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## All-in-One Beaker Method for Large-Scale Production of Metal Oxide Hollow Nanospheres Using Nanoscale Kirkendall Diffusion

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**ABSTRACT**

A simple and easily scalable process for the formation of metal oxide hollow nanospheres using nanoscale Kirkendall diffusion called the “all-in-one beaker method” is introduced. The  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{NiO}$ , and  $\text{Co}_3\text{O}_4$  hollow nanospheres are successfully prepared by all-in-one beaker method. The detailed formation mechanism of aggregate-free hematite hollow nanospheres is studied. Dimethylformamide solution containing Fe acetate, polyacrylonitrile (PAN), and polystyrene (PS) transforms into aggregate-free  $\text{Fe}_2\text{O}_3$  hollow nanospheres. The porous structure formed by the combustion of PS provides a good pathway for the reducing gas. The carbon matrix formed from PAN acts as a barrier, which can prevent the aggregation of metallic Fe nanopowders by surrounding each particle. The Fe-C bulk material formed as an intermediate product transforms into aggregate-free  $\text{Fe}_2\text{O}_3$  hollow nanospheres by the nanoscale Kirkendall diffusion process. The mean size and shell thickness of the hollow  $\text{Fe}_2\text{O}_3$  nanospheres measured from the TEM images are 52 and 9 nm, respectively. The discharge capacities of the  $\text{Fe}_2\text{O}_3$  nanopowders with hollow and dense structures and the bulk material for the 200<sup>th</sup> cycle at a current density of 0.5 A g<sup>-1</sup> are 1012, 498, and 637 mA h g<sup>-1</sup>, respectively, and their capacity retentions calculated compared to those in the second cycles are 92, 45, and 59 %, respectively. Additionally,  $\text{Fe}_2\text{O}_3$  hollow nanospheres cycled at 1 A g<sup>-1</sup> after 1000 cycles showed a high discharge capacity of 871 mA h g<sup>-1</sup> (capacity retention was 80 % from the second cycle). The  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{NiO}$ , and  $\text{Co}_3\text{O}_4$  hollow nanospheres show excellent cycling performances for lithium-ion storage because they have a high contact area with the liquid electrolyte and space for accommodating a huge volume change during cycling.

## INTRODUCTION

Hollow nanospheres with controllable size and composition have received great attention because of their distinct morphological advantages over filled nanopowders in diverse applications such as energy storage, solar cells, photocatalysis, gas sensors, and biomedical applications.<sup>1-11</sup> The fabrication of hollow nanospheres generally employs removable templates with a spherical shape and uniform size distribution. Organic polymer and silica nanobeads have been widely used as sacrificial templates because their size and morphology can be easily controlled in laboratory-scale synthesis.<sup>12-18</sup> However, templating methods for hollow nanospheres are usually time consuming and costly. Therefore, the template-free method employing nanoscale Kirkendall diffusion has received significant attention as a method for producing hollow nanospheres.<sup>2,19-25</sup> In this process, the preparation of aggregate-free metal nanopowders with a dense structure by a well-controlled liquid solution process is an essential requirement. Otherwise, metal nanopowders decorated with carbon-related materials, which are mainly graphene or graphene oxide, are transformed into hollow nanospheres by the nanoscale Kirkendall diffusion process. Recently, Kang et al. reported spherical and nanofiber-type aggregates of hollow nanospheres with various compositions.<sup>23</sup> The formation of a carbon matrix embedded with metal nanopowders as an intermediate product was the key idea for the formation of spherical and nanofiber-type aggregates of hollow nanospheres. However, the preparation process of aggregation-free hollow structured nanopowders by using carbon matrix originated from the polymeric precursors has not yet been researched. In addition, in the previous studies, it was essential to utilize the additional equipment of electrospinning or spray pyrolysis process for the preparation of precursor product.<sup>23-25</sup> Therefore, the development of a highly efficient and cost-effective process for large-scale production of hollow nanospheres without a supporting matrix is required in various application fields including energy storage.

In this study, a simple and easily scalable process for metal oxide hollow nanospheres using the nanoscale Kirkendall diffusion process called the “all-in-one beaker method” is introduced. All-in-one-beaker method does not need additional equipment for the preparation of the precursor product. The overall process for the preparation of hollow nanospheres was performed sequentially in only one glass beaker in a static furnace. The viscous solution containing the metal salt and organic polymer transformed into aggregate-free metal oxide hollow nanospheres in the glass beaker by a simple drying and thermal treatment process. Transition metal oxide materials has been extensively used in lithium-ion batteries, catalysts, gas sensors, and biomedical applications.<sup>24-35</sup> Therefore, in this study, Fe<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, NiO, and Co<sub>3</sub>O<sub>4</sub> hollow nanospheres were selected as the first target materials. The detailed formation mechanism of aggregate-free metal oxide hollow nanospheres by the nanoscale Kirkendall diffusion process using organic polymers as additives was studied. In addition, the electrochemical properties of the metal oxide hollow nanospheres for lithium-ion storage were compared with those of the filled metal oxide nanopowders.

## EXPERIMENTAL SECTION

### Sample preparation

Hollow  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{SnO}_2$ , and  $\text{Co}_3\text{O}_4$  hollow nanospeheres were synthesized in only one glass beaker in a static furnace via an “all-in-one beaker method.” For this, the precursor solution was prepared in a quartz glass beaker by dissolving 5 g of metal salt in 100 mL of N,N-dimethylformamide (DMF), and adding 5 g of polyacrylonitrile (PAN,  $M_w$ : 150 000), and 5 g of polystyrene (PS,  $M_w$ : 192 000) with vigorous stirring overnight. Iron(III) acetylacetone [Fe(acac)<sub>3</sub>], Nickel(II) acetate tetrahydrate [ $\text{Ni}(\text{CH}_3\text{CO}_2)_2(\text{H}_2\text{O})_4$ ], Tin(II) 2-ethylhexanoate [ $\text{Sn}(\text{Oct})_2$ ], and Cobalt(II) acetate tetrahydrate [ $\text{Co}(\text{CH}_3\text{CO}_2)_2(\text{H}_2\text{O})_4$ ] were applied as the source materials for  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{NiO}$ , and  $\text{Co}_3\text{O}_4$ , respectively. Then, the glass beaker containing the solution was transferred to the static tube furnace, in which the solution was sequentially post treated in three steps by changing gases. In the first step, the solution was dried for 1 h at 150 °C in air to evaporate the solvent, DMF. Second, the dried powders were reduced at 500 °C for  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$ , and  $\text{Co}_3\text{O}_4$ , and at 400°C for  $\text{SnO}_2$  at a heating rate of 5 °C min<sup>-1</sup> for 3 h under an atmosphere of 10% H<sub>2</sub>/Ar gas mixture. In the final step, the reduced powders were subsequently oxidized at 400 °C for 3 h identically for all samples at a heating rate of 5 °C min<sup>-1</sup> in air for the nanoscale Kirkendall diffusion effect to occur, and then were finally cooled down to room temperature. Dense  $\text{Fe}_2\text{O}_3$  nanopowders were also prepared by heat treatment of the dried powders directly at 400 °C for 3 h in air (5 °C min<sup>-1</sup>) without the reduction process as a sample for comparison. Additionally, to investigate the effect of polystyrene (PS) in the above solution, which is expected to form voids in bulk during the process, iron oxide powders were synthesized from a solution without PS by the all-in-one beaker method.

### Characterization

The microstructures of the metal oxide hollow nanospheres were observed by field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi) and field-emission transmission electron microscopy (FE-TEM, JEM-2100F, JEOL). In addition, their crystal phases were evaluated by X-ray diffractometry (XRD, X’Pert PRO MPD) using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at the Korea Basic Science Institute (Daegu). X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) with a focused monochromatic Al K $\alpha$  at 12 kV and 20

mA was used to analyze the composition of the specimens. The surface areas of the nanopowders were measured by the Brunauer–Emmett–Teller (BET) method, using N<sub>2</sub> as the adsorbate gas. Thermogravimetric analysis was performed using a Pyris 1 TGA (Perkin Elmer) over a temperature range of 25–650 °C and at a heating rate of 10 °C min<sup>-1</sup> under static air atmosphere.

