Controllable fabrication of hollow In$_2$O$_3$ nanoparticles by electron beam irradiation

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A growth strategy is presented for controllable fabrication of hollow In$_2$O$_3$ nanoparticles (NPs) via oxidation of In nanocrystals under electron beam irradiation. The morphology of the NPs can be tailored by changing the electron beam energy and current density. Yolk–shell NPs are preferentially formed under 200 keV electron beam irradiation, while hollow NPs are preferentially formed at 300 keV. This work confirms that electron beam irradiation is a valuable method for the engineering and modification of nanomaterials.

1. Introduction

Indium oxide (In$_2$O$_3$), a typical n-type transparent semiconductor with a wide direct bandgap, has been widely used in solar cells, optical and electrical devices, and photocatalysis because of its unique electronic and optical properties.\(^1-4\)

In$_2$O$_3$ is also a sensing material; various nanostructured In$_2$O$_3$ materials have been used in gas sensors\(^5-7\) and the performance of sensors is closely correlated with the morphology and structure of In$_2$O$_3$. Consequently, the development of synthesis methods for creating In$_2$O$_3$ nanostructures is essential and significant.

Among various nanostructures, hollow nanoparticles (NPs) exhibit a much lower density and larger surface area compared to dense solid NPs with equal volume, and have attracted growing attention.\(^8-11\) The most popular approach for the synthesis of hollow NPs involves coating of designed materials onto a sacrificial template and selective removal of the template core via chemical etching or thermal decomposition. However, the conventional template-based strategy is inconvenient in some cases and the as-formed NPs are often larger than the typical size of nanocrystals.\(^12\) An alternative strategy is direct conversion of solid NPs into hollow NPs via ion exchange, the nanoscale Kirkendall effect, and galvanic replacement.\(^12,13-14\) Examples are metal oxide hollow NPs resulting from the oxidation of some metal NPs (Fe, Co, Ni, etc.)\(^15-17\). Those metal NPs react with oxygen precursors on their surface to produce an initial oxide shell, and further reaction continues by faster outward diffusion of metal species through the oxide layer, which yields hollow oxide NPs. But for some other metal NPs in which oxidation proceeds via oxygen penetration through the growing oxide layer (Pb, In, etc.)\(^18,19\), additional treatment is required to form hollow structures.\(^20,21\)

Here, a novel strategy is presented for controllable fabrication of hollow In$_2$O$_3$ structures via oxidation of In NPs under electron beam irradiation. Specifically, using a transmission electron microscope (TEM) we observed the morphology evolution in real time and concluded that the NPs can be tailored by changing electron beam parameters. Yolk–shell NPs (regarded as special hollow NPs with interior cores) were preferentially formed under 200 keV electron beam bombardment and the oxidation kinetics was in good agreement with the Cabrera–Mott theory. Hollow NPs were preferentially formed under 300 keV electron beam irradiation. This work confirms...
that electron beam irradiation is a valuable method to tailor nanostructures.

2. Experimental section

The simplified illustration in Fig. 1a shows the controllable fabrication of yolk–shell and hollow In$_2$O$_3$ NPs at room temperature. In NPs were synthesized using electron beam irradiation inside the TEM.$^{22-24}$ After intense electron beam irradiation, In NPs with a wide size distribution (Fig. 1b) were formed around initial InP microparticles due to either electron-beam heating or electrostatic charging/discharging.$^{25}$ Because of the existence of residual oxygen in the TEM chamber or/and on the TEM grid coated with a thin film of carbon, In NPs might be oxidized under electron beam irradiation,$^{26}$ resulting in the formation of core–shell NPs with an indium oxide outer layer. The oxidation was performed under a parallel electron beam with a current in the range of 0.1 to 10 A cm$^{-2}$ inside the TEM (FEI Tecnai G20 operating at 200 kV, FEI Titan 80–300 operating at 300 kV), and the subsequent morphology evolution was observed in TEM mode. Although STEM mode is more preferable for the control of the electron beam, carbon contamination is not eliminated and surface contamination will obstruct the oxidation and evolution of NPs.

3. Results and discussion

The enlarged image in Fig. 1c demonstrates that the oxide shell is composed of a large number of small islands or clusters. Such an oxide shell provides numerous fast transport paths between its inside and outside. Continuous electron beam irradiation promoted outward indium diffusion, which results in the formation of uniform yolk–shell (Fig. 1d) and hollow (Fig. 1e) NPs in the irradiated area. The high resolution TEM image (Fig. 1e) confirms that the as-formed oxide shell is cubic In$_2$O$_3$.

