Supporting Information

A Novel and Facile Solution-Phase Deposition Approach to Porous Selenium Materials

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S1. Scheme illustrating the synthesis of selenium materials using the novel solution-phase deposition approach.

![Scheme](image)

**Figure S1-1.** Scheme illustrating the synthesis of selenium materials using the novel solution-phase deposition approach. From this scheme, it is reasonable to expect that the dimension-constrained role of different amine-containing molecules coordinated with metal ions may result in the differences in Se samples’ morphologies.

![Images](image)

**Figure S1-2.** Scheme illustrating the structures of hydrazine hydrate and EDTA molecule.
S2. SEM images of the as-prepared porous flower-like Se patterns

Figure S2. Higher magnification SEM image of porous flower-like Se patterns, indicating that the flower-like pattern is composed of nanoflakes with the thickness of ~300 nm.

S3. TEM images of the porous Se materials prepared by this facile solution-phase deposition method.

Figure S3. TEM images of porous flower-like Se patterns (a) and porous apple-like microspheres. The inset in Figure S3a is the SAED pattern. Figure S3a and the inset show that the flower-like patterns are composed of selenium with high crystallinity. Figure S3b indicate that the apple-like microspheres are hollow. Due to the samples’ large size and instability of selenium when exposed to electron beam, it is difficult to discern the porous structure and obtain the SAED pattern.
S4. XRD patterns of the as-prepared porous selenium microspheres.

Figure S4. XRD pattern of the as-prepared porous apple-like Se microspheres. Different from that of Figure 2b, this porous Se sample is carefully scraped from the Zn substrates, and then washed three times each with dilute acid, water and absolute ethanol. This shows that the pure porous selenium samples can be easily separated from the substrate.

S5. Raman spectra of the as-prepared porous selenium products.

Figure S5. XPS (a) and Raman (b) spectra of the porous apple-like Se microspheres. In the XPS spectrum, the peak centered at 54.71 eV can be attributed to Se3d and no obvious peak from Se-O are observed, indicating the high purity of the products. Typically, the resonance peak of t-Se is located at ~235 cm\(^{-1}\) whereas those of amorphous selenium and monoclinic selenium are centered at ca. 250 cm\(^{-1}\) and ca. 260 cm\(^{-1}\), respectively. As shown in Figure S5, only one peak at about 234 cm\(^{-1}\) is observed in the frequency region between 200 cm\(^{-1}\) and 300 cm\(^{-1}\), which is assigned to the characteristic mode of t-Se. This testifies that the as-prepared t-Se porous products have a high crystal quality and purity, as revealed in the XRD patterns. Note that the XPS and Raman spectra of the flower-like Se pattern are similar.
S6. SEM images of the porous lotus-root-like selenium microspheres.

**Figure S6.** SEM images of porous lotus-root-like microspheres prepared in the presence of 0.254 g Zn foil, 0.358 g Na₂SeO₃, 0.577 g EDTA and 40 mL H₂O at 180 °C, clearly suggesting the porous structure of the Se materials. Figure S6b, Figure S6c are the side images of some porous lotus-root-like samples. Figure S6d and Figure S6e are the bottom’s images of two different lotus-root-like spheres. Note that pores only exist at the bottom of the Se porous lotus-root-like, indicating that the selenium porous microstructures formed along a certain direction.
S7. XRD pattern of porous lotus-root-like selenium microspheres.

![XRD pattern](image)

**Figure S7.** XRD pattern of the as-prepared porous lotus-root-like Se microspheres. Apart from the diffraction peaks of t-Se (JCPDS 06-0362), some weak peaks can be attributed to Zn (JCPDS 04-0831), and the Miller indexes are signed using the cyan font, indicating that the porous Se spheres are grown on the Zn foil.

S8. SEM images of the porous walnut-like spheres

![SEM images](image)

**Figure S8.** Low magnification (a) and high magnification (b) SEM images of porous walnut-like spheres prepared in the presence of 0.387 g Zn foils, 0.280 g Na$_2$SeO$_3$, 0.577 g EDTA and 40 mL H$_2$O at 150 ºC, indicating the large-scale synthesis of porous walnut-like selenium microstructures.
S9. SEM images of different selenium products prepared in the presence of EDTA at different conditions

Figure S9. SEM images of four different t-Se samples obtained at different conditions. a) The mixture of particles, spheres and threads, prepared in the presence of 0.254 g Zn foil, 0.358 g Na₂SeO₃, 0.577 g EDTA and 40 mL H₂O at 100 °C. These samples are obviously different from that of Figure 1c, suggesting that the hydrothermal temperature has a noticeable influence on the shapes of selenium final products. b-c) The mixtures of spheres and wires, prepared in the presence of 0.254 g Zn foil, 0.358 g Na₂SeO₃, 0.250 g EDTA and 40 mL H₂O at 150 °C, suggesting that the amount of EDTA is important to determine t-Se morphologies. d) Particles fabricated in the presence of 0.358 g Na₂SeO₃, 0.577 g EDTA and 40 mL H₂O at 150 °C. This further confirms that the coordination of EDTA molecule and Zn²⁺ are essential for controlling the porous morphologies in our solution-phase deposition methods.
S10. The effect of Zn foil on the Se sample’s morphology