## Electrochemical measurements

The electrochemical properties of the Fe<sub>2</sub>O<sub>3</sub>, NiO, SnO<sub>2</sub>, and Co<sub>3</sub>O<sub>4</sub> hollow nanospheres were analyzed by constructing a 2032-type coin cell. The anode was prepared by mixing the active material, carbon black, and sodium carboxymethyl cellulose (CMC) in a weight ratio of 7:2:1. Li metal and microporous polypropylene film were used as the counter electrode and the separator, respectively. The electrolyte was 1 M LiPF<sub>6</sub> dissolved in a mixture of fluoroethylene carbonate/dimethyl carbonate (FEC/DMC; 1:1 v/v). The discharge/charge characteristics of the samples were investigated by cycling over the 0.001–3.0 V potential range for Fe<sub>2</sub>O<sub>3</sub>, NiO, and Co<sub>3</sub>O<sub>4</sub> hollow nanopowders and 0.001–1.0 V potential range for SnO<sub>2</sub> hollow nanopowders at various current densities. Cyclic voltammograms (CV) were measured at a scan rate of 0.07 mV s<sup>-1</sup>. The dimensions of the anode were 1 cm × 1 cm and the mass loading was approximately 1.2 mg cm<sup>-2</sup>. The electrochemical impedance was measured using electrochemical impedance spectroscopy (EIS) over the frequency range of 0.01 Hz–100 kHz.

## RESULTS AND DISCUSSION

A schematic of the formation mechanism of the aggregate-free metal oxide hollow nanospheres by the all-in-one beaker method is shown in Scheme 1. Upon drying the dimethylformamide (DMF) solution containing metal salt, polyacrylonitrile (PAN), and polystyrene (PS) contained in a glass beaker at 150 °C, the metal salt-PVP-PS composite was obtained (Scheme 1a-① and 1a-②). Carbonization of PAN during the reduction process produced the bulk carbon matrix (Scheme 1a-②). The complete decomposition and reduction of metal salt into metallic nanopowders occurred during the reduction process under 10% H<sub>2</sub>/Ar atmosphere (Scheme 1a-③). The complete elimination of PS is achieved by combustion into gases even under a reducing atmosphere (Scheme 1a-③). Therefore, the channels formed by combustion of PS supplied a good pathway for the reducing gas during the Kirkendall diffusion in bulk material (Scheme 1b-②, ③, and ④). Therefore, the metal nanopowders grown uniformly were distributed all over the amorphous carbon matrix during the reduction process. The carbon matrix formed from PAN played the role of a barrier, which can prevent the aggregation of metal nanopowders by surrounding each particle. Thermal treatment of the glass beaker containing the metla-C bulk material under air produced aggregate-free metal oxide hollow nanospheres (Scheme 1a-⑤). Dense metal nanopowders embedded within the carbon matrix transformed into metal oxide hollow nanospheres by the well-known nanoscale Kirkendall diffusion process.

The detailed formation mechanism of the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres, which were studied as the main example, is shown in Schme 1b. Surface oxidation of metallic Fe nanopowder during oxidation resulted in Fe@Fe<sub>2</sub>O<sub>3</sub> nanopowder with a core-shell structure (Scheme 1b-③). The outward diffusion of the smaller Fe cations (Fe<sup>2+</sup> = 76 pm, Fe<sup>3+</sup> = 65 pm) occurred faster than the inward diffusion of oxygen anions (O<sup>2-</sup> = 140 pm). Accordingly, Kirkendall voids were generated near the Fe/Fe<sub>2</sub>O<sub>3</sub> interface during vacancy-assisted exchange of the

material *via* bulk interdiffusion (Scheme 1a-④ and 1b-④), which gives rise to coarsening and enhancement of pore growth in the spheres (Scheme 1b-⑤). Complete conversion of metallic Fe into  $\text{Fe}_2\text{O}_3$  by the nanoscale Kirkendall diffusion process resulted in hollow nanospheres. Combustion of amorphous carbon during the nanoscale Kirkendall diffusion process resulted in the aggregate-free  $\text{Fe}_2\text{O}_3$  hollow nanospheres. In summary, DMF solution containing  $\text{Fe}(\text{acac})_3$ , PAN, and PS transformed into the aggregate-free  $\text{Fe}_2\text{O}_3$  hollow nanospheres by a static three-step post-treatment process inside a glass beaker as described in Figure S1. The contents of the glass beaker during the preparation of the aggregate-free  $\text{Fe}_2\text{O}_3$  hollow nanospheres were not disturbed in any manner.

The formation mechanism of the aggregate-free  $\text{Fe}_2\text{O}_3$  hollow nanospheres by the all-in-one beaker method is investigated based on the morphologies and crystal structures of the materials obtained in each step. The photographs of the beakers containing the product obtained in each step are shown in Figure S1. The SEM image of the bulk of the sample formed by drying at 150 °C is shown in Figure S2. The TG curves of PAN and PS obtained in  $\text{N}_2$  atmosphere are shown in Figure S3. Decomposition of PAN and PS started at a temperature of 240 and 320 °C, respectively. Therefore, decomposition of PAN and PS did not occur during the drying stage of the solution. The XRD pattern of the dried sample shown in Figure S4 revealed small peaks of  $\text{Fe}_3\text{O}_4$  formed by partial decomposition of  $\text{Fe}(\text{acac})_3$ . Therefore, the product formed by the drying process was  $\text{Fe}(\text{acac})_3\text{-Fe}_3\text{O}_4\text{-PAN-PS}$  composite. The weight loss due to complete carbonization of PAN to form carbon, which occurred below 500 °C under  $\text{N}_2$  atmosphere, was 58 wt%. On the other hand, PS completely decomposed into gaseous products under  $\text{N}_2$  atmosphere at a temperature of around 400 °C. The TG curve of the product formed by a drying process measured in air showed a three-step weight loss below 500 °C (Figure S5a) because of the decomposition of  $\text{Fe}(\text{acac})_3$  into  $\text{Fe}_2\text{O}_3$ .

and combustion of PAN and PS into gases. From the TG results of PAN and PS, the reduction temperature of the dried material was selected as 500 °C, when amorphous carbon was formed by carbonization of PAN and channels for the hydrogen gas pathway were formed by decomposition of PS. The XRD patterns of the reduced sample at 500 °C had small peaks of metallic Fe and Fe<sub>3</sub>C, as shown in Figure S4. Carbonization of metallic Fe to form the Fe<sub>3</sub>C layer occurred with amorphous carbon formed by the carbonization of PAN. The broad XRD pattern revealed the ultrafine sizes of the metallic Fe and Fe<sub>3</sub>C crystals.

The morphologies of the sample obtained from the beaker after the reduction process is shown in Figure 1. The reduced sample was crushed well by hand due to the complete transformation of the organic polymer into amorphous carbon during the reduction process. The SEM and low-resolution TEM images shown in Figures 1a and 1b revealed the porous structure of the bulk material. The ultrafine nanopowders with a dense structure are uniformly distributed all over the semitransparent amorphous carbon matrix, as shown in Figures 1b and 1c. Graphitic carbon formed by the iron catalyst was observed around the Fe nanopowders as shown by arrows in Figures 1c and 1d. The nanopowder shown in Figure 1d had a clear core-shell structure with the configuration Fe@Fe<sub>3</sub>C. The TEM image shown in Figure 1d shows lattice fringes separated by 0.14 and 0.24 nm, which correspond to the (200) and (121) crystal planes of metallic Fe and Fe<sub>3</sub>C, respectively. Carbidation of the surface of the Fe nanopowder formed the core-shell-structured nanopowder. However, the nanopowder shown in Figure 1e had the pure crystalline structure of metallic Fe. The high-resolution TEM image shown in Figure 1e shows clear lattice fringes separated by 0.203 nm, which corresponds to the (110) crystal plane of metallic Fe. The selected area electron diffraction (SAED) pattern shown in Figure 1f revealed the mixed crystalline structure of the Fe and Fe<sub>3</sub>C phases. Therefore, some of the Fe nanopowders transformed into the Fe@Fe<sub>3</sub>C nanopowders by carbidation during the reduction process. The elemental mapping images shown in Figure 1g showed a trace amount

of oxygen and revealed the formation of a carbon matrix with uniform distribution of Fe nanopowders. The TG curve of the product formed by the reduction process measured under air showed a one-step weight loss below 400 °C, as shown in Figure S5b, because of the combustion of the carbonaceous material formed by carbonization of PAN. The weight loss caused by the combustion of the carbon material was slightly offset by oxidation of Fe and  $\text{Fe}_3\text{C}$ .

