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## ARTICLE

# Template free synthesis of hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres and their application in electrocatalysts for glucose

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Hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres are successfully synthesized via a simple hydrothermal method and calcination in air. It is found that the as-prepared hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres exhibit good catalytic activity toward the oxidation of glucose, it shows a fast amperometric response time of less than 5 s, and the detection limit is estimated to be 0.125 μM. More importantly, compared with other normally co-existing electroactive species (such as ascorbic, uric acid and acid dopamine), the electrode modified with hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres shows good selectivity. These results suggest that hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres have promising application in electrocatalysts for quantitative determination of glucose with high sensitivity and selectivity.

## 1. Introduction

In recent years, the design and synthesis of hollow micro/nanostructure materials with desired size, morphology and composition have received considerable attention because of their promising use in many fields such as sensor, energy storage, drug delivery and waste water treatment.<sup>1-6</sup> The success of these applications strongly depends on the size of the hollow structure, and also on the nanostructure of the shell. Above all, hierarchically hollow spheres with the shell composed of nanosized building blocks (e.g., nanosheets, nanorods, or nanoparticles) should be of great importance for finding and making use of their novel properties, which could provide the advantages of both nanometer-sized building blocks and micro- or submicrometer-sized assemblies.<sup>7-10</sup> Moreover, porous materials are of great significance, because porous materials with high porosity and specific surface area are able to interact with liquids not only at the surface, but also in the inner part of the bulk, and thus, porous materials generally exhibit enhanced chemical-physical performance over their solid counterparts.<sup>11-17</sup> Therefore, preparation of hierarchically hollow spheres with porous has been a research hot spot.

It is no doubt that reliable and fast monitoring of glucose is vital in clinical diagnostics, biotechnology, and the food industry. Therefore, continuous efforts have been made to develop electrochemical glucose sensors. Over the past few years, the conventional glucose biosensors based on glucose oxidase (GOD) exhibits high sensitivity and selectivity.<sup>18</sup> However, these enzymatic

glucose sensors usually suffer from the fatal drawback of poor stability due to the intrinsic nature of enzymes, which limit their wide applications. To overcome these problems, considerable interest has been paid on development of non-enzymatic glucose sensor for practical applications. Recent research has shown that nanomaterials can be employed as electrocatalysts for the oxidation of glucose owing their novel physical and chemical properties, and these nanomaterials also exhibit good performance for the detection of glucose.<sup>19-24</sup> The results demonstrate that nanostructured materials are potential candidates as the electrocatalysts materials for practical glucose monitoring.

Herein, We present that the synthesis of hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres through hydrothermal route and subsequent calcinations. Benefitting from hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres with porous structure, the synthesized products were applied as electrocatalysts for the oxidation of glucose. Cyclic voltammetry and amperometry were used to evaluate the electrocatalytic activities of the hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres towards glucose. It is found that the detection limit is estimated to be 0.125 μM. Moreover, the electrode modified with hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres is also highly selective to the target analyt. The hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres hold potential application in electrocatalysts for glucose.

## 2. Experimental

### 2.1 Materials synthesis

All the reagents used were of analytical grade and used without further purification. Hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres were successfully prepared via combining a hydrothermal route and calcination treatment in air process. In a typical synthesis experiment, 0.110 g cobalt (II) chloride hexahydrate, 0.846 g sodium tartaric and 0.15 g sodium pyrophosphate were added into 20.0 mL  $\text{H}_2\text{O}$  and stirred for 30 min. The mixture solution was then transferred into a 35 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 24 h. After being cooled to room temperature, the resulting precipitate were obtained by centrifugation and washed with ethanol and water for three times, and then dried at 50 °C for 12 h. Subsequently, the products were further calcined at 550 °C for 30 min at a heating rate of 1 °C  $\text{min}^{-1}$  in air to obtain hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres.

### 2.2 Preparation of the hierarchically porous $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$ hollow microspheres/GC.

The glassy carbon (GC) electrode (3 mm diameter) was polished using a polishing cloth with alumina slurry (1.0, 0.3, and 0.05 mm in sequence), and rinsed fully with deionized  $\text{H}_2\text{O}$  and ethanol solution, then allowed to dry at room temperature. To prepare the GC electrode modified with the hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres material, an aqueous dispersion of the  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  (1 mg  $\text{mL}^{-1}$ ) was prepared, and then the suspension (5  $\mu\text{L}$ ) was cast onto the surface of the pretreated GC electrode. The solvent was allowed to evaporate at room temperature, leaving the hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres material immobilized on the GC electrode surface.

