Supplemental Information
Hierarchically Structured Porous Cadmium Selenide Polycrystals Using Polystyrene Bilayer Templates

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Conditions for CdSe Deposition

Using cyclic voltammetry, CdSe crystallization was performed at a potential range of 0 V and -1.1 V. During the cathodic scanning, a visible yellowish orange film was formed on the ITO substrate at -0.73 V (onset voltage of reduction), reducing cadmium ions (Cd\(^{2+}\)) to cadmium elements. Oxidation peaks appeared after the first scan shifted to positive potential (-0.46 V to -0.4 V), indicating that the CdSe film grows on the substrate. The crystallization starts forming at a potential of -0.68 V (versus Ag/AgCl). An applied potential influences the properties of CdSe deposited film (single crystal or dendrite-type cadmium metal).\(^1\) On the other hand, a potentiostatic method allowed for more precisely controlled electrodeposition conditions for a specific CdSe phase. Thus, considering electrochemical behaviors of CdSe crystal growth,\(^2\) potentiostatic electrodeposition was performed, applying a constant voltage of -0.655V (versus Ag/AgCl) in an aqueous solution of CdSO\(_4\) and SeO\(_2\) (pH = 2.5, controlled by H\(_2\)SO\(_4\)) for 7 min.

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\begin{align*}
\text{Cd}^{2+} + 2e^- & = \text{Cd} - 0.402 \text{ V} \\
\text{Se}^{2-} + 2e^- & = \text{Se} + 0.74 \text{ V}
\end{align*}
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Imprinting and Fabrication Process

Using soft imprint lithography, PS lines (W = 780 nm, P = 1450 nm, and H = ~137 nm) were first patterned on ITO-coated glass substrates by spin-coating with a solution of PS in PGMEA
and then immediately imprinting with a pre-patterned PDMS mold (P = 1600 nm, W = 400 nm, and H = 220 nm) for 1 min. To make homogenously periodic PS patterns with minimized residual layers over a large area (1.5 × 1.5 cm²), various spin-coating speeds (3500-5000 rpm for 5 sec) were tested to find the optimized stamping conditions. The PS lines were formed in all cases regardless of the tested speeds (see Figure S3). However, we note that spinning-speeds slower than 2000 rpm causes the resulting PS lines to form thick and irregular residual scum layers. After 18 sec of O₂ plasma etching, the residual scum layer was completely removed to expose the underlying ITO in the PS trenches for use as the working electrode for subsequent electrochemical deposition, which provides the bottom-up filling of the trenches with CdSe crystals. Assuming that the thickness of the lines formed was constant for the same electrochemical deposition time (150 sec), the height between the PS and the CdSe lines slightly varies within ± 13-16 nm depending on the exact height of the etched patterned PS films.

References

Figure S1. Cyclic voltammogram of growing CdSe nanocrystals in an aqueous solution of 0.25 M CdSO₄ and 0.25 mM SeO₂ (pH = 2.5, controlled by H₂SO₄) with a scanning range of 0 and -1.1 V (vs. Ag/AgCl).
Figure S2. AFM micrographs of the PS arrays with hexagonal structures [(a) $d = 1000$ nm, (b) $d = 750$ nm, (c) $d = 500$ nm, and (d) $d = 200$ nm]. The scale bars are 1 µm.
Figure S3. AFM micrographs of the PS line strips obtained from solvent-assisted stamping with a patterned PDMS mold on PS film. A PGMEA solution of 4 wt% PS was used for spin-coating [(a) 3500, (b) 4000, (c) 4500, and (d) 5000 rpm for 5 sec] on ITO substrates. After spinning, the PDMS stamp was immediately placed on the substrate keeping a good contact under a certain pressure. The scale bars are 2 µm.
Figure S4. AFM micrographs of the CdSe line strips grown cathodically from the PS trenches using potentiostatic method [-0.655V vs. Ag/AgCl in an aqueous solution of 0.25 M CdSO$_4$, 0.25 mM SeO$_2$ for electrodeposition time of 150 sec (pH = 2.5, controlled by H$_2$SO$_4$)]. The residual layer on the PS template was removed by a reactive ion etching process (pressure: 200 mTorr, ICP power: 20 W, RIE power: 90 W, O$_2$: 49 sccm, and etching time: 18-24 sec). The scale bars are 2 µm.
Figure S5. AFM micrographs of the CdSe line strips with nano/microperiodic porous structures after being grown cathodically on a second PS colloid template arranged on alternating PS/CdSe stripes using potentiostatic method (-0.655V vs. Ag/AgCl in an aqueous solution of CdSO$_4$ and SeO$_2$ (pH = 2.5, controlled by H$_2$SO$_4$), followed by removing the PS bilayered templates. PS line template (bottom): $W = 780$ nm, $P = 1450$ nm, and $H = 140$ nm and PS colloid template (top): (a) $d = 1000$ nm, (b) $d = 750$ nm, and (c) $d = 500$ nm. The scale bars are 2 $\mu$m.
Figure S6. AFM micrographs of microperiodic porous CdSe strips grown cathodically from the PS stripe/colloid template (T1). Electrochemical deposition was performed at -0.655V (vs. Ag/AgCl) in an aqueous solution of CdSO$_4$ and SeO$_2$ (pH = 2.5, controlled by H$_2$SO$_4$) for 1500 sec. The scale bars are 3 µm.
Figure S7. AFM micrographs of (a) the twisted ellipsoidal patterned PS bottom template ($W_1 = 500$ nm, $W_2 = 750$ nm, $P = 1500$ nm, and $H = 120$ nm) and (b) CdSe microstructures electrodeposited cathodically on the PS bilayered template [ellipsoidal feature/colloid ($d = 750$ nm)]. Electrodeposition time: 1000 sec. The scale bars are 3 µm.