The product obtained by the reduction process was oxidized at 400 °C under air, as shown in Figure S1. The bulky black material transformed into a small volume of red-brown colored powders. Combustion of the carbon material and oxidation of the Fe component resulted in  $\text{Fe}_2\text{O}_3$  powders, as confirmed by the color of the product and XRD pattern shown in Figure S4c. The morphologies of the  $\text{Fe}_2\text{O}_3$  powders formed by the all-in-one beaker method are shown in Figure 2. The SEM and low-resolution TEM images shown in Figures 2a and 2b revealed the formation of aggregate-free  $\text{Fe}_2\text{O}_3$  hollow nanospheres by the all-in-one beaker method. The TEM images shown in Figures 2b and 2c revealed the hollow and thin-walled structure of the  $\text{Fe}_2\text{O}_3$  nanospheres. The Fe nanopowders dispersed within the carbon matrix transformed into the hollow  $\text{Fe}_2\text{O}_3$  nanospheres by the nanoscale Kirkendall diffusion process as described in Scheme 1b. The high-resolution TEM images shown in Figures 2d and 2e revealed a crystalline structure of the hollow  $\text{Fe}_2\text{O}_3$  nanospheres. The high-resolution TEM image showed clear lattice fringes separated by 0.270 nm and 0.252 nm, which correspond to the (104) and (110) crystal planes of rhombohedral  $\alpha\text{-Fe}_2\text{O}_3$ , respectively. The SAED pattern shown in Figure 2f also revealed the presence of the phase pure  $\text{Fe}_2\text{O}_3$  nanospheres. The oxidation of Fe into  $\text{Fe}_2\text{O}_3$  is further supported by the Fe 2p XPS spectrum shown in Figure S6b. There are two peaks at binding energies of 711 eV for Fe 2p<sub>3/2</sub> and 724 eV for Fe 2p<sub>1/2</sub>, and a shakeup satellite at 719 eV, which are the characteristic peaks of Fe(III) in  $\alpha\text{-Fe}_2\text{O}_3$ . No components related to zero-valent Fe and  $\text{Fe}^{2+}$

are observed.<sup>24-26,30,36</sup> Trace amount of carbon which is graphitic carbon formed by graphitization of amorphous carbon during the reduction process, in which metallic iron acted as catalyst for graphitization was detected in the survey spectrum (Figure S6a). The elemental mapping images shown in Figure 2g also revealed the presence of carbon in the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres. However, the TG curve shown in Figure S5c revealed the trace amount of carbon in the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres. The mean size and shell thickness of the hollow Fe<sub>2</sub>O<sub>3</sub> nanospheres measured from the TEM images were 52 and 9 nm, respectively. The BET surface area of the hollow Fe<sub>2</sub>O<sub>3</sub> nanospheres was 21 m<sup>2</sup> g<sup>-1</sup>.

The morphologies of the Fe<sub>2</sub>O<sub>3</sub> nanopowders formed as a sample for comparison prepared by the all-in-one beaker method, where nanoscale Kirkendall diffusion was not applied, are shown in Figure 3. The product obtained by the drying process, shown in Figure S2, was directly post-treated at 500 °C under air without the reduction process not to apply nanoscale Kirkendall effect. The SEM and TEM images shown in Figures 3a–c revealed aggregated Fe<sub>2</sub>O<sub>3</sub> nanopowders with a dense structure. The high-resolution TEM image shown in Figure 3d revealed clear lattice fringes separated by 0.221 and 0.252 nm, which correspond to the (113) and (110) crystal planes of rhombohedral α-Fe<sub>2</sub>O<sub>3</sub>, respectively. The SAED and XRD patterns shown in Figures 3e and 3f, respectively, revealed the formation of phase pure Fe<sub>2</sub>O<sub>3</sub> nanopowders. Figure S7 shows the morphologies of the Fe<sub>2</sub>O<sub>3</sub> powders prepared from the solution without polystyrene (PS) that provides a good pathway for the reducing gas. The post-treatment of Fe(acac)<sub>3</sub>-PAN composite powders without PS at 500 °C under air produced formless bulk iron oxide. The XRD pattern shown in Figure S7d revealed the mixed crystal structure of the Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> phases. The oxygen poor Fe<sub>3</sub>O<sub>4</sub> phase was formed because oxygen gas did not penetrate the inside of the dried bulk material well. Therefore, PS played a key role in the preparation of Fe<sub>2</sub>O<sub>3</sub> nanopowders with hollow and dense structures by the all-in-one beaker method as shown in Figure 1 and 2.

The electrochemical properties of the  $\text{Fe}_2\text{O}_3$  hollow nanospheres for use in lithium-ion storage were compared to those of the nanopowders with a dense structure and the bulk material (Figure 4). The cyclic voltammogram (CV) curves of the  $\text{Fe}_2\text{O}_3$  hollow nanospheres formed by the nanoscale Kirkendall diffusion process for the first five cycles at a scan rate of  $0.07 \text{ mV s}^{-1}$  over the voltage range of  $0.001\text{--}3 \text{ V}$  are shown in Figure 4a. The first reduction peak observed around  $1.6 \text{ V}$  in the first cathodic sweep corresponded to the initial lithium insertion into  $\text{Fe}_2\text{O}_3$  and the reduction of iron from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  without structural change. The second reduction peak observed at around  $0.9 \text{ V}$  was due to the phase transformation from hexagonal  $\text{Li}_x\text{Fe}_2\text{O}_3$  to cubic  $\text{Li}_x\text{Fe}_2\text{O}_3$ .<sup>37-40</sup> The third obvious reduction peak observed at around  $0.6 \text{ V}$  corresponded to the reduction of iron from  $\text{Fe}^{2+}$  to  $\text{Fe}^0$  metal nanograins.<sup>32,41-</sup><sup>43</sup> The two broad oxidation peaks observed at around  $1.6$  and  $1.9 \text{ V}$  in the anodic sweeps were attributed to the oxidation of  $\text{Fe}^0$  to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .<sup>37-40</sup> From the second cycle onward, the reduction peak shifted to a higher potential, around  $0.8 \text{ V}$ , because of the conversion of  $\text{Fe}_2\text{O}_3$  into ultrafine nanocrystals during the first cycle.<sup>44-46</sup> The initial charge and discharge profiles of the three samples at a current density of  $0.5 \text{ A g}^{-1}$  are shown in Figure 4b. The three samples had similar shapes and capacities in their initial charge and discharge profiles irrespective of their morphologies. The initial discharge and charge capacities of the  $\text{Fe}_2\text{O}_3$  hollow nanospheres were  $1356$  and  $1078 \text{ mA h g}^{-1}$ , respectively; and their corresponding initial Coulombic efficiency was  $79\%$ . However, the cycling performances of the three samples were strongly affected by their morphologies, as shown in Figure 4c. The  $\text{Fe}_2\text{O}_3$  hollow nanospheres showed good cycling performance over  $200$  cycles. The  $\text{Fe}_2\text{O}_3$  nanopowders with a dense structure decreased during the first  $20$  cycles because of partial destruction of their structure during cycling. However, they later showed good cycling performance during the further  $100$  cycles. However, the discharge capacities of the iron oxide bulk material decreased continuously during the first  $75$  cycles, and then the capacities

