## Template-free single-step electrochemical synthesis of ZnO hollow nanospheres: Self-assembly of hollow nanospheres from nanoparticles<sup>†</sup>

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The present work demonstrates for the first time a template-free, single-step electrochemical method to synthesize ZnO hollow nanospheres with diameter in the range of 20–200 nm, which are formed by self-assembly of ZnO nanoparticles of <10 nm diameter.

Hollow nanospheres (NSs) are an important class of materials because their hollow structures provide low density and large surface-area-tovolume ratio for potential applications in catalysis, fillers, drug delivery, gas sensors, and photonics.1 The spherical geometry facilitates the highest possible packing density and low light scattering surface properties.<sup>2</sup> A large variety of inorganic hollow spheres have been prepared by employing hard templates such as silica,<sup>3</sup> polystyrene spheres,<sup>4</sup> resin spheres,<sup>5</sup> and carbonaceous polysaccharide microspheres,<sup>6</sup> and soft templates such as emulsions<sup>7</sup> and ethanol droplets.<sup>8</sup> The use of templates to synthesize hollow spheres requires multiple steps, which are time-consuming and expensive, and sometimes involve environment-hostile chemicals. The nature of the templates could also influence the properties of the resulting hollow spheres, which are of great concern for the targeted applications. The thermal treatment process, normally used to remove the templates, often leads to agglomeration of the product materials and reactions of the adsorbed species with the surface of nanoparticles (NPs).9 Despite the large effort towards the synthesis of hollow spheres, a single-step method for producing hollow spheres remains an important challenge. To date, only a limited number of studies involving single-step methods, such as hydrothermal,<sup>10</sup> solid-state pyrolysis<sup>11</sup> and thermal evaporation techniques,12 have been reported for the production of self-assembled mesospheres with hollow structures, with diameters mostly larger than 200 nm. In particular, Gao et al. and Umar et al. reported the formation of ZnO spherical cages and shells of 1.0-5.0 µm in diameter using a thermal evaporation method at a temperature in the range of 500-1150 °C.12 Recently, Zhou et al. and Wang et al. prepared ZnO hollow spheres of 1.2-1.5 µm and 0.2-1.5 µm in diameter using Streptococcus thermophilus and colloidal carbon spheres, respectively, as templates in a hydrothermal method (at 90-180 °C).13 Deng et al. obtained good photocatalytic activity of ZnO hollow spheres (0.45-1.1 µm in diameter) synthesized by a hydrothermal technique at 70 °C using sulfonated polystyrene templates.14 Therefore, it is of scientific interest to find new methods to produce hollow NSs using a simpler and single-step process. In the present work, we demonstrate a single-step, template-free electrochemical

WATLab and Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada. E-mail: tong@uwaterloo.ca; Fax: (+1) 519-746-0435 process for the preparation of ZnO hollow NSs at 70 °C and with the average diameter (20–200 nm) considerably smaller than the previous studies that employed either a hydrothermal or a thermal evaporation method.<sup>10–14</sup> The present electrodeposition process also does not require the use of any catalyst or toxic precursors, making it a facile, more environmentally friendly method.

Since the pioneering work of electrochemical synthesis of ZnO nanostructures by Peulon et al. and Izaki et al. over a decade ago,15 a diverse range of nanostructures have been obtained by controlling the electrodeposition parameters.<sup>16</sup> For instance, one-dimensional and two-dimensional ZnO nanostructures can be obtained by changing the zinc electrolyte concentration over the 0.5-10 mM and 50-500 mM ranges, respectively.16 To date, no ZnO hollow NSs has been obtained using the electrochemical technique. In the present work, by using a lower  $Zn(NO_3)_2 \cdot 6H_2O$  electrolyte concentration ( $\leq 0.25$  mM), we were able to deposit (zero-dimensional) ZnO NPs that self-assemble to (three-dimensional) hollow NSs on several substrates, including indium-tin-oxide coated glass (ITO-glass), indium oxide, and Au-coated polyethylene terephthalate (PET). Fig. 1a and b show the scanning electron microscopy (SEM) images of ZnO hollow NSs deposited on ITO-glass for 120 minutes in 0.1 mM electrolyte. These hollow NSs are discrete and uniformly deposited with a size distribution of 20-100 nm in diameter. Upon increasing the electrolyte concentration to 0.25 mM, the hollow NSs increase in diameter to 20-200 nm (Fig. 1c, d), with less homogeneity along with the emergence of sparsely grown nanotube-like structures. Although all the broken NSs seen in the insets of Fig. 1a and c indicate the hollow nature, some of



