

Short Communication

# One-step Nanocasting Route for the Synthesis of Hierarchically Mesoporous Magnetic Nanocrystalline Ni@C/Graphitic Carbon Nanocomposite and Electrochemical Performance

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In this paper, we have reported a simple method for the preparation of hierarchically mesoporous magnetic nanocrystalline Ni@C/graphitic carbon nanocomposite by one-step nanocasting route for the first time. X-ray diffraction, nitrogen adsorption-desorption, transmission electron microscopy and thermogravimetric analysis techniques were used to characterize the sample. It was observed that magnetic metallic Ni nanocrystals of 10-15 nm in diameter, which were covered by a nanometer-thick graphitic carbon layer, were well dispersed in the hierarchically mesoporous graphitic carbon matrix, and the as-obtained nanocomposite with hierarchical mesoporous structure and high specific surface area showed good electrochemical properties, giving the material potential application as an electrode material for electrochemical sensing.

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**Keywords:** hierarchically mesoporous; graphitic carbon; Ni nanocrystal; one-step nanocasting.

## 1. INTRODUCTION

Magnetically separable mesoporous carbon nanocomposites have received much attention in recent years because of the combined functionalities of magnetic nanoparticle and mesoporous carbon, which endow them with many potential applications in adsorption, catalysis, separation, and electrochemical sensors [1-4]. Until now, three approaches have been used to synthesize magnetic mesoporous carbon nanocomposites: 1) incorporating magnetic nanoparticles into the pre-synthesized

mesoporous carbons using the incipient-wetness impregnation procedure [5-7], 2) using one-step blockcopolymer self-assembly strategy to create mesoporous carbon nanocomposites with magnetic metal nanoparticles dispersed in the composites [8-10], 3) employing co-casting method by infiltration of an appropriate carbon precursor and metal source into the channels of mesoporous silica template, followed by polymerization, carbonization and subsequent removal of the silica framework [4, 11-15]. However, most of the above methods were either too costly or too synthetically complicated to be viable for a large-scale production, which may severely hamper the broad applications of these composite materials. Therefore, development of a simple and effective method for the synthesis of magnetic mesoporous carbon composites remains necessary and challenging in this field. Moreover, the stability of magnetic nanoparticles in the most mesoporous carbon composites is not very good since the lack of a suitable protective layer, which makes them easily oxidized by air or dissolved into an acid/alkaline solution for the practical applications.

Herein, we report a simple method for the synthesis of magnetic nanocrystalline Ni@C/graphitic carbon nanocomposite with hierarchical mesostructure by a simple one-step nanocasting route. The synthesis was achieved using nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and soybean oil as nickel source and carbon precursor, respectively, for the gelation reaction of tetraethyl orthosilicate (TEOS) and citric acid. One of the most prominent advantages of this method is its easy operation and enlargement, and the formed magnetic metallic Ni nanocrystals covered by a nanometer-thick graphite carbon layer were well dispersed in the hierarchically mesostructured graphitic carbon matrix. Furthermore, the structural and electrochemical properties of the obtained hierarchically mesostructured magnetic nanocrystalline Ni@C/graphitic carbon nanocomposite were investigated.