increased with increasing number of cycles because of the formation of a polymeric gel-like film on the active material as well as electrolyte decomposition. The discharge capacities of the Fe<sub>2</sub>O<sub>3</sub> nanopowders with hollow and dense structures, and the bulk material after the 200th cycle were 1012, 498, and 637 mA h g<sup>-1</sup>, respectively, and their capacity retentions calculated compared to the second cycles were 92, 45, and 59 %, respectively. The rate performances of the three samples are shown in Figure 4d, in which the current density is increased step-wise from 0.3 to 3.0 A g<sup>-1</sup>. The Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres showed superior rate performance compared with the nanopowders with dense structure and the bulk material. The final discharge capacities of the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres at current densities of 0.3, 0.7, 1.5, 2.0, and 3.0 A g<sup>-1</sup> were 1095, 1074, 1027, 993, and 915 mA h g<sup>-1</sup>, respectively. The discharge capacities decreased slightly with increasing current densities. In addition, the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres showed good capacity recovery when the current density returns to 0.3 A g<sup>-1</sup> even after cycling at high current densities. The long-term cycling performance and Coulombic efficiencies of the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres cycled at 1 A g<sup>-1</sup> are shown in Figure 4e. The Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres showed high Coulombic efficiencies above 99 % from the second cycle onward. The initial discharge and charge capacities of the hollow nanospheres were 1327 and 1057 mA h g<sup>-1</sup>, respectively. However, the initial capacity loss of the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres was attributed to the partial destruction of the internal structure, the irreversible electrochemical decomposition of electrolyte and the subsequent formation of a solid-electrolyte interphase (SEI) layer on the surface. Then, the slight decrease of the capacity after 400 cycles was due to the structure destruction owing to the stress forming by uptake of Li ion upon repeated further cycles. After 1000 cycles, the hollow nanospheres showed a high discharge capacity of 871 mA h g<sup>-1</sup> and their corresponding capacity retention calculated from the second cycle was 80 %.

Electrochemical impedance spectroscopy (EIS) measurements before and after 1, 50, and

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4 100 cycles were performed to reveal the superior electrochemical properties of the Fe<sub>2</sub>O<sub>3</sub>  
5 hollow nanospheres compared with those of the nanopowders with dense structure and the  
6 bulk material. The Nyquist plots shown in Figures 5a-d display compressed semicircles in the  
7 medium-frequency range, which describe the charge-transfer resistance ( $R_{ct}$ ) of the  
8 electrode.<sup>29,47,48</sup> The aggregate-free Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres with a high surface area had  
9 the minimum charge-transfer resistance before cycling, as shown in Figure 5a. However, the  
10 bulk material with a low contact area with liquid electrolyte had the highest charge-transfer  
11 resistance before cycling. The charge-transfer resistances of the three samples decreased after  
12 the first cycle because of the formation of ultrafine nanocrystals during the first discharge and  
13 charge processes. The low charge-transfer resistance of the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres with  
14 high structural stability was maintained during cycling for 100 cycles, as shown in Figure 5b.  
15 However, the charge-transfer resistances of the nanopowders with a dense structure and the  
16 bulk material increased with increasing number of cycles, as shown in Figures 5c and 5d. The  
17 morphological changes of the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres and the Fe<sub>2</sub>O<sub>3</sub> nanopowders with a  
18 dense structure obtained after 200 cycles were investigated by TEM in Figure S8. The Fe<sub>2</sub>O<sub>3</sub>  
19 hollow nanospheres maintained their overall morphology even after repeated lithium  
20 insertion and desorption processes. On the other hand, Fe<sub>2</sub>O<sub>3</sub> nanopowders with a dense  
21 structure lost their original morphology and aggregated after cycling. The Fe<sub>2</sub>O<sub>3</sub> hollow  
22 nanospheres having a high contact area with the liquid electrolyte and space for  
23 accommodating huge volume change during cycling showed excellent cycling and rate  
24 performance for lithium-ion storage (Figure S9). Graphitic carbon coating layer formed by  
25 graphitization of amorphous carbon also improved the electrochemical properties of the  
26 Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres.

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30 Furthermore, the strategy described in this study has generally applied to various metal  
31 oxide hollow nanospheres. We successfully synthesized many other metal oxide hollow  
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nanospheres, such as NiO, SnO<sub>2</sub>, and Co<sub>3</sub>O<sub>4</sub> in Figure 6. The XRD patterns of the reduced samples at 500 °C for NiO and Co<sub>3</sub>O<sub>4</sub> and at 400°C for SnO<sub>2</sub> hollow nanospheres had peaks of metallic Ni, Co, and Sn, respectively, as shown in Figure S10. The TEM images of the NiO, SnO<sub>2</sub>, and Co<sub>3</sub>O<sub>4</sub> nanopowders obtained after further oxidation process at 400 °C under air showed hollow structure as shown in Figure 6. The NiO, SnO<sub>2</sub>, and Co<sub>3</sub>O<sub>4</sub> hollow nanospheres were formed by the same formation mechanism of the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres above studied. The cycling performances of the three samples at a current density of 1.0 A g<sup>-1</sup> are also shown in Figure 6. The initial discharge capacities of the NiO, SnO<sub>2</sub>, and Co<sub>3</sub>O<sub>4</sub> hollow nanospheres were 1074, 2098, and 1248 mA h g<sup>-1</sup>, respectively, and their corresponding initial Coulombic efficiencies were 75, 42, and 76%, respectively. The discharge capacities of the NiO, SnO<sub>2</sub>, and Co<sub>3</sub>O<sub>4</sub> hollow nanospheres for the 250<sup>th</sup> cycles were 763, 845, and 1128 mA h g<sup>-1</sup>, respectively, and their corresponding capacity retentions calculated from the second cycle were 94, 91, and 114%, respectively. The NiO, SnO<sub>2</sub>, and Co<sub>3</sub>O<sub>4</sub> hollow nanospheres prepared by all-in-one beaker method had also excellent lithium-ion storage properties.

## CONCLUSIONS

In this study, a new process denoted as an “all-in-one beaker method” for aggregate-free metal oxide hollow nanospheres was studied. The viscous solution containing metal salt and organic polymers transformed into aggregate-free metal oxide hollow nanospheres in the glass beaker in a static furnace by simple drying and a thermal treatment process. The polyacrylonitrile (PAN) and polystyrene (PS) polymers played key roles in the formation of metal oxide hollow nanospheres. In particular, PS, which can be decomposed under a reducing atmosphere, enabled the formation of bulk C material decorated uniformly with the metal nanopowders. In addition, PAN, which is decomposed to carbon matrix, prevented the aggregation of metal nanopowders by surrounding each particle. The metal oxide hollow nanospheres formed by applying the nanoscale Kirkendall diffusion process had a regular morphology and excellent lithium-ion storage properties. The simple process developed in this study can be efficiently applied in the large-scale production of aggregate-free metal oxide nanospheres for various applications including lithium-ion batteries.

**ASSOCIATED CONTENT**

Supporting Information.

