

Hollow Nano Spheres for Lithium-ion Batteries

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Abstract: Technology in the Twentieth century requires miniaturization of devices into nanometer sizes while their ultimate performance is dramatically enhance. This raises many issues regarding to new materials for achieving specific functionality and selectivity. Nanomaterials a new branch of materials research are attracting a great deal of attention because of their potential applications in areas such as Electronics. There are two ways of approaching the properties of nanoscale objects: the bottom-up approach and the top-down approach. In the first, one assembles atoms and molecules into objects whose properties vary discretely with the number of constituent entities, and then increases the size of the object until this discretisation gives way in the limit to continuous variation. The relevant parameter becomes the size rather than the exact number of atoms contained in the object. In the second case, one considers the evolution of the properties of a sample as its size is whittled down from macroscopic toward nanometric lengths. It is this approach that we shall examine here, whilst mentioning zones of overlap and exclusion between the two approaches. Nanomaterials plays a very important role in various applications. One of the best applications of Nanomaterials is for Energy Storage Applications. Since the surface reactivity increases in Nano dimensions, their structures play a very important role under these dimensions. The Nanoparticles shape and morphology can also help to improve the performance of the devices. This paper mainly deals with the importance of Nanoparticles, particularly Hollow Nanospheres helps the movement of ions to circulate between the hollow spaces and to act as a transport media for the ions. Various methods are adopted for the synthesis of Hollow Nanospheres, The best methods among these are Hydrothermal Sol-gel Method, SoftMicelle template method, Hard Micelle Template method. One of these Soft Micelle template methods is reported in this paper.

Keywords: Nanotechnology, Nanomaterials, Hollow Nanospheres, Soft micelle template method.

1. Introduction

Nanomaterials are classified into Nanostructured materials and Nanophase/Nanoparticle materials. The former refer to condensed bulk materials that are made of Grains with grain size in the nanometer range, while latter are the usually dispersive nanoparticles. The nanometer range here covers a wide range which can be as large as 100-200 nm. To distinguish nanomaterials from bulk, it is vitally important to distinguish the unique properties of nanomaterials and their prospective impact in the field of Science and Technology. Nanomaterials plays a very important role in various applications. One of the best applications of Nanomaterials is for Energy Storage Applications. Since the surface reactivity increases in Nano dimensions, their structures play a very important role under these dimensions. The Nanoparticles shape and morphology can also help to improve the performance of the devices. This paper mainly deals with the importance of Nanoparticles, particularly Hollow Nanospheres helps the movement of ions to circulate between the hollow spaces and to act as a transport media for the ions. Hollow colloidal particles are exceptionally promising materials in diverse fields of technology, including catalysis, drug delivery, photonics, biotechnology, and electrochemical cells [1-7]. This promise has motivated intense research efforts by groups, worldwide, seeking to develop both specific and general strategies for synthesizing hollow nanostructures,[8-13] and for functionalizing their interior and exterior spaces with desirable chemistries.[13-15]

Hollow colloidal particles are exceptionally promising materials in diverse fields of technology, including catalysis, drug delivery, photonics, biotechnology, and electrochemical cells. Various methods are adopted for the synthesis of Hollow Nanospheres, The best methods among these are Hydrothermal Sol-gel Method, Soft Micelle template method, Hard Micelle Template methods. One of these Soft Micelle template methods is reported in this paper. Hollow colloidal particles are exceptionally promising materials in diverse fields of technology, including catalysis, drug delivery, photonics, biotechnology, and electrochemical cells. A common difficulty in template-based syntheses arises from the well-known challenge of creating uniform coatings of desired materials (or their precursors) on the corresponding templates. In many cases incompatibility between the substrate and coating material requires prior surface modification/ functionalization before the coating step can be performed. Preparation of hollow particles with nonspherical shapes introduces additional challenges. These range from the difficulty in forming a uniform coating around surfaces with large variation in curvature to the paucity of nonspherical templates available for the synthesis. [15-17].