## 2. EXPERIMENTAL

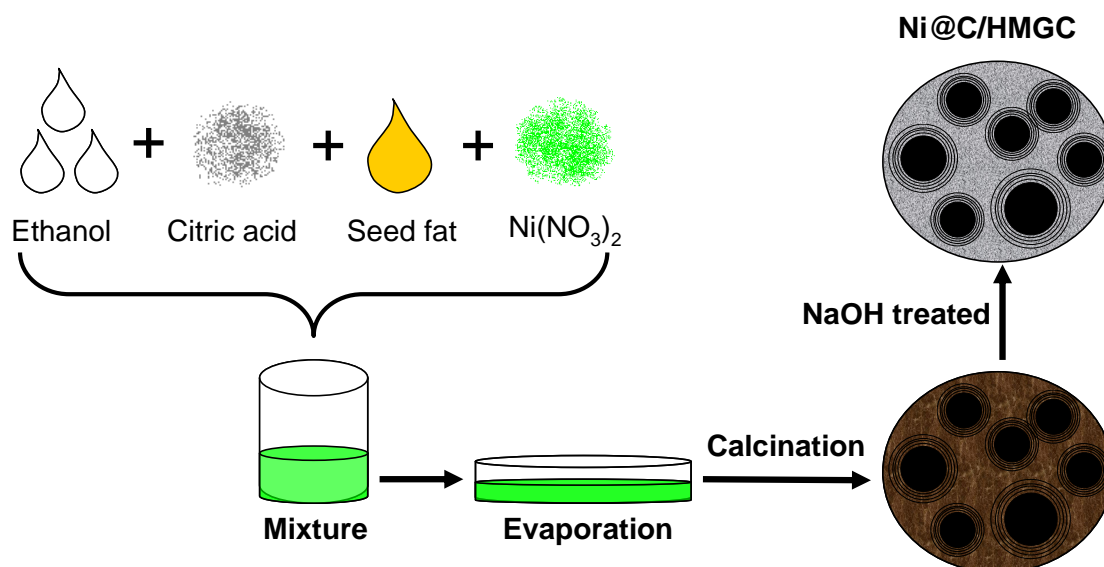
### 2.1. Chemicals

Citric acid, tetraethoxysilane (TEOS), ethanol,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and sodium hydroxide were purchased from Shanghai Chemical Corp. Soybean oil was obtained from Shanghai Wal-mart supermarket. All chemicals were used as received without further purification.

### 2.2 Materials preparation

Hierarchically mesostructured magnetic nanocrystalline Ni@C/graphitic carbon nanocomposite was prepared by a simple one-step nanocasting route (illustrated in Fig. 1). In a typical synthesis, 20 mmol of citric acid was dissolved in 40 mL of ethanol, which was stirred for several minutes at room temperature to get a transparent solution. Then, 4.2 g of soybean oil, 10mmol of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and 20 mmol of TEOS were sequentially added to the above solution under vigorous stirring, after stirring for 120 min, the mixture was transferred to a clean flat Petri dish (diameter: 10 cm) and underwent solvent evaporation at room temperature for a day to get a rigid gel. This gel was calcined at 900 °C under Ar flow for 4 hours with a heating ramp of 1 °C /min to decompose and carbonize the

precursors. Finally, the silica matrix was removed using a 2 M NaOH aqueous solution and this etching process was repeated three times. The resulting nanocomposite material is denoted as Ni@C/HMGC.



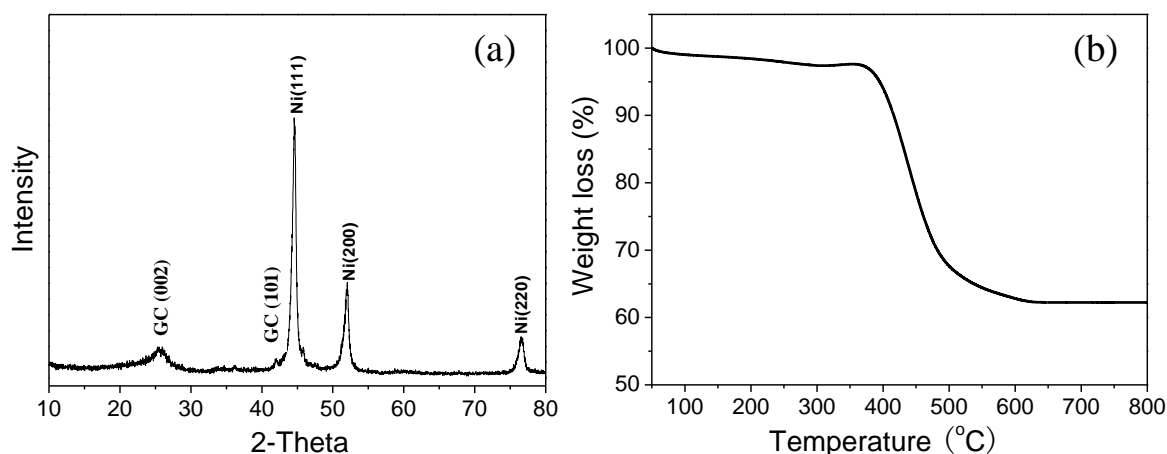
**Figure 1.** Schematic illustration of the synthesis process of hierarchically mesostructured magnetic nanocrystalline Ni@C/graphitic carbon nanocomposite by one-step nanocasting route.