Fig. 2a shows the formation of yolk–shell NPs under 200 keV electron beam irradiation with a current density of $\sim 3.4$ A cm$^{-2}$. An $\sim 2$ nm uniform layer of indium oxide was formed on the surface at the early stage, and then the growth rate of the oxide shell decreased exponentially as the thickness increased (Fig. 2b). The parabolic growth behavior indicates that the oxidation of In NPs is controlled by ion diffusion, and the growth kinetics is in good agreement with the simplified theory of Cabrera and Mott.$^{27}$ The electric field in the oxide layer, created by a positive surface charge on the metal and a negative one on the oxide/vacuum interface, effectively lowered the energy barriers for the migration of In cations and O anions through the oxide.$^{28}$ The inward transportation of oxygen anions and the outward diffusion of In cations could lead to further growth of the oxide layer either at the metal/oxide interface or the oxide/vacuum interface, respectively.

Meanwhile, voids start to develop and emerge at the metal/oxide interface (Fig. 2a), which indicates that the outward diffusion of In ions is faster than the inward diffusion of O ions. It should be noted that room temperature oxidation of In
NPs under ambient conditions proceeds primarily via oxygen penetration through the growing oxide,\(^{19}\) that is, the inward diffusion of O ions is faster. The difference in the diffusion rate may be due to electron beam induced heating and the structure of the oxide shell. It is expected that the electron beam induced local temperature rise can promote the outward diffusion of In ions.\(^{29}\) However, the electron beam cannot induce the formation of voids in In@In\(_2\)O\(_3\) core–shell NPs formed in air.\(^{19}\) The oxide shell formed in air is single crystalline, while the as-formed shell formed under electron beam irradiation in this work is a polycrystalline structure with a crystal domain size of 3–5 nm (Fig. 1c and d); the grain boundaries may provide a fast diffusion path especially for the outward In species.

The preferred outward diffusion of In leads to the growth and merging of voids, leaving bridges between the core and the shell (Fig. 2a). These bridges, which provide a fast transport path for the outward diffusion of In atoms that can then spread on the inner shell surface, are expected to persist until the core is completely consumed, resulting in the formation of hollow NPs. However, in our experiments, no hollow NPs were observed even under a 200 keV electron beam for 1 hour. In terms of Cabrera–Mott theory, the electric field in the shell gets weaker with the growth of oxide, and the additional effect of the electric field diminishes. The growth will stop when the shell reaches a uniform limiting thickness, and after that the electric field diminishes. The growth will stop when the carbon film radius, \(r_0\), is the upper limit of thickness, \(X_1\) is the diameter of the as-formed yolk–shell NPs, \(\Delta T\) is the temperature rise associated with the electron beam bombardment is taken into account. The maximum temperature rise \(\Delta T\) can be estimated using the following equation:\(^{30}\)

\[
\Delta T = \frac{I}{\pi \kappa e} \left( \frac{\Delta E}{e} \right) \ln \frac{b}{r_0}
\]  

(1)

where \(I\) is the beam current, \(\kappa\) is the thermal conductivity, \(b\) is the carbon film radius, \(r_0\) is the beam radius, and \(e\) is the electron charge. \(\Delta E\) is the total energy loss per electron in a sample of thickness \(t\), normally a few eV nm\(^{-1}\), which is given by the stopping power for the electrons. With an electron beam current density of 3.4 A cm\(^{-2}\), \(I = 9.6\) nA, \(b = 1.5\) mm, \(r_0 = 300\) nm, \(\kappa = 1.0\) W m\(^{-1}\) K\(^{-1}\), and \(\Delta E/t = 1.0\) eV nm\(^{-1}\), which was calculated from the Bethe–Bloch equation\(^{10}\) assuming that the mean excitation energy is 373 eV,\(^{12}\) the temperature rise will be 26 K.

According to the Cabrera–Mott model, the limiting thickness \(X_t\) is dependent on the temperature and given by:\(^{26}\)

\[
X_t = X_1/\left( \frac{W}{kT - 39} \right)
\]  

(2)

where \(X_t\) is the upper limit of thickness, \(W\) is the activation energy for the motion of In cations across the oxide, \(k\) is the Boltzmann constant, and \(T\) is the absolute temperature. Taking \(W = 1.6\) eV\(^{13}\) and \(X_t = 3.5–4\) nm at room temperature,\(^{19}\) \(X_t\) is estimated to be 4.5–5.1 nm at 324 K, which is consistent with our experimental measurement.