Generally, it is believed that when material sizes are reduced down to nanometer scale, usually exhibit significantly enhanced functionalities in their properties. For instance, hollow nanoparticles with spherical morphology are unique candidates with high mechanical strength, surface permeability, and high surface area. Hollow nanospheres with thin shell domain not only enhance the fast lithium insertion/deinsertion kinetics but also the hollow void could serve as an effective buffering medium [18]. Recently, we have reported the fabrication TiO₂, La₂O₃ and V₂O₅ hollow nanospheres using anionic polymeric micelles with *core-shell-corona* architecture [19-21]. Herein, we report the fabrication of ZnO hollow nanospheres using anionic micelles through electrostatic interaction of Zn²⁺ ions with anionic micelles followed by precipitation under mild alkaline conditions. ABC triblock copolymer poly(styrene-*b*-acrylic acid-*b*-ethylene oxide)(PS-PAA-PEO) with anionic COO⁻ was used as a template and Zn(OAc)₂ was used as metal source. The hollow nanospheres were characterized by TEM, XRD, FTTR, SEM/EDX, thermal analysis with TG/DTA and nitrogen sorption analyses. The electrochemical characteristics of ZnO hollow nanospheres were further investigated as anode materials for rechargeable lithium-ion batteries.

2. Experimental

The fabrication of hollow zinc oxide nanospheres with micelles of poly(styrene-*b*-acrylic acid-*b*-ethylene oxide) (PS-*b*-PAA-*b*-PEO) using zinc acetate as metal precursor was carried out as follows. Polymeric micelles solution was prepared by dissolving the required amount of the above polymer in distilled water and then transferred to a volumetric flask to obtain a stock solution with a concentration of 0.5 gL⁻¹. The micelle solution was adjusted to pH 9 by using dilute NaOH solution. On addition of zinc salt solution, the clear micelle solution slowly turns to turbid due to formation of Zn(OH)₂ in *shell* domain of micelles and the contents were gently stirred for overnight at room temperature using a magnetic stirrer. The synthesis protocol was tuned by changing the ratio of Zn²⁺/PAA between 5 and 10 to obtain monodispersed hollow nanospheres. The composite particles were repeatedly washed with distilled water and ethanol and dried at 60 °C to remove moisture. In order to remove the polymeric template as well as to crystallize the ZnO hollow particles, the composite particles were calcined at 500 °C for 4 h in a muffle furnace under air.

Hydrodynamic diameter (D_h) of the template micelles of PS-PAA-PEO was measured with an Otsuka ELS-800 instrument. Wide-angle X-ray diffraction (WAXRD) patterns were recorded using CuK α radiation with a Shimadzu XRD-7000 diffractometer. The textural properties such as BET surface area and mesopore-size distribution were obtained using nitrogen adsorption/desorption isotherms with a BELSORB instrument. The morphology of the samples was observed from JEOL TEM-1210 (acceleration voltage: 80 KV) and JEOL TEM-2100 electron microscopes (acceleration voltage: 200 KV). FTIR spectra were recorded on a Jasco FTIR-7300 spectrometer. TG and DTA analyses were carried out using MAC Science TG-DTA 2100. Energy dispersed X-ray analysis was carried out with Hitachi S-3000N.

For lithium insertion studies, the zinc oxide hollow nanosphere (5 mg) was mixed mechanically with teflonized acetylene black (TAB-2, 3 mg) and then the mixture was pressed on a stainless steel mesh as the current collector under a pressure of 500 kg/cm² and dried at 160 °C for 4 hours under vacuum. The electrochemical characterizations were carried out using CR-2032 coin type cells with lithium as an anode. The electrolyte used was 1M LiPF₆-EC: DMC (1:2 volume ratios, Ube Chemicals Co. Ltd.). The coin cell assembling was performed in a glove box filled with argon (dew point, lower than -80 °C). The galvanostatic charge-discharge tests of the coin cell were performed at the constant current density of 0.5 mAcm⁻². The cyclic voltammograms (CV) were recorded with a Hokuto Denko HSV-100 in a beaker type cell containing zinc oxide hollow nanospheres as working electrode and a lithium foil as a counter and reference electrodes. *The charge-discharge performance was carried out in the voltage range of 3.0-0.05 V.*

3. Results and Discussion

The hydrodynamic diameter D_h (67 nm) and the ζ -potential (-56 mV) of the micelles (pH 9) were obtained from dynamic light scattering (DLS) and electrophoretic light scattering (ELS) experiments, respectively. Nearly monodispersed spherical micelles with average diameter *ca.* 46 ± 1 nm estimated from TEM image (not shown) were used as template for fabrication hollow nanospheres. The difference in the micelle particle's size between DLS and TEM is due to the fact that the latter accounts for only the *core-shell* part and excludes *corona* part of the micelle [22-25]. **The TG/DTA analyses of ZnO/polymer composite particles revealed that all the organic contents were decomposed between 200 and 420 °C (not shown) and the total organic content was found to be 16.2 %. Thus the calcination step is essential to create a hollow void space by removing the core-domain of polymeric micelles.** The absence of C-H, -C=C-, and -COOH bond stretching vibrations of phenyl groups of polymer backbone in the FTIR spectrum of the calcined sample (not shown) is also consistent with the thermal analyses [26]. **The phase purity and crystallinity of zinc oxide**