Schematic diagram for static three-step post-treatment process inside a glass beaker and photographs of the beakers containing the product obtained in each step, SEM image of the sample formed by drying process at 150 °C, TG curves of PAN and PS obtained in N<sub>2</sub> atmosphere, XRD patterns of the powders obtained by drying process, subsequent reduction process, and final oxidation process, TG analyses of the powders obtained after drying process, subsequent reduction process, and final oxidation process, Fe 2p XPS spectrum of the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres obtained by all-in-one beaker method, Morphologies and XRD pattern of the materials formed by all-in-one beaker method from the solution without polystyrene (PS), Morphologies of the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres and Fe<sub>2</sub>O<sub>3</sub> nanopowders with a dense structure obtained after 200 cycles, Schematic diagram for the mechanism of the lithium ion transport diffusion and storage in hollow nanosphere, XRD patterns of the metal-C composite powders obtained by reduction process and metal oxide hollow nanopowders obtained by further oxidation process during the all-in-one beaker method: (a) Ni, NiO, (b) Sn, SnO<sub>2</sub>, and (c) Co, Co<sub>3</sub>O<sub>4</sub>, TEM images of the Fe<sub>2</sub>O<sub>3</sub> hollow nanopowders formed by all-in-one beaker method with different reduction temperatures, XRD patterns of the powders formed by all-in-one beaker method from the precursor solution without polystyrene (PS), TG analyses of the Fe<sub>2</sub>O<sub>3</sub> nanopowders with dense structure obtained by direct oxidation process of the dried powders at 400 °C and bulk material prepared from the solution without PS, N<sub>2</sub> adsorption-desorption isotherms measured at 77 K for the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres, Fe<sub>2</sub>O<sub>3</sub> dense nanopowders, and bulk material. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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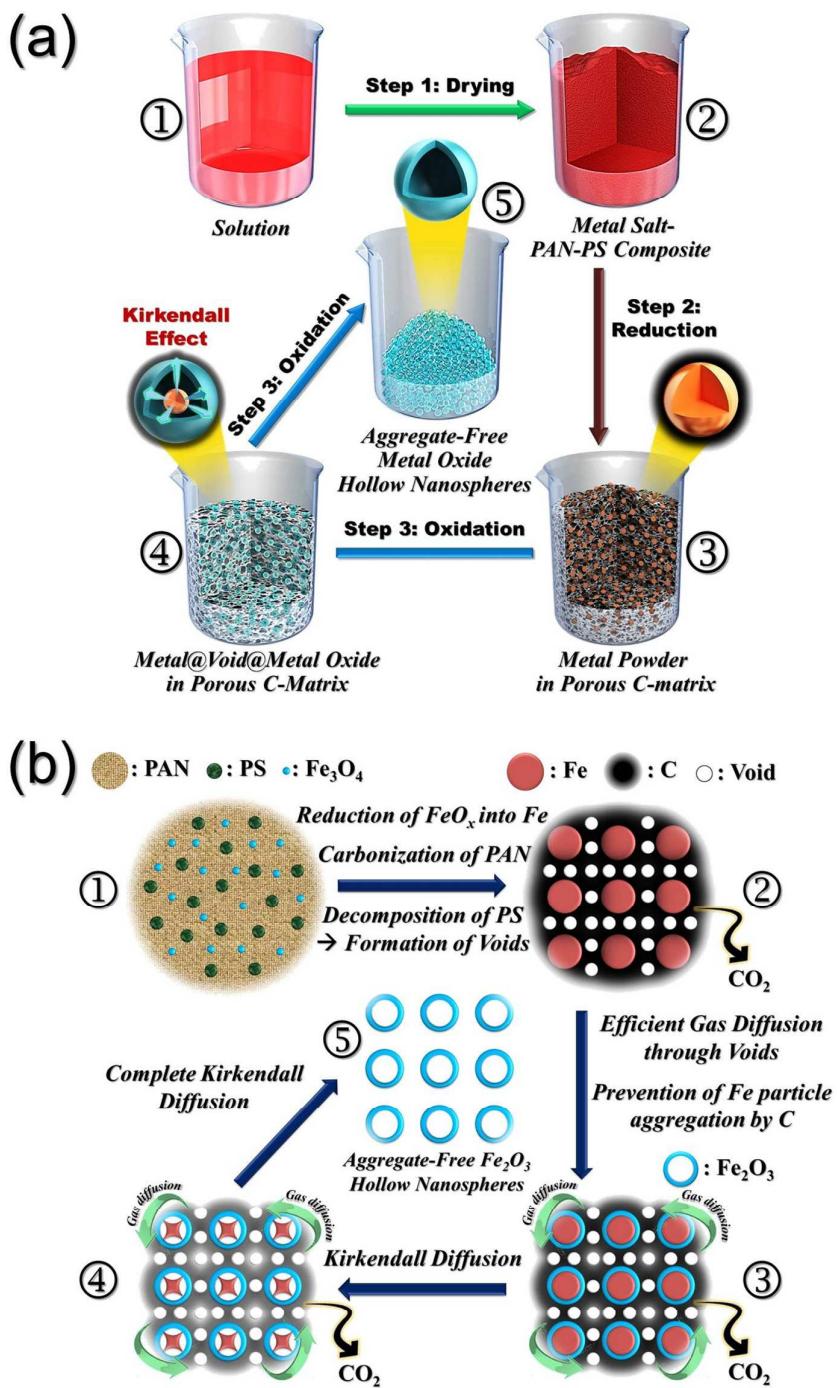
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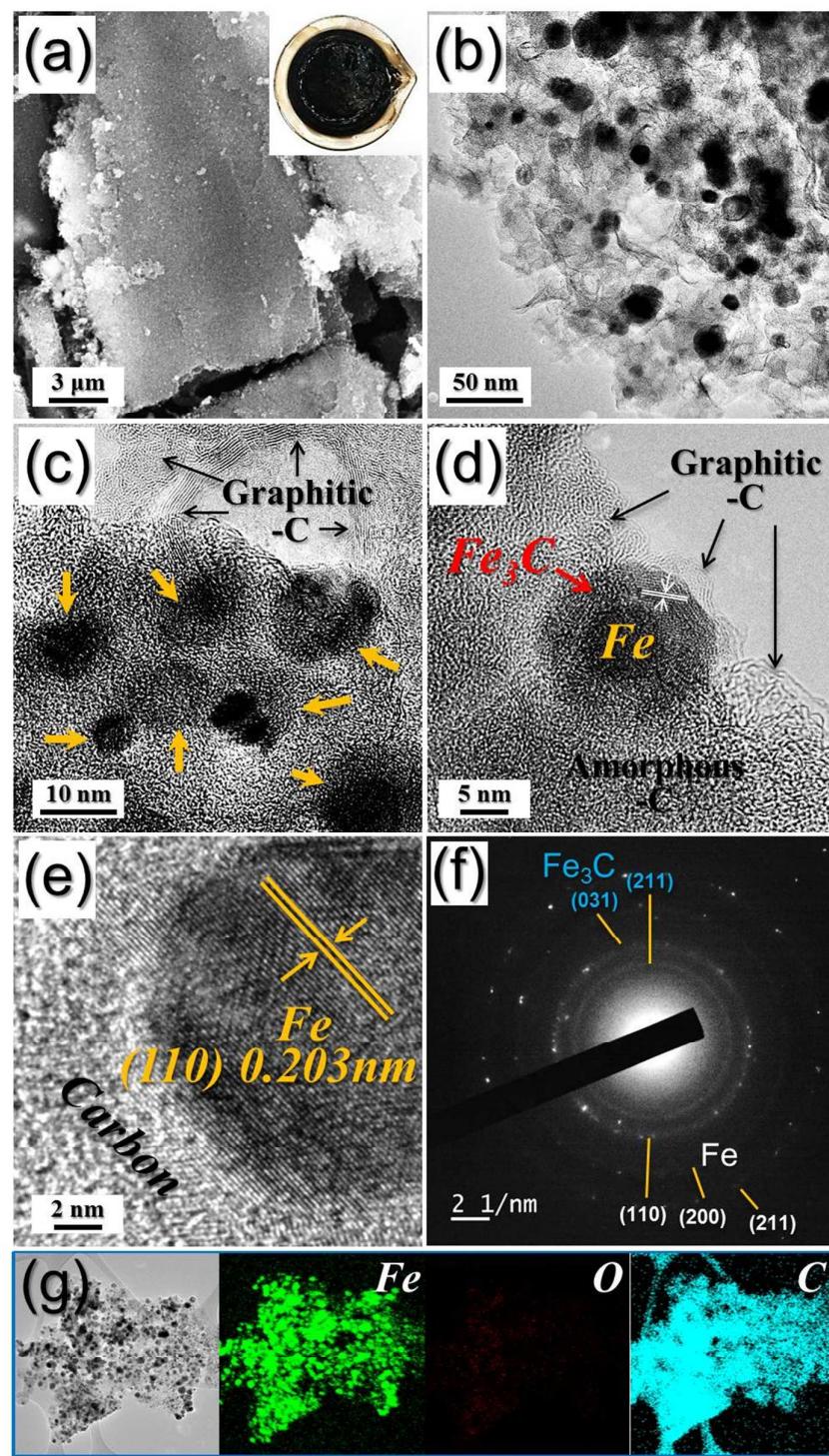
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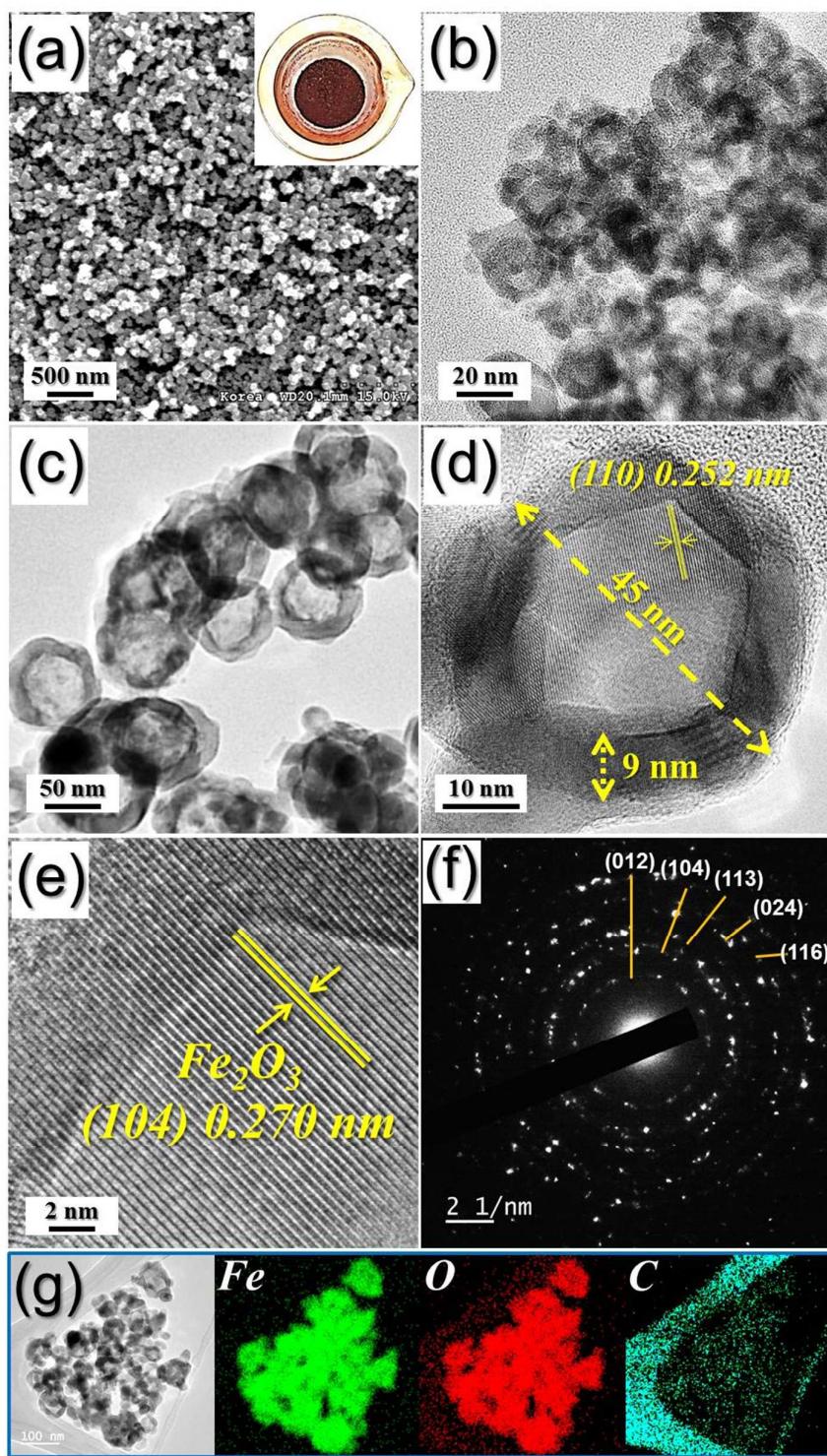
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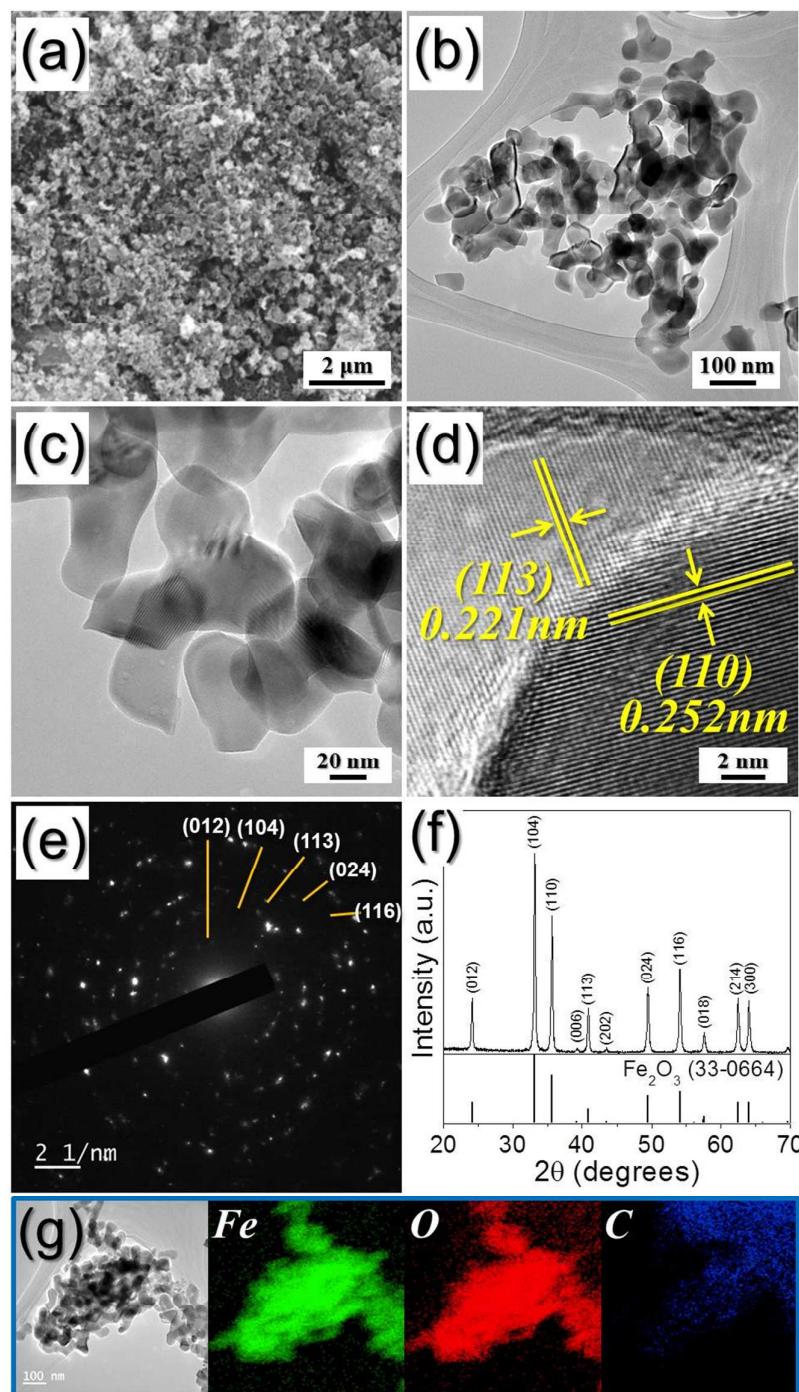
**Scheme 1.** (a) Schematic diagram for the formation mechanism of the aggregate-free metal oxide hollow nanospheres by all-in-one beaker method and (b) detail formation mechanism of the  $\text{Fe}_2\text{O}_3$  hollow nanospheres by Kirkendall diffusion effect in a static furnace and the roles of polystyrene (PS) and polyacrylonitrile (PAN) polymers contained in a beaker.