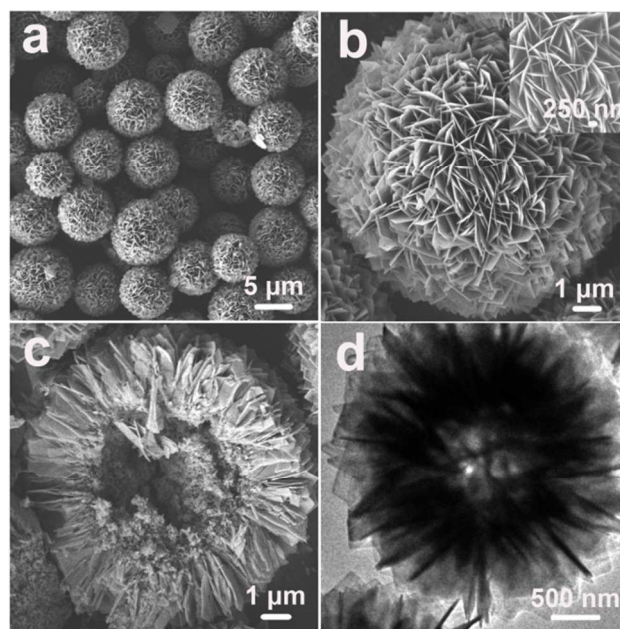
### 2.3 Materials characterization

The phase and compositions of the samples were examined via X-ray diffraction (XRD) on a Rigaku-Ultima III with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The morphologies and microstructures of the products were characterized using a field-emission scanning electron microscope (FESEM, JEOL JSM-6701F), transmission electron microscope (TEM, JEOL-2010). The surface area, pore size, and pore size distribution of the samples were determined by Brunauer-Emmett-Teller (BET)  $\text{N}_2$  adsorption/desorption and Barrett-Joyner-Halenda (BJH) methods on a Micromeritics ASAP2020 physisorption analyzer. Electrochemical measurements were conducted on a CHI 660D electrochemical station (CH Instruments, Shanghai, China), a three-compartment electrochemical cell containing a modified GC electrode as the working electrode, a Ag/AgCl electrode as the reference electrode, and platinum foil as the auxiliary electrode.

## 3. Results and discussion

Hierarchically hollow microspheres constructed by nanosheets can be easily synthesized when the mixture solution is hydrothermally treated at 200 °C for 24 h. The hierarchically hollow microspheres are characterized by field-emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). A panoramic view of the sample (Fig. 1a) presents that these

microspheres with a diameter of about 5-8  $\mu\text{m}$ . The microspheres with rough surface are interconnected. As shown in the Fig. 1b, the microsphere is constructed by nanosheets with smooth surface and the thickness is about 30 nm (the inset in Fig. 1b). A typical broken microsphere is shown in Fig. 1c, which reveals the hollow interior of the hierarchical microspheres. The hollow nature of the as-prepared hierarchical microspheres can also be further proved by transmission electron microscopy. It was found that the contrast between the central portion and the edge of the hierarchical microspheres strongly confirms the formation of hollow nature (Fig. 1d).