Figure S10. Low magnification (a) and high magnification (b) SEM images of selenium spheres in the presence of 0.189 g Zn(NO$_3$)$_2$, 0.358 g Na$_2$SeO$_3$, 0.577 g EDTA and 40 mL H$_2$O at 150 ºC, where the Zn foil was replaced by Zn(NO$_3$)$_2$. As shown in Figure S10, the as-prepared samples are Se spheres, and almost no porous structures can be observed, obviously different from apple-like microspheres displayed in Figure 1c and Figure 1d. This manifests that the Zn substrate and the soft-template, formed through zinc ions adsorbed on Zn foil substrate and EDTA molecules, is very important for the synthesis of the porous Se materials in the solution-phase deposition method.
S11. SEM images of different selenium products prepared in the presence of N₂H₄·H₂O at different conditions

Figure S11-1. SEM images of four different t-Se samples synthesized at different conditions. 

a) The mixture of flakes, turbine and crystals (the higher SEM image is also shown in Figure S11-2), prepared in the presence of 0.254 g Zn foil, 0.358 g Na₂SeO₃, 0.8 mL N₂H₄·H₂O and 40 mL H₂O at 120 °C. This indicates that the hydrothermal temperature has a noticeable influence on the shapes of selenium final products. 

b) Crystals prepared in the presence of 0.254 g Zn foil, 0.358 g Na₂SeO₃, 0.8 mL N₂H₄·H₂O and 40 mL H₂O at 90 °C. This confirms that the hydrothermal temperature are significant in controlling the shapes of selenium final products.

c) Flakes with irregular arrangements, prepared in the presence of 0.254 g Zn foil, 0.358 g Na₂SeO₃, 0.3 mL N₂H₄·H₂O and 40 mL H₂O at 150 °C. This indicates that the amount of N₂H₄·H₂O has important effect on the Se morphologies and shows that the coordination of N₂H₄·H₂O and Zn²⁺ are important for the growth of flower-like Se pattern.

d) Particles synthesized in the presence of 0.358 g Na₂SeO₃, 0.8 mL N₂H₄·H₂O and 40 mL H₂O at 150 °C. This confirms that the coordination of N₂H₄·H₂O and Zn²⁺ is essential for our solution-phase deposition methods.
Figure S11-2. High-magnification SEM images of selenium flakes, turbine and crystals, prepared in the presence of 0.254 g Zn foil, 0.358 g Na$_2$SeO$_3$, 0.3 mL N$_2$H$_4$·H$_2$O and 40 mL H$_2$O at 150 °C. This shows the coexistence of three kinds of morphologies in the products.
S12. XRD patterns of the intermediates collected in the formation of the porous t-Se apple-like microspheres

**Figure S12.** XRD patterns of the intermediates of porous t-Se microspheres, prepared in the presence of 0.254 g Zn foil, 0.358 g Na₂SeO₃, 0.577 g EDTA and 40 mL H₂O at 150 °C, collected at different reacting mages. a) 1h; b) 4h; c) 8h; d) 24h.
S13. SEM images of the selenium nanoparticles.

Figure S13. SEM image of the t-Se nanoparticles prepared through hydrothermal treatment of 0.4 g SeO₂, 0.5 mL N₂H₄·H₂O and 20 mL H₂O for 24 h.
S14. Summary of the shapes of t-Se porous microstructures obtained under various conditions.

Table S1. Summary of the shapes of t-Se porous materials obtained under various conditions.

<table>
<thead>
<tr>
<th>Amine-containing compounds</th>
<th>Amount of amine-containing compounds</th>
<th>Metal foil</th>
<th>Amount of Na$_2$SeO$_3$(g)</th>
<th>Temperature (°C)</th>
<th>Morphologies</th>
<th>SEM images</th>
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<tr>
<td>N$_2$H$_4$H$_2$O</td>
<td>0.8 ml</td>
<td>0.254 g Zn</td>
<td>0.358</td>
<td>150</td>
<td>Porous flower-like patterns</td>
<td>Figure 1a,b</td>
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<td></td>
<td>0.64 ml</td>
<td>0.242 g Zn</td>
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<td>Ear-like microstructures</td>
<td>Figure 4c,d</td>
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<td>0.8 ml</td>
<td>0.254 g Zn</td>
<td>0.358</td>
<td>120</td>
<td>Mixture of flakes, turbine and crystals</td>
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<td>0.8 ml</td>
<td>0.254 g Zn</td>
<td>0.358</td>
<td>50</td>
<td>Crystals</td>
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<td>Particles</td>
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<td>EDTA</td>
<td>0.577 g</td>
<td>0.254 g Zn</td>
<td>0.358</td>
<td>150</td>
<td>Apple-like microspheres</td>
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<td>0.577 g</td>
<td>0.254 g Zn</td>
<td>0.358</td>
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<td>Porous lotus-coconut-like microspheres</td>
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<tr>
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<td>Microspheres</td>
<td>Figure 4a,b</td>
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</table>

*Zn foil was replaced by 0.189 g Zn(NO$_3$)$_2$
S15. SEM images of porous Te products prepared by the solution-phase deposition method.

Figure S15. Different-magnification SEM images of porous tellurium samples using the novel solution-phase deposition approach. The samples were prepared in the presence of 0.254 g Zn foil, 0.1 g H₂TeO₃, 0.8 mL N₂H₄·H₂O and 40 mL H₂O at 150 °C.