hollow nanospheres was investigated by powder X-ray diffraction (XRD). Comparison of wide-angle X-ray diffraction (WXRD) patterns of zinc oxide nanospheres (after calcination) and composite particles (before calcination) (Figure 1) suggested highly pure zincite crystalline phase. All diffraction peaks can be indexed as the hexagonal phase of ZnO with the lattice constants $a = 0.325$ nm and $c = 0.521$ nm, which is in good agreement with the JCPDS data, No. 36-1451.

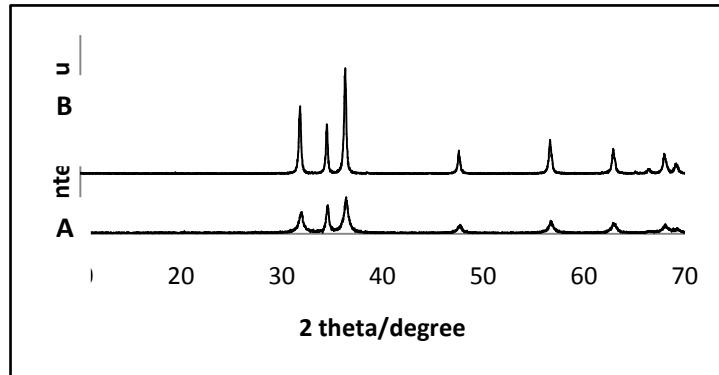


Fig. 1: Powder X-ray diffraction patterns of: (A) ZnO-composites and (B) ZnO hollow nanospheres.

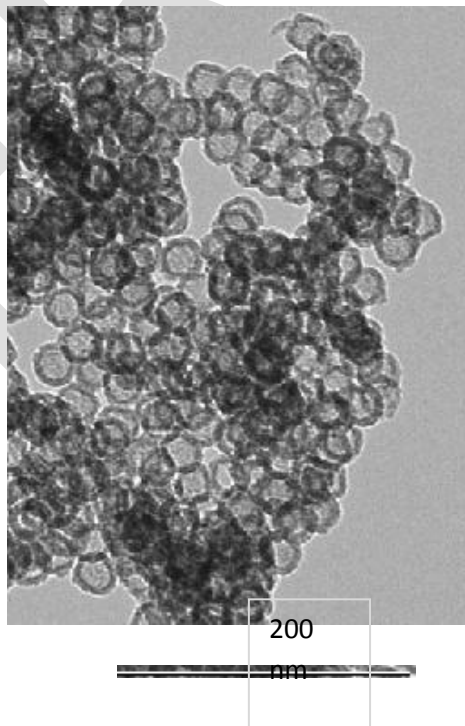


Fig. 2: TEM image of ZnO hollow nanospheres ($Zn^{2+}/PAA = 8$)

Figure 2 exhibits TEM image of material with $\text{Zn}^{2+}/\text{PAA}$ mole ratio of 8. The average particle size and void space diameter were found to be 32 ± 2 and 18 ± 1 nm, respectively. The wall thickness estimated by TEM (Figure 2) was approximately 7 ± 1 nm. However, at lower $\text{Zn}^{2+}/\text{PAA}$ ratios ($\text{Zn}^{2+}/\text{PAA} = 3$ and 5), the degree of aggregation of nanospheres is relatively low compared to $\text{Zn}^{2+}/\text{PAA} = 10$, due to deposition of zinc precursor species outside micelle domain. Furthermore, the PS block core size estimated from the TEM observation was found to be 23 ± 1 nm; however, after calcinations the void space diameter was approximately 18 ± 1 nm due to shrinkage. In addition, for hollow particles with high precursor concentration ($\text{Zn}^{2+}/\text{PAA} = 10$), the shell thickness increased marginally to 8 ± 1 nm. In addition, the pore sizedistribution curves based on BJH model showed disordered mesopores. The total pore volume and BET surface area were found to be $0.59 \text{ cm}^3 \text{ g}^{-1}$ and $119 \text{ m}^2 \text{ g}^{-1}$, respectively. The high-resolution transmission electron microscope (HRTEM, not shown) allows the resolution of lattice fringes of the crystals to be correlated to the (110) planes of the zincite lattice structure. Furthermore, energy-dispersive X-ray spectroscopy spectrum (EDX, not shown) shows strong peaks for zinc and oxygen suggestive of the pure zinc oxide phase confirming the highly pure zinc oxide hollow nanospheres.