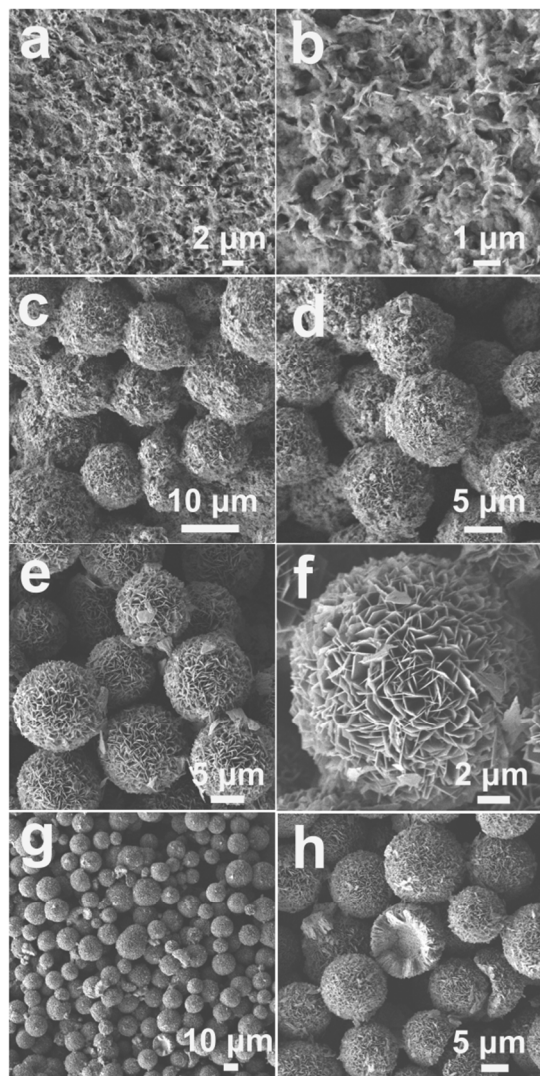


**Fig. 1** FESEM (a-c) and TEM (d) images of the precursor 3D hierarchical hollow microspheres.

In this work, sodium tartaric plays an important role in the preparation of the hierarchically hollow microspheres precursors. Without adding sodium tartaric, the as-prepared sample with urchin-like morphology can be obtained (Fig. S1, ESI†). FTIR spectra of sodium tartaric and hierarchically hollow microspheres precursors are shown in Fig. S2. The peaks at 2974 and 2929  $\text{cm}^{-1}$  are assigned to the stretching vibration of C-H. The band at 1610  $\text{cm}^{-1}$  is assigned to the C=O. The peak at 1380  $\text{cm}^{-1}$  is attributed to the stretching vibration of the C-O. We therefore concluded that sodium tartaric plays a key role for the formation of hierarchically hollow microspheres precursors. To investigate the influence of the reaction temperature on the hierarchically hollow microspheres precursors, we carried out a series of experiments by varying the reaction temperature. When the reaction temperature is increased to 220 °C, the microstructure of the precursors had no obvious variation. In contrast, when the reaction temperature is 160 °C, nanosheets were obtained (Fig. S2). It is believed that the reaction temperature played an important role in the formation of hierarchically hollow microspheres morphology feature. To well understand the formation process of the hierarchically hollow microspheres, a series of time-dependent experiments were carried out. The samples obtained after



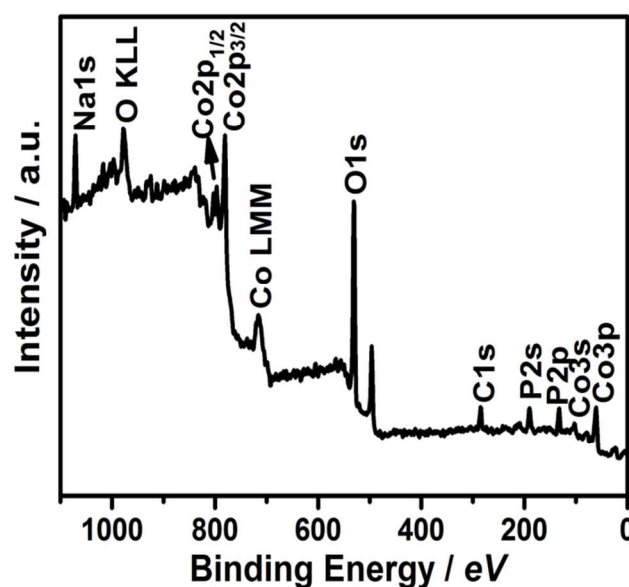
reaction for different times under 200 °C have been examined. Nanosheets were firstly formed after a reaction time of 1 h (Fig. 2a and b). After reaction for 6 h, microspheres constructed by nanosheets come into being (Fig. 2c and d). When the reaction time was further prolonged to 12 h, solid microspheres with nanosheets were formed (Fig. 2e and f). As the reaction proceeds, the hierarchically hollow microspheres were appeared (Fig. 2g and h). During a longer reaction time, the small crystallites in the core region of the solid hierarchically microsphere are selectively dissolved according to a well-known Ostwald ripening process.<sup>25</sup> The hollowing process continues with longer reaction times until well-defined hierarchically hollow microspheres are formed (Fig. 1).



**Fig. 2** SEM images of the samples obtained after reaction for (a and b) 1 h; (c and d) 6 h; (e and f) 12 h; (g and h) 18 h.

The thermal treatment of pre-obtained precursor micro/nano structures is a simple route to synthesize tailored micro/nano structured materials.<sup>25, 26</sup> The thermal behaviours of the pre-obtained hierarchical hollow microspheres have been examined by thermogravimetric analysis. As presented in Fig. S4, The weight loss at low temperature (below 250 °C) was mainly attributed to the