### 2.3 Materials characterization

X-ray diffraction (XRD) pattern was collected in  $\theta$ - $2\theta$  mode using Rigaku D/MAX-2550VB/PC diffractometer ( $\text{CuK}\alpha_1$  radiation,  $\lambda=1.5406\text{\AA}$ ), operated at 40 kV and 100 mA (scanning step:  $0.02^\circ$  per second). Thermogravimetric (TG) analysis was carried out using a Mettler Toledo TGA-SDTA851 analyzer (Switzerland) from 25 to  $800^\circ\text{C}$  in an air flow of  $80\text{ mL min}^{-1}$  at a heating rate of  $5^\circ\text{C min}^{-1}$ . Transmission electron microscope (TEM) images were taken using a JEOL JEM-2010 electron microscope with an acceleration voltage of 200 kV. Nitrogen sorption isotherms were measured at  $-196^\circ\text{C}$  on a Micromeritics ASAP 2000 apparatus. Before measurements, the sample was degassed in vacuum at  $200^\circ\text{C}$  for 6 h. The Brumauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. The pore size distributions were derived from the desorption branches of the isotherms using the Barrett–Joyner–Halanda (BJH) method. The total pore volume ( $V_t$ ) was estimated at a relative pressure of 0.98. Electrochemical experiments were performed with CHI 440A electrochemical analyzer (ChenHua Instruments Co. Ltd., Shanghai, China) with a conventional three-electrode setup. The working electrode was a Ni@C/HMGC modified carbon paste electrode (CPE). An Ag/AgCl and a platinum electrode were used as the reference and the auxiliary electrode, respectively. The experiments were carried out at room temperature.

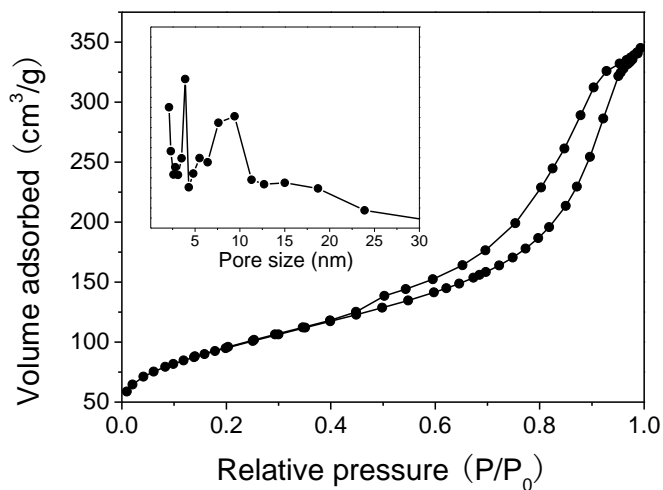
### 3. RESULTS AND DISCUSSION

The XRD pattern of the synthesized Ni@C/HMGC nanocomposite is shown in Fig. 2a, it can be seen that in addition to the two weak peaks at around 23 and 43° which can be respectively indexed to the (002) and (101) reflections for typical graphitic carbon [16], all diffraction peaks correspond to the fcc Ni form by comparison with the JCPDS card file no. 04-0850 and no evidence of nickel oxide is detected. The crystallite size estimated from the line broadening of the Ni (111) reflection plane ( $2\theta=44.5^\circ$ ) is about 12.6 nm. TG result (Fig. 2b) under air atmosphere exhibits that this Ni@C/HMGC nanocomposite has a chemical composition of about 48.5 wt% metallic Ni and 51.5 wt% graphitic carbon.

