Electronic Supplementary Information (ESI) for

**Generation and Superhydrophobicity of Complex PbSe Crystalline Nanodendrites**

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**Experimental Section**

**Synthesis.** Pb(NO_3)_2 (analytic reagent, AR), selenophene (C_4H_4Se, AR), and aniline (C_6H_5NH_2, AR) were purchased and used without further purification. In a typical synthesis, 1 mmol Pb(NO_3)_2 was added into 20 mL C_6H_5NH_2 with stirring for 1h to form solution A, while 1 mmol C_4H_4Se was dissolved into 20 mL C_6H_5NH_2 with stirring 30 min and then to from solution B. Solution B was added into stirred solution A in 30 min at room temperature. The resulting mixture was transferred to and sealed in a Teflon-lined autoclave, heated to 240 °C, and maintained at this temperature for 24 h. After the autoclave was cooled down to room temperature naturally, the products were collected and washed via centrifugal method with 5000 r/min for 5 min by using deionized water and then absolute alcohol. The washing cycle was repeated two times. Because Pb(NO_3)_2 reacted with C_4H_4Se in the presence of C_6H_5NH_2 as solvent, elementary Pb and Se were generated. So, the products were treated by 1M HCl for 0.5 h for dissolving Pb and 20 M NaOH for 1h for dissolving Se, respectively, followed washing by using deionized water four times. After that, the products were washed by using absolute alcohol followed by drying at 60 °C for 6 h, and the yield of about 3%.

**Materials Characterization.** The X-ray powder diffraction patterns were obtained on X-ray diffractometer (Drucker D8 Advance) with Cu Kα radiation (λ = 1.54056 Å, operating at 40 kV × 40 mA) in 2θ ranging from 10° to 70°. Raman spectrum (Renishaw, RM 1000) was recorded by using excitation from the 514.5 nm line of an Ar-ion laser with a power of about 5 mW. The scanning electron microscopy (SEM) was carried out by a KYKY-2000 instrument. Field emission electron microscopy (FE-SEM) was carried out by a FESEM, JSM-7401F instrument. Transmission electron microscopy (TEM) was carried out by a JEOL, JEM-1200 instrument, using an accelerating voltage of 120 kV. High-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL JEM-2010 Electron Microscope, operating at 200 kV. Photoluminescence (PL) spectra were carried out with a fluorescence spectrophotometer (LS55 Luminescence Spectrometer, Perkin Elmer).

**Water contact angle (CA) Measurement.** The CA measurement and sliding angle were carried out on water droplet with drop volume 8 μL or 9 μL, on an optical contact angle meter (Data physics Inc., OCA 20), after five days of
the as-synthesized PbSe nanostructures treatment followed by $^{1}H,^{1}H,^{2}H,^{2}H$-perfluorodecyltriethoxysilane $[\{(C_2H_5O)\}_3Si(CH_2)\_2C_8F\_17\}$ treatment at ambient temperature. A methanol solution of $^{1}H,^{1}H,^{2}H,^{2}H$-perfluorodecyltriethoxysilane $[\{(C_2H_5O)\}_3Si(CH_2)\_2C_8F\_17\}$, PDES] (volume ratio of PDES to methanol = 2 : 98) was used to modify the glass coated with as-synthesized PbSe nanostructures at room temperature for 1 h, and subsequently heated at 120°C for 1 h.

**Figure S1.** a) Low magnification SEM image, b) High magnification SEM image, c) HRTEM image of the PbSe complex nanostructures.

**Figure S2.** SEM images of a) PbSe-1, b) PbSe-2, c) PbSe-3, d) PbSe-4, and e) PbSe-5, respectively.

We carried out a series of experiment for understand the growth mechanism. The first study was the effect of the reaction time, Figure S2 shows SEM images of the final PbSe products synthesized in identical concentrations ($Pb^{2+}$ concentration = 1 mmol/40 ml, $C_4H_4Se$ concentration =1 mmol/40 ml) and identical reaction temperature of 240 °C, but for different reaction times, that is, 5 h, 10 h, and 24 h, with these being denoted as PbSe-1, PbSe-2, and PbSe-3 (i.e, the sample in the main text), correspondingly (Figure S2a, S2b, and S2c). According to SEM observation, the morphology of the product appeared as a dendrite like complex architecture. The product synthesized at 24 h (PbSe-3) is more homogeneous, while the product synthesized at 5 h (PbSe-1) are not perfect with some half-baked dendrite like complex architecture with thorns. And the diameters of thorns of PbSe are ca. 0.4-1.5 μm, 0.3-1μm, and 100 nm for PbSe-1, PbSe-2, and PbSe-3, correspondingly. That means the diameters of the thorns of the dendrite like PbSe complex architectures decreased accompanying with prolonging the reaction time.
We also investigate the effect of the ratio of the reaction agents \((\text{Pb}^{2+}/\text{C}_4\text{H}_4\text{Se})\) changing from 1:1 (PbSe-2, Figure S2b) to 2:1 (termed as PbSe-4, Figure S2d) \((\text{Pb}^{2+} \text{ concentration } = 2 \text{ mmol}/40 \text{ ml}, \text{C}_4\text{H}_4\text{Se concentration } = 1 \text{ mmol}/40 \text{ ml})\) (Figure S1d) with the identical reaction temperature of \(240 \degree C\) and the identical reaction time of 10 h. We can observe there are some small fragments of thorns besides the dendrite like PbSe complex architectures. That means lower ratio of the reaction agents \((\text{Pb}^{2+}/\text{C}_4\text{H}_4\text{Se})\) favors the growth of dendrite like PbSe complex architectures, which demonstrated the dendrite like PbSe complex architectures generated by self assembly manner from nanorods.

We also investigated the effect of the reaction temperature changing from \(240 \degree C\) (PbSe-2, Figure S2b) to \(260 \degree C\) (PbSe-5, Figure S2e) with identical reaction time of 10 h and reaction ratio of the reaction agents \((\text{Pb}^{2+}/\text{C}_4\text{H}_4\text{Se})\) of 1:1. We can also find faulty dendrite like PbSe complex architectures with some small fragments of thorns besides the dendrite like PbSe complex architectures. That means lower reaction temperature favors the growth of dendrite like PbSe complex architectures. All these data support the growth mechanism of the dendrite like PbSe complex architectures.

![Figure S3. PL properties of the PbSe complex nanostructures.](image)

**Movie S1** The movie of the sliding angle measurement of the as-synthesized PbSe nanostructures.