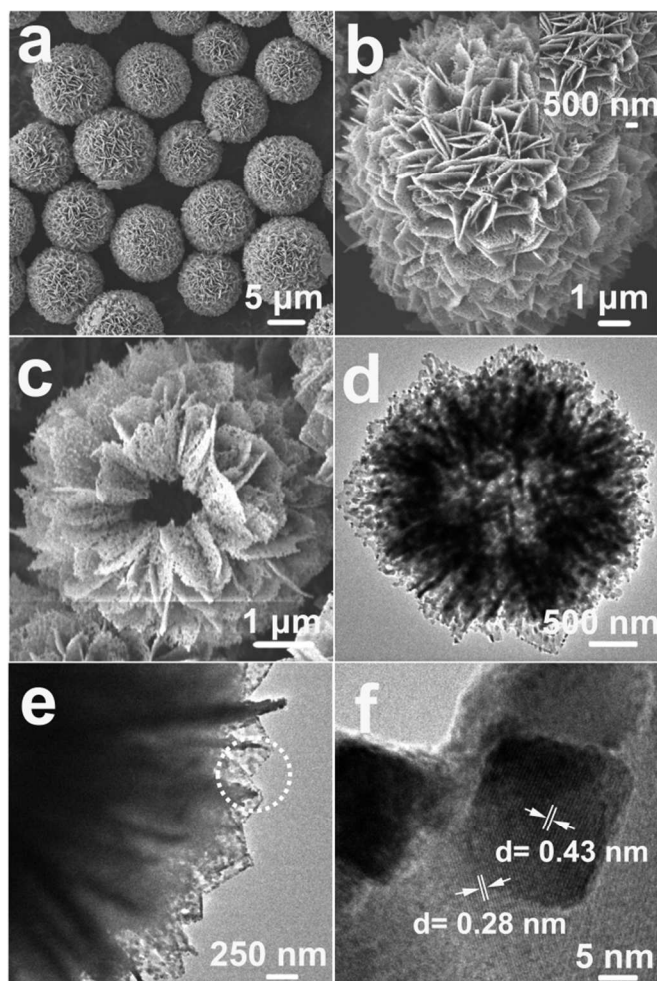
removal of absorbed water on the sample surface. After that, the weight loss was determined to be about 13 % between 250 and 600 °C in air, and thus we choose 550 °C as the calcination temperature to prepare hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres. The composition of the calcined sample was determined by X-ray diffraction (XRD) analysis. A typical XRD pattern of the as-obtained hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres is demonstrated in Fig. S5. The diffraction peaks in the XRD pattern are in good agreement with Co<sub>3</sub>O<sub>4</sub> (JCPDS cards: no. 43-1003) and NaCoPO<sub>4</sub> (JCPDS cards: no. 87-1017 and 88-0481). X-ray photoelectron spectroscopy (XPS) was also used to further determine the chemical composition of the composites (Fig. 3). The peak observed at 132.7 eV (Fig. S6b) can be ascribed to the P2p, which demonstrates that all P atoms have a valence of +5 state.<sup>27</sup> The sharp peak at binding energies of 1070.8 eV is indexed to the characteristic peak of Na 1s (Fig. S6c).<sup>28</sup> The spectra show peak positions at binding energies of 780.3 eV and 795.7 eV which correspond to Co2p<sub>3/2</sub> and Co2p<sub>1/2</sub>, respectively, and with a spin-orbit splitting of 15.4 eV, confirming the presence of both Co(II)/Co(III) in the composites (Fig. S6d).<sup>29, 30</sup>



**Fig. 3** X-ray photoelectron spectroscopy (XPS) survey scan spectra of the NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> composites.

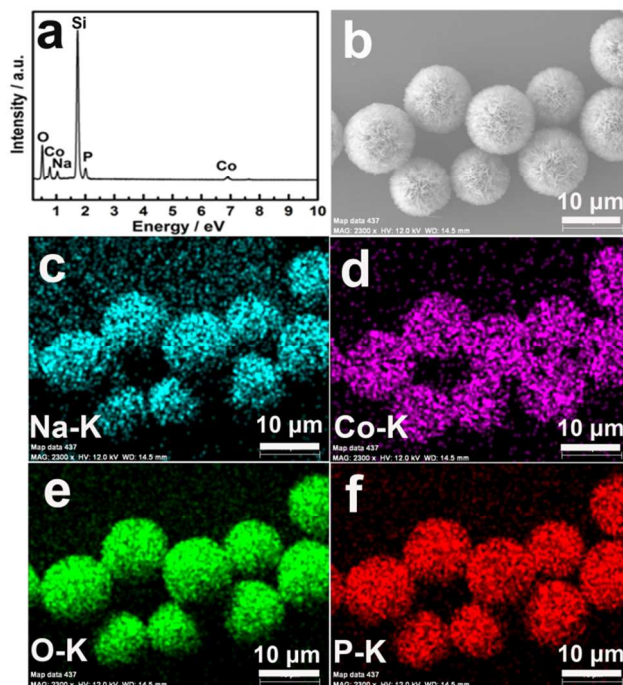
The morphology of the as-prepared NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> was observed by FESEM. After subsequent treatment, basal hierarchical hollow microspheres structures are not changed (Fig. 4a-c), and they show good consistency with that of the hydrothermal pre-obtained samples. However, we find that the nanosheets as building blocks are not as smooth as before (the inset of Fig. 4b), and the nanosheet is assembled by little nanoparticles. The hollow interior of hierarchically NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> microspheres was further confirmed by TEM (Fig. 4d), which obviously showed them to have a void space. In addition, a TEM image (Fig. 4e) showed that the nanosheets were porous and composed of small nanoparticles after

calcination. The HRTEM image obtained for the area marked with a white circle (Fig. 4e) is shown in Fig. 4f. There are two different lattice fringes in the HRTEM image, the lattice fringes spacing of 0.28 nm belongs to the (220) plane of the  $\text{Co}_3\text{O}_4$ , while 0.43 nm indexes to the (101) plane of  $\text{NaCoPO}_4$  (JCPDS cards: no. 88-0481).