Fig. 1 SEM images of ZnO hollow nanospheres electrodeposited in (a,b)  $1.0 \times 10^{-4}$  M and (c,d)  $2.5 \times 10^{-4}$  M Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (with 0.1 M KCl) on ITO-glass at 70 °C for 120 minutes.

<sup>†</sup> Electronic supplementary information (ESI) available: Experimental details; further SEM images. See DOI: 10.1039/b904965g

them can be solid with voids (discussed later). Careful examination of the magnified SEM images as shown in the insets of Fig. 1b and d reveals that the shells of the hollow NSs are constructed from very fine NPs of <10 nm in diameter. In addition, most of the larger NSs appear to have fused together, indicating further clustering of NSs. Fig. 2 shows the size distributions of ZnO NSs obtained at two different electrolyte concentrations. Evidently, a narrower size distribution with smaller NSs is obtained at 0.1 mM than that obtained at 0.25 mM Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O electrolyte concentration. Further increasing the concentration to 0.5 mM produces ZnO nanowires of diameter 40-50 nm uniformly grown over the substrate (ESI,† Fig. S1). A similar observation on the change in shape from ZnO NPs to nanowires with increasing concentration of the zinc acetate dihydrate precursor in a sol-gel process has been reported.<sup>17</sup> The precursor concentration therefore plays an important role in building different nanostructured materials. Similar results can also be obtained on indium oxide or Au-coated PET substrates, suggesting that the substrate does not play a significant role in the formation of ZnO nanostructures.

The transmission electron microscopy (TEM) images of ZnO hollow NSs obtained with 0.25 mM  $Zn(NO_3)_2 \cdot 6H_2O$  show a relatively darker outer regions (shells) of most of the NSs (marked in Fig. 3a,b) indicating the hollow nature of the observed structures. However, some of these ZnO NSs (without the marks) also appear not completely hollow at their center, and the voids and pores inside



Fig. 2 Size distributions of ZnO nanospheres obtained at electrolyte concentrations of (a)  $1.0 \times 10^{-4}$  M and (b)  $2.5 \times 10^{-4}$  M Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (with 0.1 M KCl) on ITO-glass at 70 °C for 120 minutes.



**Fig. 3** TEM images of ZnO hollow nanospheres electrodeposited in 2.5  $\times 10^{-4}$  M Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (with 0.1 M KCl) on ITO-glass at 70 °C for 120 minutes. (a,b) Low-magnification images, with the projected hollow regions of the nanospheres highlighted by dashed-line circles. (c) High-resolution image of the edge region of a hollow nanosphere, with the corresponding selected area electron diffraction pattern shown as inset.

the NSs can be clearly discerned. The voids and pores in these NSs indicate that they were in the process of self-assembling towards the formation of hollow NSs. It should be noted that these "non-hollow" ZnO nanospheres appeared to be similar to the mesoporous  $SnO_2$ microspheres formed by assembly of nanoparticles in a carbonmatrix-assisted hydrothermal process.<sup>18</sup> These SnO<sub>2</sub> samples with their porosity and the nanosized building blocks were reported to show significant improvement in the electrochemical performance when compared with a nonporous micrometer-sized commercially available SnO<sub>2</sub> sample.<sup>18</sup> This indicates that even though the NSs may not be entirely hollow, they show promise for further performance improvement in potential applications. The corresponding high-resolution TEM image of the shell region of a hollow ZnO NS (Fig. 3c) shows clear and continuous lattice planes (marked by circles), indicating that the individual ZnO NPs are nearly perfect single crystals. The size of the individual NPs is measured to be 5-6nm, with a lattice spacing of 2.8 Å corresponding to the (100) crystal plane of ZnO. The selected area electron diffraction (SAED) pattern of the hollow NSs shows a series of rings, indicating the polycrystalline nature arising from the constituent single-crystal NPs.