Figure 3A exhibits the cyclic voltammograms (CV) of ZnO hollow nanospheres measured between 0 and 3 V at a scan rate of 3 mV/min. In the first cathodic scan, there is a major strong peak at 0.23 V and a minor peak at 0.57 V, which are related to the electrochemical process of the ZnO material. This process contains

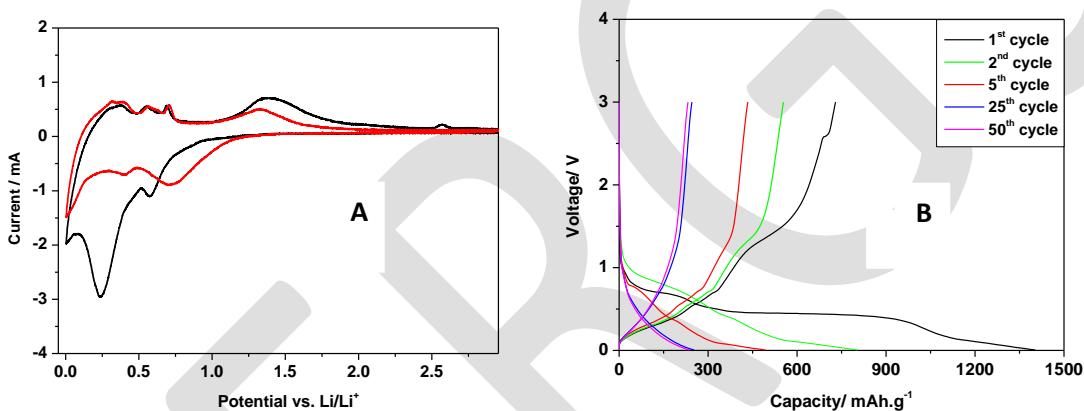


Fig. 3: (A) CV curves of ZnO hollow nanospheres in 1.0 m LiPF_6 (EC/DMC = 1/2 (v/v)) at a 3 mV/min sweep rate and (B) The Charge/discharge profiles ZnO hollow nanospheres at 0.25 C rate in the voltage region of 0.005-3.0 V.

the reduction of ZnO into Zn, the formation of Li-Zn alloy, and the growth of the gel-like solid electrolyte interphase (SEI) layer. The potentials of these reactions are very close, so it shows one major broad peak and a minor shoulder. In the first anodic scan, the four peaks located at 0.38 (broad), 0.51, 0.68, and 1.37 V are attributed to the multi-step dealloying process of Li-Zn alloy [27]. The second cathodic sweep differs from the first one; the major peak at 0.23 V is vanished and new peaks at 0.4 and 0.72 V (broad) were appeared for the second cycles. The anodic peaks of the second cycle, however, are more similar to that of first cycle according to literature [28].

Figure 3B shows discharge-charge curves in the voltage window of 0.005–3.0 V (vs. Li) at a rate of 0.25 C up to 50 cycles and for clarity, only selected cycles are shown in the voltage versus capacity profiles. It is worth to note that the plateaus on the voltage profiles coincide with the cathodic and anodic peaks in the CV curves (Fig.3A). A very obvious long plateau located at about 0.5 V appears in the first discharge curve. However, in the first charge curve, the plateaus are not so obvious. It can be seen four slopes, which are located at 0.28, 0.45, 1.33, and 2.5 V, respectively. After the first cycle, the slopes in discharge curves are around 0.8 and 0.4 V, and the curves are similar in shape, indicating that the reactions become more reversible. The ZnO hollow nanospheres deliver a first discharge capacity of 1304 mAh.g^{-1} , and a first charge capacity of 730 mAh.g^{-1} . It is important to mention that the very high discharge-capacity observed in the first cycle must originate from electrolyte decomposition in the low-potential region and subsequent formation of solid electrolyte interphase (SEI) on the hollow nanospheres [29]. The discharge capacities of the ZnO

hollow particles based electrode (Fig.4) in the 1st, 2nd, 5th, 25th, and 50th cycles are 1304, 804, 494, 252 and 249 mAh g⁻¹, respectively. The corresponding charge capacity values are 730, 554, 434, 251, and 248, mAh g⁻¹ for the 1st, 2nd, 5th, 25th, and 50th cycles, respectively. The coulombic efficiency of first cycle was found to be 62.5 %. However, the dense ZnO powder exhibited significantly lower charge-discharge capacities (not shown) compared to ZnO hollow nanospheres under similar experimental conditions. For instance, the discharge capacities of ZnO dense particles are 471, 352, 214, 151, and 144 mAh.g⁻¹ for 1st, 2nd, 5th, 25th, and 50th cycles; whereas the corresponding charge capacities were found to be 275, 210, 162, 141, 139 mAh.g⁻¹ for 1st, 2nd, 5th, 25th, and 50th cycles, respectively.