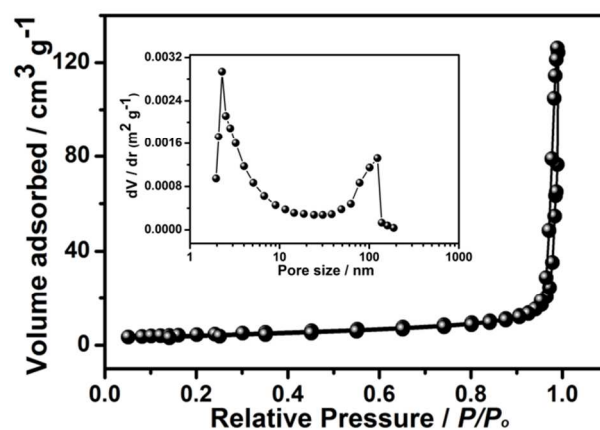


**Fig. 4** (a-c) FESEM images of the hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres; TEM (d, e) and HRTEM (f) images of the hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres.

Fig. 5a shows the electron dispersive spectroscopy (EDS) of the annealed products, which shows the peaks of O, Co, Na and P elements, further confirming that the products are  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  composites. To better investigate the spatial distribution of  $\text{NaCoPO}_4$  and  $\text{Co}_3\text{O}_4$  in the obtained hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres, EDS mapping analysis is necessary. Fig. 5b-f shows the EDS mapping images of Co, Na, O, and P elements, proving that the generally uniform distribution of  $\text{NaCoPO}_4$  and  $\text{Co}_3\text{O}_4$  within hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres.



**Fig. 5** (a) EDS spectrum of the hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres composites; (b) FESEM image and EDS-elemental mapping images (c-f) of the hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres shown in (b).

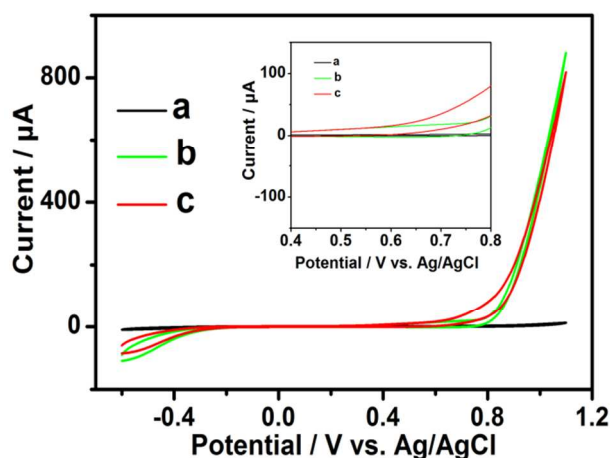


**Fig. 6**  $\text{N}_2$  adsorption-desorption isotherms of the as-prepared  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  (the inset is size distribution curves of the as-prepared  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$ ).

The specific surface areas and porosity of the as-synthesized hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres were analyzed by  $\text{N}_2$  adsorption-desorption measurements. As shown in Fig. 6, the  $\text{N}_2$  adsorption-desorption isotherms can be ascribed to type IV, suggesting the presence of macropores in the hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres, and the specific surface area is  $15.49 \text{ m}^2 \text{ g}^{-1}$ . The pore size distribution curve exhibits multi-modal and hierarchical porosity (mesopores together with macropores) and the average pore size is 49.6 nm. Considering its hierarchically porous hollow structure, which can provide sufficient



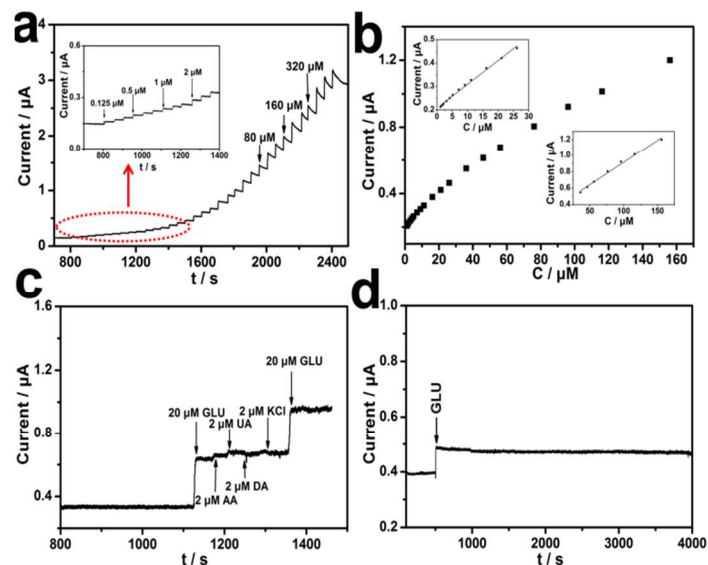
surface/interface electroactive sites and favoring the diffusion of ions/electrons, so the hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres are expected to have a potential application in electrochemical sensors.<sup>31, 32</sup>



**Fig. 7** Cyclic voltammetry (CV) traces: (a) bare GC electrode in 5 mM glucose and 0.1 M NaOH; GC electrode modified with  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  composites in 0.1 M NaOH in the absence (b) and presence of glucose (c). The inset is the CVs in the potential window ranging from 0.4 to 0.8 V.