Fig. 4a shows the corresponding glancing-incidence X-ray diffraction (GIXRD) pattern of the ZnO hollow NSs (Fig. 1a, b),



**Fig. 4** (a) GIXRD spectrum and (b) depth-profiling O1s XPS spectra of ZnO hollow nanospheres electrodeposited in  $1.0 \times 10^{-4}$  M Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (with 0.1 M KCl) on ITO-glass at 70 °C for 120 minutes.

which exhibits three prominent diffraction features in good accord with the wurtzite crystal structure (JCPDS 01-074-0534). Furthermore, the O 1s X-ray photoelectron spectra (XPS) collected as a function of sputtering time are shown in Fig. 4b. As shown in the inset of Fig. 4b, each O 1s envelope is found to consist of two components corresponding to Zn(OH)<sub>2</sub> at 531.6 eV and ZnO at 530.7 eV, in good agreement with the literature values.<sup>19</sup> The Zn(OH)<sub>2</sub> component is found to weaken while the ZnO component strengthens with increasing sputtering time, which indicates the presence of a Zn(OH)<sub>2</sub> rich surface region.

The growth evolution of the hollow NSs as a function of deposition time from 30 minutes to 120 minutes (ESI,† Fig. S2) is shown in Fig. 5a-c [and to 240 minutes (ESI, † Fig. S3)], and schematically in Fig. 5d. After 30 minutes of deposition (Fig. 5a), the formation of NPs of  $\sim 10$  nm in diameter is evident. Some of these NPs are found to form nanoclusters, many of which appear to form the base of the emerging hollow spherical structures. As Zn(OH)<sub>2</sub> is an intermediate in the electrodeposition of ZnO,<sup>15</sup> the hydroxyl group at the surface of the NP can act as a binder with another NP to form the clusters, which have been observed for the aggregation of metal oxide NPs.20 After 60 minutes of deposition (Fig. 5b), the aggregated clusters of NPs have evidently self-assembled to hollow spherical nanostructures. Further deposition produced hollow NSs over extended areas of the substrate after 120 minutes (Fig. 5c) and increased film thickness after 240 minutes (ESI,† Fig. S3). The presence of Zn(OH)<sub>2</sub> on the surface of the hollow NSs has been confirmed in the XPS spectra (Fig. 4b), supporting its role as the binder for producing the nanoclusters and other nanostructures.

As suggested by Park et al.,<sup>21</sup> the shape of the nanostructures generally depends on the competition between the rate of formation of the NPs and the rate of self-organization of these NPs. Given that



Fig. 5 Growth evolution of ZnO hollow nanospheres on ITO-glass upon electrochemical deposition in 0.1 mM Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O at 70 °C for (a) 30, (b) 60, and (c) 120 minutes. A schematic growth model of this selfassembly process is shown in (d).

the electrolyte concentration is directly related to the deposition rate of ZnO NPs,<sup>16</sup> the use of an extremely slow deposition rate likely provides sufficient time for the NPs to self-organize leading to the hollow NS structures. The NSs found with voids in the TEM images (Fig. 3a and b) are believed to be under the process of self-assembling from clusters of NPs to hollow NSs. Furthermore, the formation of NSs appears to follow a size-limited progressive growth mechanism with the number of hollow NSs increasing with deposition time and the size of the hollow NSs restricted to a concentration-dependent optimal regime.

In summary, the present work illustrates that a template-free, single-step electrochemical method can be used to produce ZnO hollow NSs with diameters in the range 20-200 nm. The growth of these hollow NSs follows a size-limited progressive growth mechanism involving self-assembly of NPs (<10 nm in size). The production of these distinct ZnO hollow nanostructures offers potential applications in nanophotonics, catalysis, and nanomedicine.

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