The oxidation of In NPs under a 300 keV electron beam with a current density of \(-0.16\) A cm\(^{-2}\) presents different morphology evolution (Fig. 3a). Some oxide islands nucleated on the surface at the early stage followed by growth and coalescence to form a non-continuous shell with gaps. It should be noted that NPs under 300 keV electron beam irradiation undergo obvious deformation (Fig. 3a), which may also lead to the formation of gaps. The gaps provide fast surface diffusion paths for the core materials and favor the nucleation of voids nearby, which is distinct from the oxidation under 200 keV electron beam irradiation. As In species diffuse outwards and react with O species on the outer surface, the voids become bigger while the oxide shells become thicker and more non-uniform, leaving hollow NPs. After the core is completely consumed or the gaps are filled, the as-formed hollow NPs do not undergo changes in size and morphology. Although the oxidation still obeys parabolic kinetics (Fig. 3b), the Cabrera–Mott mechanism is invalid, which can also be confirmed from Fig. 3c. According to the Cabrera–Mott model, for temperatures below the critical temperature \(W/39k\) the oxide grows up to limiting thickness and then stops. The local temperature

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rises associated with 200 keV and 300 keV electron irradiation are almost the same; consequently, the oxide layer should have a critical thickness independence on the particle size. However, the experimental result in Fig. 3c is inconsistent with the expectation, which confirms that the Cabrera–Mott mechanism is invalid in this case.

The difference in the oxidation behavior under 200 keV and 300 keV electron beams may stem from beam induced mass transport. Considering that the elastic scattering cross-section increases and the inelastic scattering cross-section decreases with the increase of electron energy, elastic scattering damage is a predominant factor for much severe deformation under 300 keV. Using the elastic collision model, the maximum transferred energy from the incident electron to the atom can be calculated using:

\[
E_{\text{max}} = \frac{2E_0(E_0 + 2mc^2)}{(Mc^2)}
\]

(3)

where \(E_0\) is incident electron energy, \(m\) is the mass of the electron, \(M\) is the mass of the target atom in the material and \(c\) is the speed of light in a vacuum. The maximum energies transferred from 200 keV electrons to In and O are 4.6 and 32.7 eV, while those from 300 keV electrons are 7.4 and 53.0 eV, respectively. The threshold displacement energy for In atoms at the surface, taken as 1.5 times the sublimation energy,\(^{34,35}\) is 4.2–4.4 eV. For either 200 or 300 keV electron, the transferred energy to In nuclei is larger than the threshold energy; consequently, the electron beam can knock In atoms away from the surface at the early stage of the oxidation, leading to the mass loss and deformation of NPs. However, obvious deformation is only observed at 300 keV (Fig. 3a), which is attributed to the fact that the displacement cross section of In under 300 keV electron beam irradiation is two orders of magnitude higher than that at 200 keV.\(^{36}\) In fact, both oxidation and atomic displacement occurred simultaneously on the surface of In NPs at the early stage. The oxidation plays a leading role at 200 keV, resulting in the rapid formation of a uniform oxide layer (Fig. 2a). At 300 keV, the electron beam induced atomic displacement cannot be ignored; the generation and aggregation of In vacancies result in an obvious mass loss locally; consequently, In NPs undergo obvious deformation (Fig. 3a).

Considering that the displacement rate is proportional to the beam current density, it is expected to modify the morphology and structure of the products by changing the beam density. It can be confirmed from Fig. 4, which shows the oxidation and structural evolution of In NPs under 300 keV electron beam irradiation with a beam current density of \(\sim 1.5\) A cm\(^{-2}\). It is very different from the phenomena in Fig. 3a that some oxides form the surrounding NPs and that the NPs evolve into a flower-like structure. It should be noted that the “petals” are deposited on the carbon supporting film rather than on the particle surface because the initial nucleation occurs at somewhere away from the particles (Fig. 4b). In atoms were knocked off and diffused outwards on the carbon substrate. The nucleation took place at someplace where the products of the reaction between In and O were deposited (Fig. 4g). With the continuous deposition of the reaction products, the petals open up gradually (Fig. 4b–f). Due to the higher displacement rate, much more In atoms were knocked off. Ultimately, the as-formed hollow structures are porous (Fig. 4e and f).

4. Conclusions

In conclusion, we have shown a novel strategy for controllable fabrication of yolk–shell and hollow In\(_2\)O\(_3\) NPs using electron beam irradiation. The morphology and structure of the NPs can be modified by changing the beam energy and the beam density. Yolk–shell NPs are preferentially formed under 200 keV electron beam bombardment, while hollow NPs are preferentially formed at 300 keV. In the case of 200 keV, the oxidation plays a leading role, and the oxidation kinetics is in good agreement with the Cabrera–Mott theory. The NPs, under 300 keV electron beam irradiation, undergo serious deformation because the beam induced mass loss cannot be ignored. This method can be further extended to other yolk–shell and hollow structures. Although the productivity is low due to the small size of the electron beam inside the TEM, the electron beam assisted method can be an extremely useful technique for large-scale synthesis of hollow nanostructures. The mass production rate can be reached up to several grams per hour in some homemade synthesis systems with electron beam reaction chambers,\(^{37}\) which is similar to that of the flame synthesis method.

**Author contributions**

T. X. and L. S. designed the experiments and supervised the project. H. Z. and T. X. performed the experiments. T. X. wrote the paper and all authors contributed to the discussions and preparation of the manuscript.
Conflicts of interest

There are no conflicts to declare.

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