To evaluate the electrochemical property of the as-synthesized hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres, we carried out the cyclic voltammogram (CV) to study glucose oxidation and reduction. For highly sensitive detection, we carried out a series of experiments by varying the mass of  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$ . The optimal mass of  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  (5.0  $\mu\text{g}$ ) used to modify GC electrodes give a maximum voltammetric signal. The signal also be sufficiently robust to accommodate slight variation in the actual mass of  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  nanoparticles deposited on the electrode surface. For these reasons, we selected 5.0  $\mu\text{g}$  of  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  nanoparticles for the modification of GC electrodes in subsequent experiments. The CVs of the bare GC electrode and the modified electrodes in 0.1 M NaOH solution in the potential window ranging from -0.6 to 1.1 V with a scan rate of 50  $\text{mV s}^{-1}$  are shown in Fig. 7. Fig. 7a and b present the CVs of a bare GC electrode and the hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres modified electrode and in the presence and absence of 5.0 mM glucose at 0.1 M NaOH solution. As shown for the bare GC electrode, there is only a small background current observed, whereas a big magnification can be noted while the electrode was modified by the prepared hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microsphere. Upon the addition of 5.0 mM glucose, a dramatic increase can be found after the GC electrode was modified, demonstrating that hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres composites plays an important role in the detection of glucose. The possible mechanism for oxidation of glucose by the hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres materials could be represented by the following reactions: First,  $\text{Co}^{2+}$  could be electro-oxidized to  $\text{Co}^{3+}$  in alkaline solution, where the

release of electron resulted in the formation of oxidation peak current. Then, glucose could be oxidized to gluconic acid by  $\text{Co}^{3+}$ , which was deoxidized to  $\text{Co}^{2+}$  at the same time.<sup>33, 34</sup> In addition, It can be obviously found that the GC electrode modified with hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres composites presents the electrocatalysts for  $\text{H}_2\text{O}$  in the range of 0.8-1.1 V. In our work, 0.65 V was chosen for the applied potential for the determination of glucose. It is seen from the insets of Fig. 7 that the activation of the electrocatalysts with  $\text{H}_2\text{O}$  can be negligible.



**Fig. 8** Current-time response diagram of the  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4\text{/GC}$  electrode upon successive addition of glucose in 0.1 M NaOH (inset: magnified diagram at glucose concentrations of 0.125-2.0  $\mu\text{M}$ ); (b) plot of electrocatalytic current of glucose versus its concentrations in the range of 0.125  $\mu\text{M}$ -0.16 mM; (c) amperometric response of  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4\text{/GC}$  electrode with successive addition of glucose, ascorbic acid (AA), uric acid (UA), dopamine (DA), KCl and glucose in 0.1 M NaOH; (d) the stability of the response current for  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4\text{/GC}$  electrode after addition of 20  $\mu\text{M}$  glucose measure over 4000 s.

Current-time responses at a potential of 0.65 V after successive injections of different amounts of glucose into the 0.1 M NaOH solution under stirring are presented in Fig. 8a. It can be seen from the insets of Fig. 8a that a GC electrode modified with hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres composites shows an obvious increase in current response after successive additions of glucose. Moreover, the as-prepared sensors can achieve a steady-state current within 5s, which is a very rapid response to the change of glucose concentrations. The corresponding calibration curve is presented in Fig. 8b, the  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4\text{/GC}$  electrode sensor presents a linear range from 1.0  $\mu\text{M}$  to 26  $\mu\text{M}$  ( $R=0.9948$ ), 36  $\mu\text{M}$  to 0.15 mM ( $R=0.9923$ ), and a detection limit of 0.125  $\mu\text{M}$ . The detection limit for glucose determination at the  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4\text{/GC}$  electrode is better than that of those previously reported glucose sensors, such as NiO hollow spheres (0.3  $\mu\text{M}$ ),<sup>35</sup> porous Cu-NiO

(0.5 μM),<sup>36</sup> CuS nanotube (0.25 μM).<sup>37</sup> However, it should be noted that the detection limit of some glucose sensors are better than our results, such as NiO/C nanobelts (9.12 nM),<sup>38</sup> porous Ni networks (0.07 μM).<sup>39</sup>

In general, easily oxidisable species such as ascorbic acid (AA), uric acid (UA), and dopamine (DA) co-exist with glucose, and the determination of glucose is usually affected by these above species. Therefore, the electrochemical response of the interfering species was also examined by adding 20 μM glucose, followed with additions of 2.0 μM AA, 2.0 μM UA, 2.0 μM DA, and 2.0 μM KCl in 0.1M NaOH. It is seen that the addition of 2.0 μM AA, UA, DA also induces the increasing the current of NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub>/GC electrode, however, the intensity increased is much smaller than that of glucose (Fig. 8c). These results indicate that NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub>/GC electrode shows good selectivity toward glucose and could be used as a good sensing material for highly selective and sensitive detection of glucose in the practical conditions.