Fig.4A shows the capacity versus cycle number plot for ZnO hollow nanospheres. As can be seen, both discharge and charge capacities decrease up to 10 cycles and thereafter the capacity stabilizes. After 100 cycles with 100 % depth of discharging and charging at a rate of 0.1 C, the electrode capacity decreased to 246 mAh g⁻¹. After about 10 cycles, the columbic efficiency, the ratio of discharge/charge capacity is nearly 100 %. However, cycle performance of dense ZnO particles was poor as the discharge capacities reduced from 1090 to 118 mAh.g⁻¹ within a few cycles of repeated charge/discharges (not shown). Fig. 4B shows the rate performance of ZnO hollow nanospheres. At a low rate of 0.1 C, hollow particles show a discharge capacity of about 1414 mAh g⁻¹. However, the discharge capacities gradually decrease to 306, 195, and 116 mA g⁻¹ at 1C, 5C and 10C, respectively. However, the ZnOhollow particle basedelectrodes almost regains their original high-capacities when the rate was again lowered to 0.1 C after being exposed to high current loads (10 C),which indicatethe high stability of hollow nanospheres based electrodes. The improved electrochemical performance is attributed to the unique hollow spherical morphology. More importantly, the void space not only effectively buffers against charge storage and local volume change but also provides better electrical contact and shorter diffusion path length providing better rate capability.

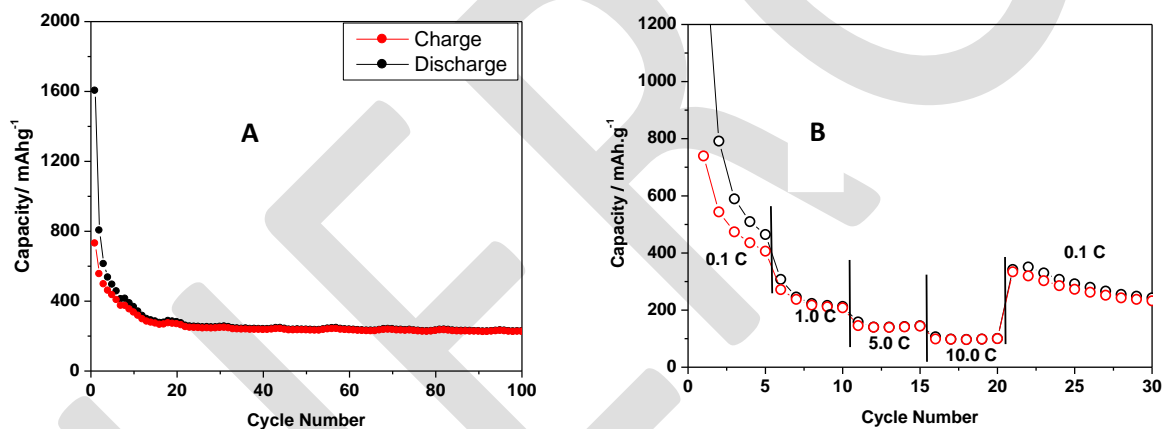


Fig. 4: (A) Charge-discharge cycling performance ZnO hollow nanospheres at 0.1 C rate in the voltage region of 0.005-3.0 V vs. Li/Li⁺ and (B) Rate performance in the voltage region of 0.005-3.0 V.

4. Conclusions

Core-shell-corona micelle obtained from poly(styrene-*b*-acrylic acid-*b*-ethylene oxide) successfully produce ZnO hollow nanosphere of size about 32 ± 2 nm. TEM, SEM/EDX, and XRD analyses confirmed the formation of hollow nanospheres and purity or crystallinity of ZnO nanoparticles. ZnOhollow nanospheres exhibited good cycling performance even after 100 cycles of repeated charge/discharges and the discharge capacity at 100th cycle was found to be 246 mAh g⁻¹. The ZnO hollow nanospheres based electrode exhibited high rate capability and cycling performance than the dense ZnO particles. The void space not only act as buffer medium against charge storage and local volume change but also provides better electrical contact and shorter diffusion path length and therefore provide better rate capability.

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