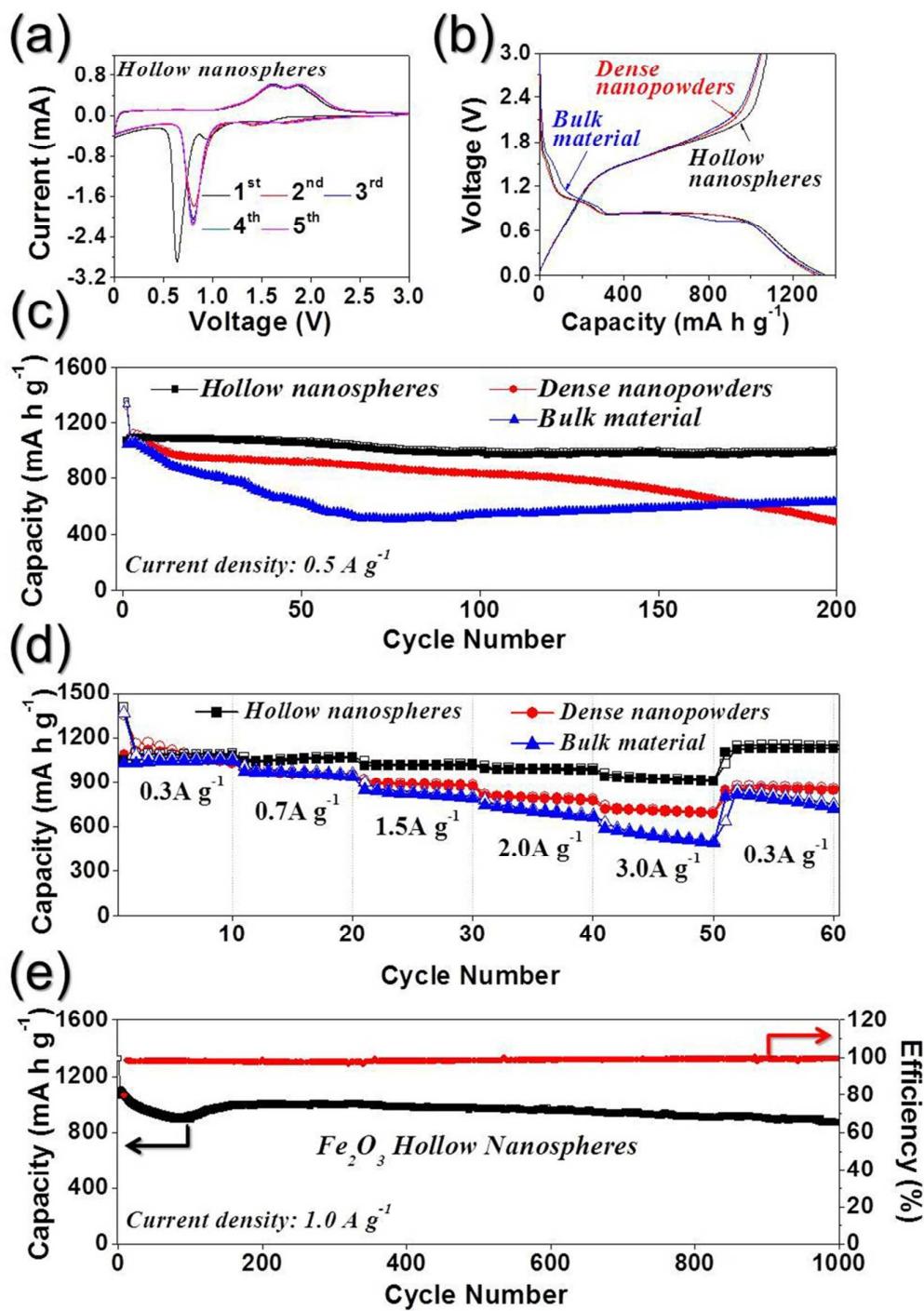
**Figure 1.** Morphologies, SAED pattern, and elemental mapping images of the powders obtained by reduction of the dried precursor powders at 500 °C under 10% H<sub>2</sub>/Ar gas: (a) SEM image, (b) - (d) TEM images, (e) HR-TEM image, (f) SAED pattern, and (g) elemental mapping images.