The reproducibility and stability of the sensor were evaluated. Seven NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> modified electrodes were prepared and their current responses to 20 μM glucose were studied. The relative standard deviation (RSD) was 1.43%, confirming the good reproducibility of NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub>/GC electrode. The stability of the sensor was evaluated by measuring its sensitivity to 20 μM glucose over 4000 s. As shown in Fig. 8d, there is only a 6.2 % loss in the specific response current of the electrode after 4000 s, which is stable enough for use as the electrocatalysts for quantitative determination of glucose.

Based on the above discussion, the as-prepared NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub>/GC electrode presents good electrocatalytic performance towards glucose. Such a good electrochemical response capability in hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres composites might be explained as follows: First, the porous hollow structure of NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> ensures that the glucose molecules can transport through not only on material surfaces, but also throughout the whole material, and thus shorten the diffusion distance for glucose molecules to access the electrode surface. Importantly, the oriented nature of hierarchical structures makes them excellent electron percolation pathways for electron/ions transfer between interfaces. Secondly, porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> composites could have novel interfaces (between the NaCoPO<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> nanoparticles), which can also provide a synergistic effect from individual constituents and efficient rapid pathways for electron/ions. Different surface/interface characteristics and conductivity will lead to different chemical-physical adsorption abilities towards glucose molecules and their diffusion paths, resulting in a better electrocatalysts detection of glucose.<sup>31, 35</sup>

#### 4. Conclusions

In summary, hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres composites were successfully prepared via a simple hydrothermal route and final heat treatment in air. As a result of its novel structure, the hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres were then used as the electrocatalysts for detection of glucose with high sensitivity and selectivity. This present study provides us an effective approach in preparing hollow structured

materials and a method for detection of glucose by using multi-component hollow spheres as sensing materials. We believe that the active hierarchically porous NaCoPO<sub>4</sub>-Co<sub>3</sub>O<sub>4</sub> hollow microspheres materials with distinct structures could serve as promising candidates in other applications, such as supercapacitors, catalysis and lithium-ion batteries.

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#### Notes and references

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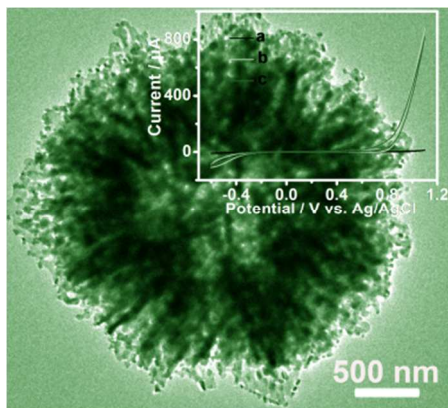
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- 1 M. Chen, C. Y. Ye, S. Y. Zhou, L. M. Wu, *Adv. Mater.*, 2013, **25**, 5343.
- 2 Y. J. Yin, Y. J. Hu, P. Wu, H. Zhang, C. X. Cai, *Chem. Commun.*, 2012, **48**, 2137.
- 3 Y. F. Zhu, J. L. Shi, W. H. Shen, X. P. Dong, J. W. Feng, M. L. Ruan, Y. S. Li, *Angew. Chem., Int. Ed.*, 2005, **44**, 5083.
- 4 X. Y. Lai, J. E. Halpert, D. Wang, *Energy Environ. Sci.*, 2012, **5**, 5604.
- 5 X. J. Feng, T. J. Latempa, J. I. Basham, G. K. Mor, O. K. Varghese, C. A. Grimes, *Nano Lett.*, 2010, **10**, 948.
- 6 C. Z. Wei, Q. Y. Lu, J. Sun, F. Gao, *Nanoscale*, 2013, **5**, 12224.
- 7 H. F. Cheng, B. B. Huang, Z. Y. Wang, X. Y. Qin, X. Y. Zhang, Y. Dai, *Chem.-Eur. J.*, 2011, **17**, 8039.
- 8 J. X. Zhu, Z. Y. Yin, D. Yang, T. Sun, H. Yu, H. E. Hoster, H. H. Hng, H. Zhang, Q. Y. Yan, *Energy Environ. Sci.*, 2013, **6**, 987.
- 9 A. Q. Pan, T. Zhu, H. B. Wu, X. W. Lou, *Chem.-Eur. J.*, 2013, **19**, 494.
- 10 G. T. Duan, W. P. Cai, Y. Y. Luo, F. Q. Sun, *Adv. Funct. Mater.*, 2007, **17**, 644.
- 11 Y. Xu, L. Zheng, C. Z. Wu, F. Qi, Y. Xie, *Chem.-Eur. J.*, 2011, **17**, 384.
- 12 C. Z. Wei, C. Cheng, J. H. Zhao, S. S. Zheng, M. M. Hao, H. Pang, *Dalton Trans.*, 2014, **43**, 5687.
- 13 X. W. Li, S. L. Xiong, J. F. Li, J. Bai, Y. T. Qian, *J. Mater. Chem.*, 2012, **22**, 14276.
- 14 Y. Qu, W. Zhou, X. H. Miao, Y. Li, L. Jiang, K. Pan, G. H. Tian, Z. Y. Ren, G. F. Wang, H. G. Fu, *Chem.-Asian J.*, 2013, **8**, 3085.
- 15 J. M. Ma, L. Chang, J. B. Lian, Z. Huang, X. C. Duan, X. D. Liu, P. Peng, T. Kim, Z. F. Liu, W. J. Zheng, *Chem. Commun.*, 2010, **46**, 5006.
- 16 X. F. Xia, Q. L. Hao, W. Lei, H. L. Wang, X. Wang, *J. Mater. Chem.*, 2012, **48**, 16844.
- 17 L. Hu, P. Zhang, H. Zhong, X. R. Zheng, N. Yan, Q. W. Chen, *Chem.-Eur. J.*, 2012, **18**, 15049.
- 18 J. Wang, *Chem. Rev.*, 2008, **108**, 814.
- 19 C. Z. Wei, Y. Y. Liu, X. R. Li, J. H. Zhao, Z. Run. H. Pang, *ChemElectroChem.*, 2014, **1**, 799.
- 20 C. T. Hou, Q. Xu, L. N. Yin, X. Y. Hu, *Analyst*, 2012, **137**, 5803.
- 21 Y. H. Ni, L. N. Jin, L. Zhang, J. M. Hong, *J. Mater. Chem.*, 2010, **20**, 6430.
- 22 Y. Ding, Y. X. Liu, J. Parisi, L. C. Zhang, Y. Lei, *Biosens. Bioelectron.*,

