purities of all the samples at room temperature. The morphology was characterized with High Resolution Transmission Electron Microscopy (HRTEM) (Philips Tecnai G2 F20 and JEM-2100F). A vibrating sample magnetometer (VSM, LakeShore 7404) was used to characterize the magnetic properties of as-synthesized samples. The magnetic hysteresis curve was obtained by changing H between +18000 Oe and −18000 Oe.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the XRD patterns of Fe_3C, $(Fe_{0.9}Mn_{0.1})_3C$ and $(Fe_{0.9}Ni_{0.1})_3C$ NPs which are prepared at the heating rates of 10 and 15 °C min^{-1}.

In Fig. 1(a), the standard XRD pattern of Fe_3C (JCPDS card No. 65-2413) is shown at the bottom, it can be seen that all of the XRD patterns which are prepared at the heating rates of 10 °C min^{-1} can be perfectly match it, confirming their single phase nature. By comparison, we can see that the peaks intensity is different, indicating that the involved of Mn or Ni may will affect the lattice parameters of Fe_3C. Furthermore, the peak at $2\theta = 26°$ which belongs to the characteristic peak of graphite carbon (JCPDS card No. 41-1487) changed weak, this may be due to that the Fe can play the role of catalyst to generate graphite carbon, when the dopants involved, they will depress the catalytic activity. Fig. 1(b) shows the XRD patterns of the three kinds of materials which are prepared at the heating rates of 15 °C min^{-1}, we can also see that all of the peaks can match the standard XRD pattern of Fe_3C well, confirming that the single phase Fe_3C, $(Fe_{0.9}Mn_{0.1})_3C$ and $(Fe_{0.9}Ni_{0.1})_3C$ NPs can be prepared at the heating rate of 15 °C min^{-1}.

TEM was performed to investigate the detailed information about the morphology of the samples. Fig. 2 shows the Fe_3C, $(Fe_{0.9}Mn_{0.1})_3C$ and $(Fe_{0.9}Ni_{0.1})_3C$ NPs embedded in an amorphous carbon. Fe_3C and $(Fe_{0.9}Ni_{0.1})_3C$ NPs possess spherical structure, and the $(Fe_{0.9}Mn_{0.1})_3C$ possess the cubic structure which is consistent with our previous reports. Moreover, the average size of Fe_3C NPs is larger than $(Fe_{0.9}Ni_{0.1})_3C$ NPs and smaller than $(Fe_{0.9}Mn_{0.1})_3C$, which is may be due to the Fe replacement with larger Mn atoms (or smaller Ni atoms) in the Fe_3C crystal lattices.

All of the Fe_3C, $(Fe_{0.9}Mn_{0.1})_3C$ and $(Fe_{0.9}Ni_{0.1})_3C$ NPs display soft magnetic properties as shown in Fig. 3. The values of M_s are 26.9, 25.3and 24.9 emu g^{-1} for the materials which are prepared at the

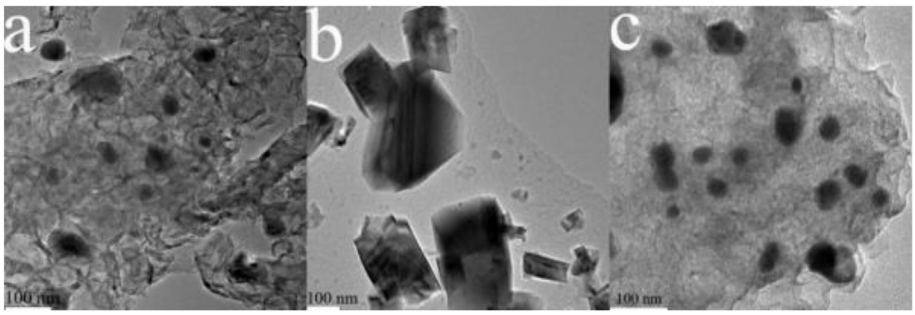

Fig. 2. TEM images of Fe_3C (a), $(Fe_{0.9}Mn_{0.1})_3C$ (b) and $(Fe_{0.9}Ni_{0.1})_3C$ NPs (c) which are prepared at the heating rates of 15 °C min^{-1}.