**Figure 2.** Morphologies, SAED pattern, and elemental mapping images of the Fe<sub>2</sub>O<sub>3</sub> hollow nanospheres formed by all-in-one beaker method: (a) SEM, (b) - (d) TEM images, (e) HR-TEM image, (f) SAED pattern, and (g) elemental mapping images.



**Figure 3.** Morphologies, SAED pattern, and elemental mapping images of the Fe<sub>2</sub>O<sub>3</sub> nanopowders with dense structure as a sample for comparison formed by all-in-one beaker method, in which nanoscale Kirkendall diffusion is not applied: (a) SEM, (b) and (c) TEM images, (d) HR-TEM image, (e) SAED pattern, (f) XRD pattern, and (g) elemental mapping images.



**Figure 4.** Electrochemical properties of the  $\text{Fe}_2\text{O}_3$  hollow nanospheres and nanopowders with dense structure and bulk material: (a) CV curves of the  $\text{Fe}_2\text{O}_3$  hollow nanospheres, (b) first charge-discharge curves at a current density of  $0.5 \text{ A g}^{-1}$ , (c) cycling performances at a current density of  $0.5 \text{ A g}^{-1}$ , (d) rate performances, and (e) long term cycling performance and Coulombic efficiencies of the  $\text{Fe}_2\text{O}_3$  hollow nanospheres at a current density of  $1.0 \text{ A g}^{-1}$ .