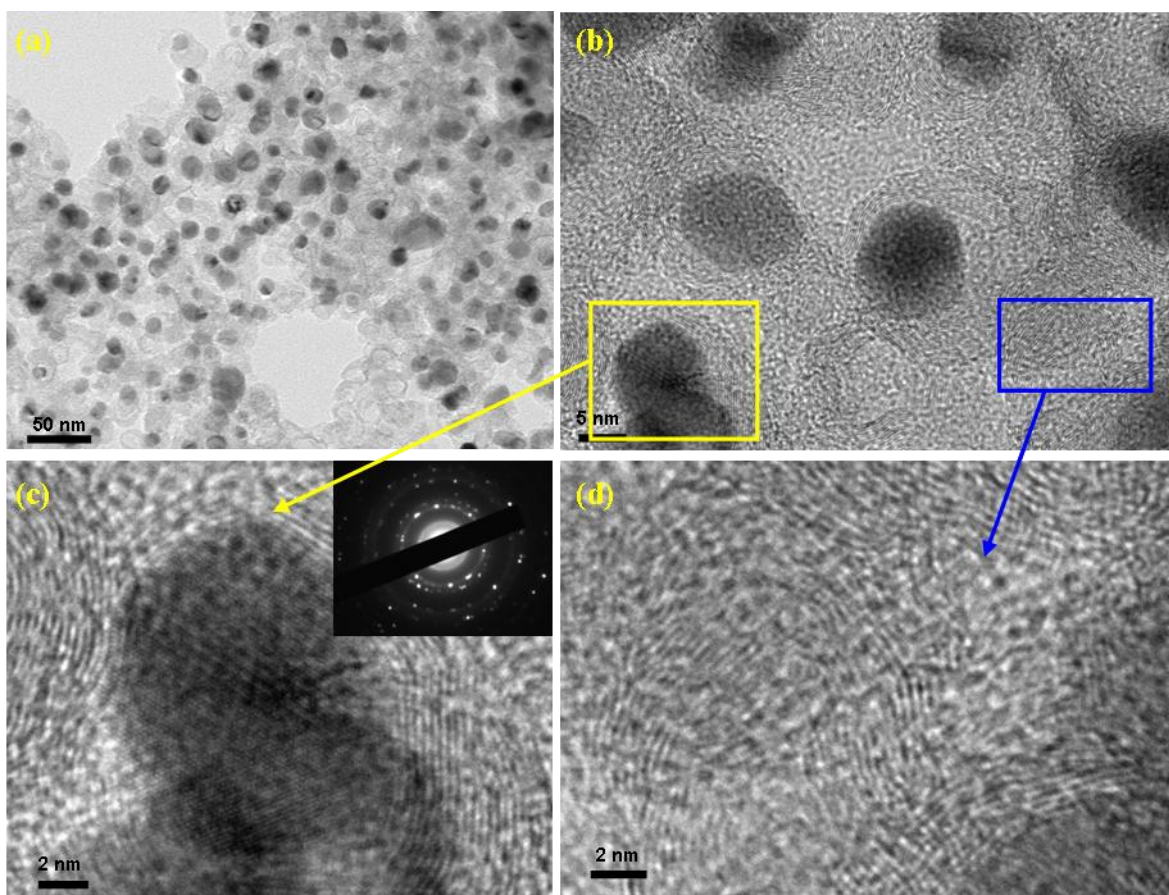


**Figure 2.** (a) XRD pattern and (b) TG curve of Ni@C/HMGC nanocomposite.

Fig. 3 shows the nitrogen adsorption-desorption isotherm and corresponding pore size distribution curve of the Ni@C/HMGC nanocomposite. The isotherm exhibits a strong uptake of  $N_2$  as a result of capillary condensation in a wide relative pressure ( $P/P_0$ ) range of 0.45-0.95, which indicates the existence of multiform pore distributions. The pore size distribution obtained from an analysis of desorption branch of the isotherm is shown in the inset of Fig. 3. It can be seen that this Ni@C/HMGC nanocomposite has a bimodal pore size distribution centered at about 3.8 and 9.3 nm which are respectively ascribed to the decomposition of citric acid template and the dissolution of the silica matrix. Such hierarchical mesostructure is especially valuable for heterogeneous reaction system since active molecular diffusion/transfer becomes easy. Additionally, this Ni@C/HMGC nanocomposite has a high BET surface  $\sim 338.9 \text{ m}^2 \text{ g}^{-1}$ , and a large pore volume  $\sim 0.534 \text{ m}^3 \text{ g}^{-1}$ , giving the material wide potential applications as catalyst support, adsorbent and electrode material.



**Figure 3.** N<sub>2</sub> adsorption-desorption isotherm and corresponding pore size distribution curve (inset) of the Ni@C/HMGC nanocomposite.