- 2011, **28**, 393.
- 23 Y. T. Zhang, L. Q. Luo, Z. Zhang, Y. P. Ding, S. Liu, D. M. Deng, H. B. Zhao, Y. G. Chen, *J. Mater. Chem. B*, 2014, **2**, 529.
- 24 P. Si, Y. J. Huang, T. H. Wang, J. M. Ma, *RSC Adv.*, 2013, **3**, 3487.
- 25 B. Wang, H. B. Wu, L. Zhang, X. W. Lou, *Angew. Chem., Int. Ed.*, 2013, **52**, 4165.
- 26 C. Z. Wei, H. Pang, C. Cheng, J. H. Zhao, P. W. Li, Y. K. Zhang, *CrystEngComm*, 2014, **16**, 4169.
- 27 J. C. Zhang, Y. Yang, Z. C. Zhang, X. B. Xu, X. Wang, *J. Mater. Chem. A*, 2014, **2**, 20182.
- 28 C. Deng, S. Zhang, *ACS Appl. Mater. Interfaces.*, 2014, **6**, 9111.
- 29 S. L. Xiong, J. S. Chen, X. W. Lou, H. C. Zeng, *Adv. Funct. Mater.*, 2012, **22**, 861.
- 30 Y. X. Ye, L. Kuai, B. Y. Geng, *J. Mater. Chem.*, 2012, **22**, 19132.
- 31 C. Z. Yuan, X. G. Zhang, L. H. Su, B. Gao, L. F. Shen, *J. Mater. Chem.*, 2009, **19**, 5772.
- 32 C. Z. Wei, C. Cheng, J. H. Zhao, Z. T. Wang, H. P. Wu, K. Y. Gu, W. M. Du, H. Pang, *ChemistryOpen*, 2014, **4**, 32.
- 33 Y. Mu, D. L. Jia, Y. Y. He, Y. Q. Miao, H. L. Wu, *Biosens. Bioelectron.*, 2011, **26**, 2948.
- 34 Y. Q. Fan, G. J. Shao, Z. P. Ma, G. L. Wang, H. B. Shao, S. Yan, *Part. Part. Syst. Charact.*, 2014, **31**, 1079.
- 35 S. Liu, B. Yu, T. Zhang, *Electrochim. Acta.*, 2013, **102**, 104.
- 36 X. J. Zhang, A. X. Gu, G. F. Wang, Y. Huang, H. Q. Ji, B. Fang, *Analyst*, 2011, **136**, 5175.
- 37 J. Liu, D. F. Xue, *J. Mater. Chem.*, 2011, **21**, 223.
- 38 D. G. Yang, P. C. Li, Y. Gao, H. Wu, Y. Cao, Q. Z. Xiao, H. M. Li, *J. Mater. Chem.*, 2012, **22**, 7224.
- 39 X. Zhu, Q. Jiao, C. Zhang, X. Zuo, X. Xiao, Y. Liang, J. Nan, *Microchim. Acta.*, 2013, **180**, 477.

### Table of Contents



Hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres are successfully synthesized via a simple hydrothermal method and calcination in air. The as-prepared hierarchically porous  $\text{NaCoPO}_4\text{-Co}_3\text{O}_4$  hollow microspheres exhibit good catalytic activity toward the oxidation of glucose, it exhibited high selectivity, a stable signal, and a low detection limit of  $0.125 \mu\text{M}$  for glucose.