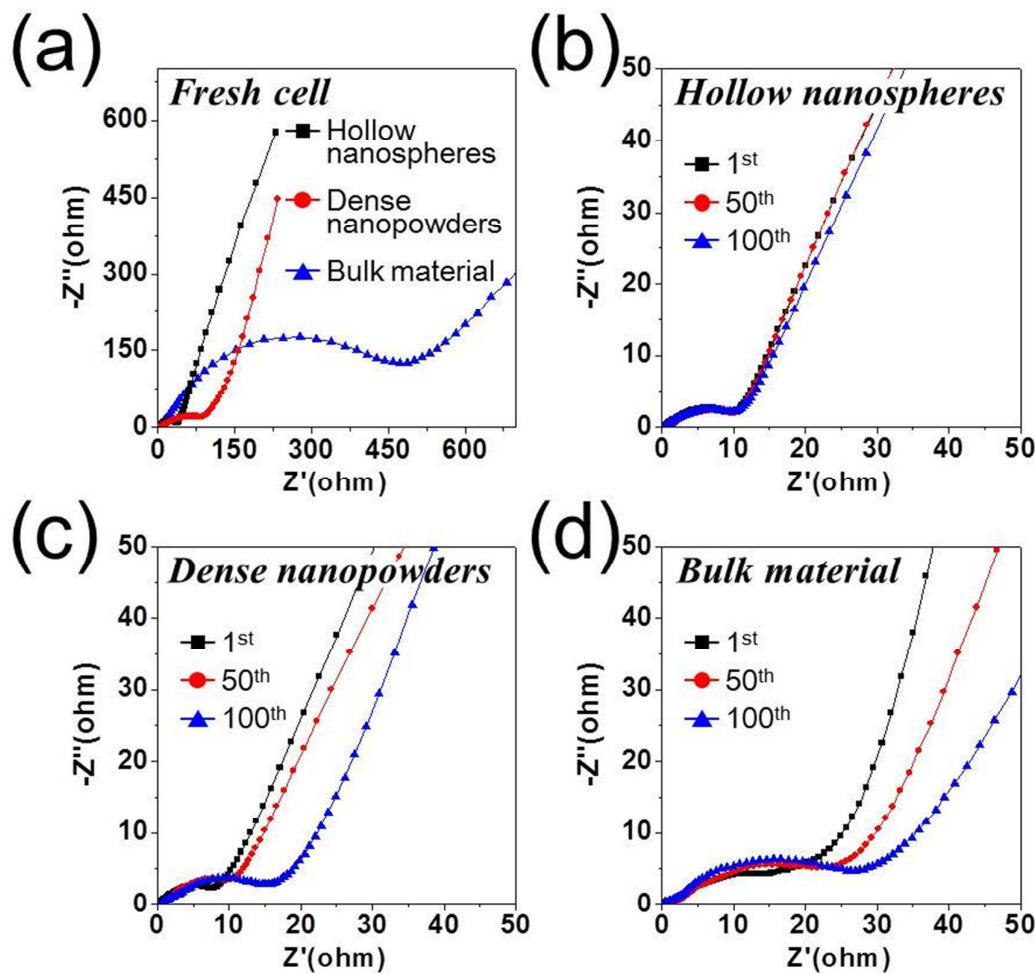
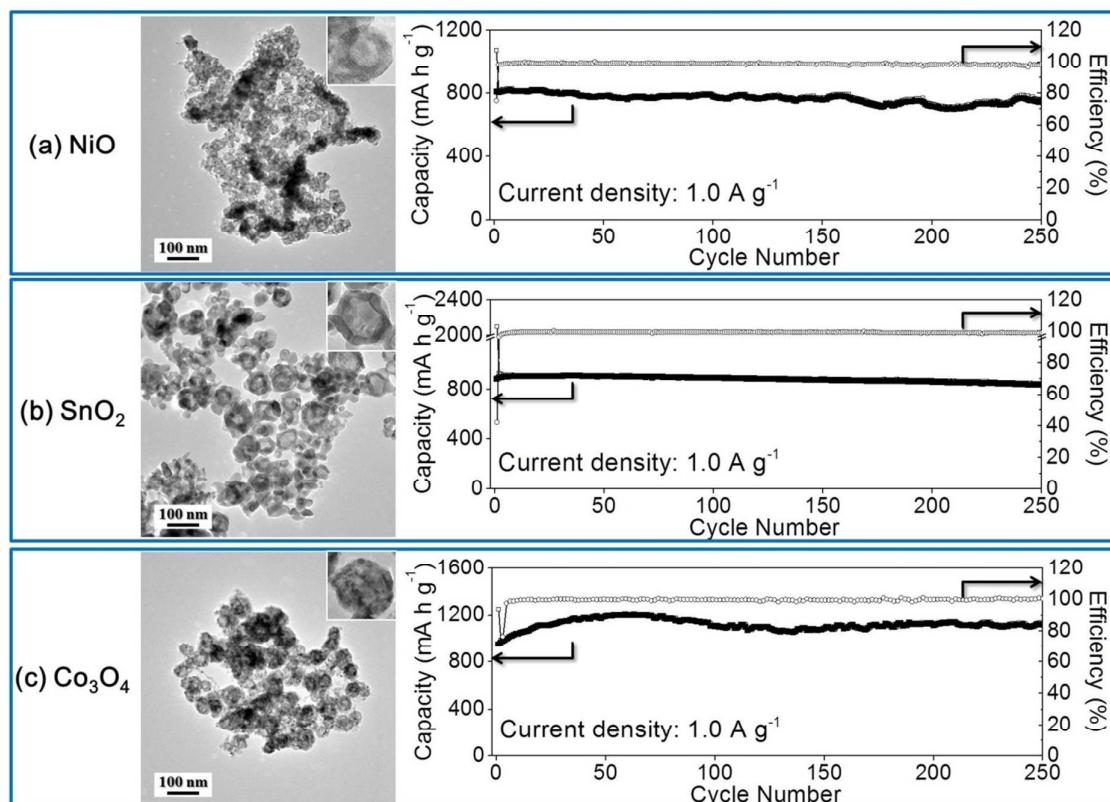


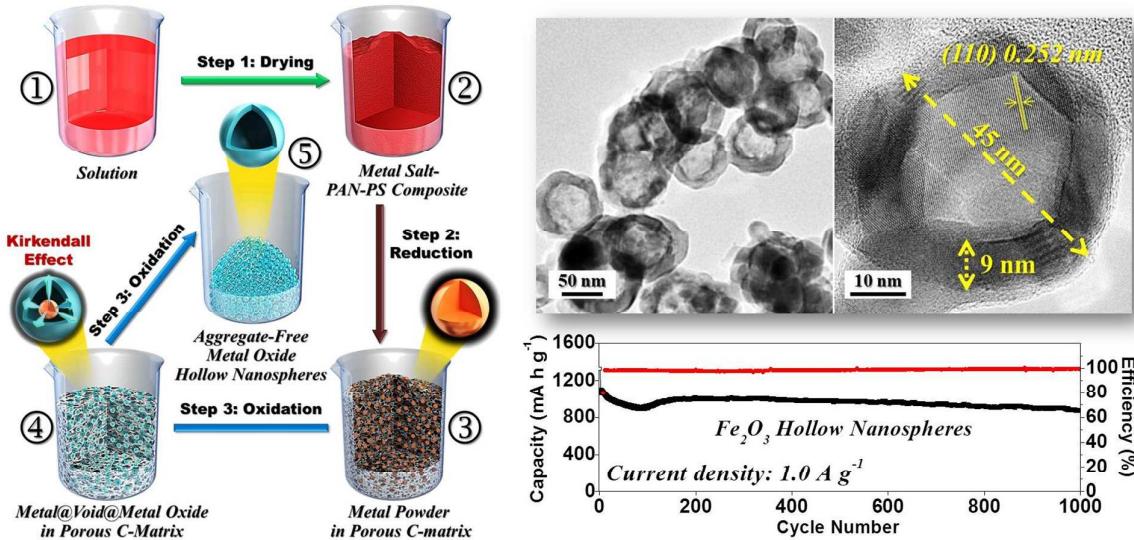
Figure 5. Nyquist plots of the  $\text{Fe}_2\text{O}_3$  hollow nanospheres and nanopowders with dense structure and bulk material: (a) before cycling, (b) after cycling of the  $\text{Fe}_2\text{O}_3$  hollow nanospheres, (c) after cycling of the  $\text{Fe}_2\text{O}_3$  nanopowders with dense structure, and (d) after cycling of the bulk material.

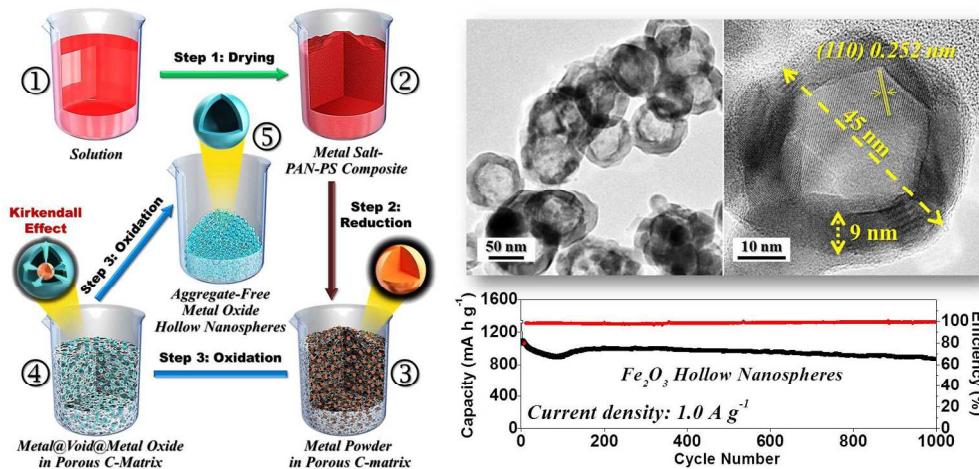


**Figure 6.** Morphologies and cycling performances at a current density of  $1.0 \text{ A g}^{-1}$  for the (a) NiO, (b) SnO<sub>2</sub>, and (c) Co<sub>3</sub>O<sub>4</sub> hollow nanospheres formed by all-in-one beaker method.

**The table of contents entry**

A simple and easily scalable process for the formation of metal oxide hollow nanospheres using nanoscale Kirkendall diffusion called the “all-in-one beaker method” is introduced. Aggregate-free  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{SnO}_2$ , and  $\text{Co}_3\text{O}_4$  hollow nanospheres with excellent cycling performances for lithium-ion storage are produced as the first target materials.





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