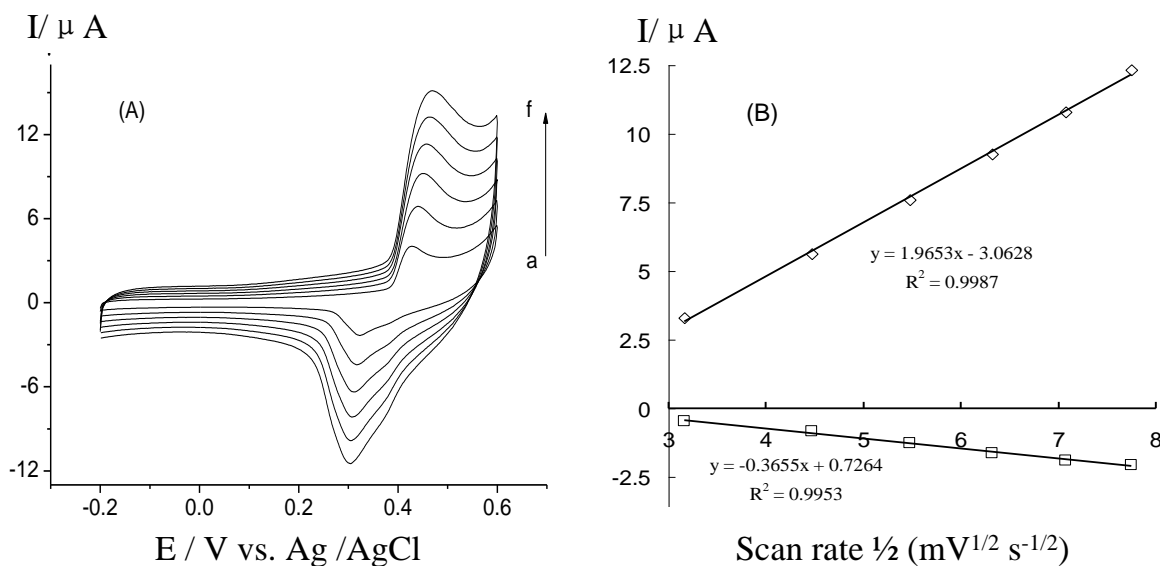


**Figure 4.** Low- (a) and high-magnification (b, c) TEM images for the Ni@C/HMGC nanocomposite. (d) is the SAED pattern of the observed metallic Ni.

The detailed structure of the Ni@C/HMGC was provided by TEM images. Low-magnification TEM image given in Fig. 4a reveals that nano-sized metallic Ni particles with the diameter of 10-15

nm are highly dispersed in the hierarchically mesostructured graphitic carbon matrix, and the high-magnification TEM (HRTEM) images (Fig. 4b and 4c) exhibit that metallic Ni nanocrystals with a monocrystalline characteristic are covered by a nanometer-thick (2-3 nm) graphite carbon layer. In addition, HRTEM image exhibits that the hierarchically mesostructured carbon matrix has a relative high graphitic degree with the  $d$  spacing of the observed lattice planes of 0.343 nm (as shown in Fig. 4d) and very close to the  $d(002)$  value (0.34 nm) of typical graphite, which is in agreement with our previous study [16]. Furthermore, the presence of the monocrystalline-like metallic nickel is also confirmed by the electron diffraction pattern taken from the region with the lattice fringes (Fig. 4c inset).

It is also found that this hierarchically mesostructured Ni@C/HMGC nanocomposite possesses good electrochemical properties. Fig. 5A depicts the cyclic voltammograms (CVs) of Ni@C/HMGC/CPE in 0.1 M NaOH at different scan rates of 10-60  $\text{mV s}^{-1}$ . It can be seen that the Ni@C/HMGC/CPE gives a well-defined redox peak with an average formal potential of 0.45 V (vs. Ag/AgCl) at a scan rate of 20  $\text{mV s}^{-1}$ , which can be assigned to the  $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$  redox couple formed in alkaline medium [17]. As can be seen from Fig. 5B, both the cathodic and anodic peak currents increased linearly with the square root of scan rate from 10-60  $\text{mV s}^{-1}$ , indicating the electron transfer of the Ni@C/HMGC/CPE in a diffusion controlled electrochemical process, which may endow the material with potential application as an electrode material for electrochemical sensing. [18].



**Figure 5.** (A) CVs of Ni@C/HMGC/CPE in 0.1 M NaOH at different scan rates (a  $\rightarrow$  f: 10, 20, 30, 40, 50, 60  $\text{mV s}^{-1}$ , respectively). (B) Plot of peak current vs.  $V^{1/2}$ .

#### 4. CONCLUSIONS

In conclusion, the hierarchically mesostructured magnetic nanocrystalline Ni@C/graphitic carbon nanocomposite was synthesized by a simple one-step nanocasting route. XRD, TG, nitrogen sorption and TEM results revealed that magnetic metallic Ni nanocrystals covered by a nanometer-

thick (2-3 nm) graphite carbon layer were well dispersed in the hierarchically mesostructured graphitic carbon matrix. Furthermore, this hierarchically mesostructured magnetic nanocrystalline Ni@C/graphitic carbon nanocomposite with high specific surface area presented a good electrochemical response in 0.1 M NaOH, which may endow it with potential application as an electrode material for electrochemical sensing.

#### ACKNOWLEDGMENTS

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