

Heterogeneous ZnS Hollow Urchin-like Hierarchical Nanostructures and their Structure-enhanced Photocatalytic Properties**

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Experimental details

In a typical run, Zn powder (2 g, 99.99%) was loaded into an alumina boat, which was placed in the central heating zone of a quartz tube in a furnace. The quartz tube was pumped out and then filled with argon. After repeating the operation three times, the quartz tube was heated to 650 °C under an argon flow of 200 standard cubic centimeters per minute (sccm) and normal pressure. After maintaining the sample at this temperature for 5 minutes, the quartz tube was rapidly cooled. Then, the products were all collected in a region about 50 cm downstream from the source. For the second step, these collected products (Zn microspheres, 0.5 g) were put into the quartz tube again, and sulphur powder (1.5 g, 99.99%) was loaded in at the leading edge of the quartz tube. The quartz tube was pumped and then filled with argon. After repeating the operation three times, the quartz tube was heated to 300 °C in 20 minutes under an argon gas flow of 100 sccm. The sulfuration time was 5 hours. Finally, the quartz tube was suddenly heated from 300 °C to 650 °C in 10 minutes, while the other experimental conditions were maintained. After a 5 minute dwell time at 650 °C, the tube was naturally cooled. Then, the products were collected. If oxygen is used instead of sulphur vapor in the experimental process, hollow ZnO urchin-like hierarchical nanostructures can also be obtained by this method.

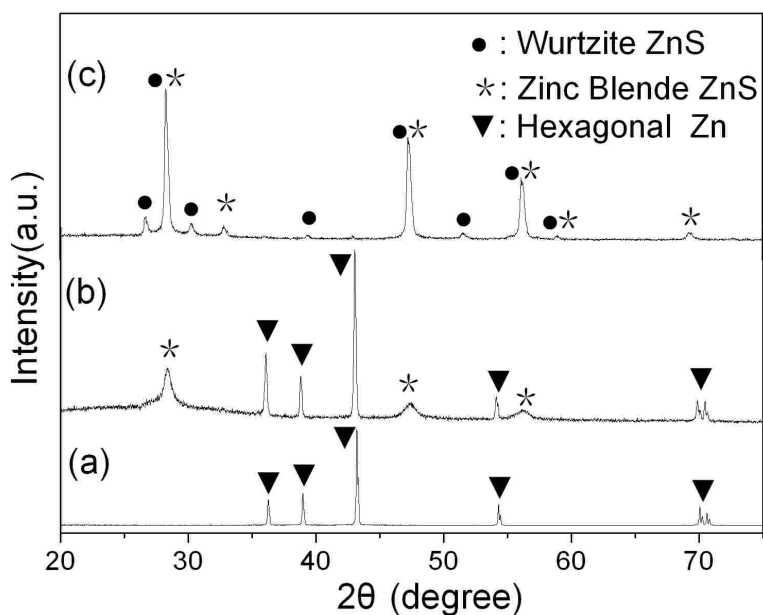


Figure SI-1. X-ray diffraction patterns (XRD) of the products in each step. The inverted triangles (▼) are XRD peaks of Zn, the asterisks (*) are peaks of cubic zinc-blende ZnS, and the filled circles (●) are peaks of hexagonal wurtzite ZnS. (a) The products obtained in the first step are single-phase Zn; (b) Zn products annealed for 5 hours at 350 °C under sulphur vapor atmosphere in the second step; (c) the products obtained at 650 °C in the third step.

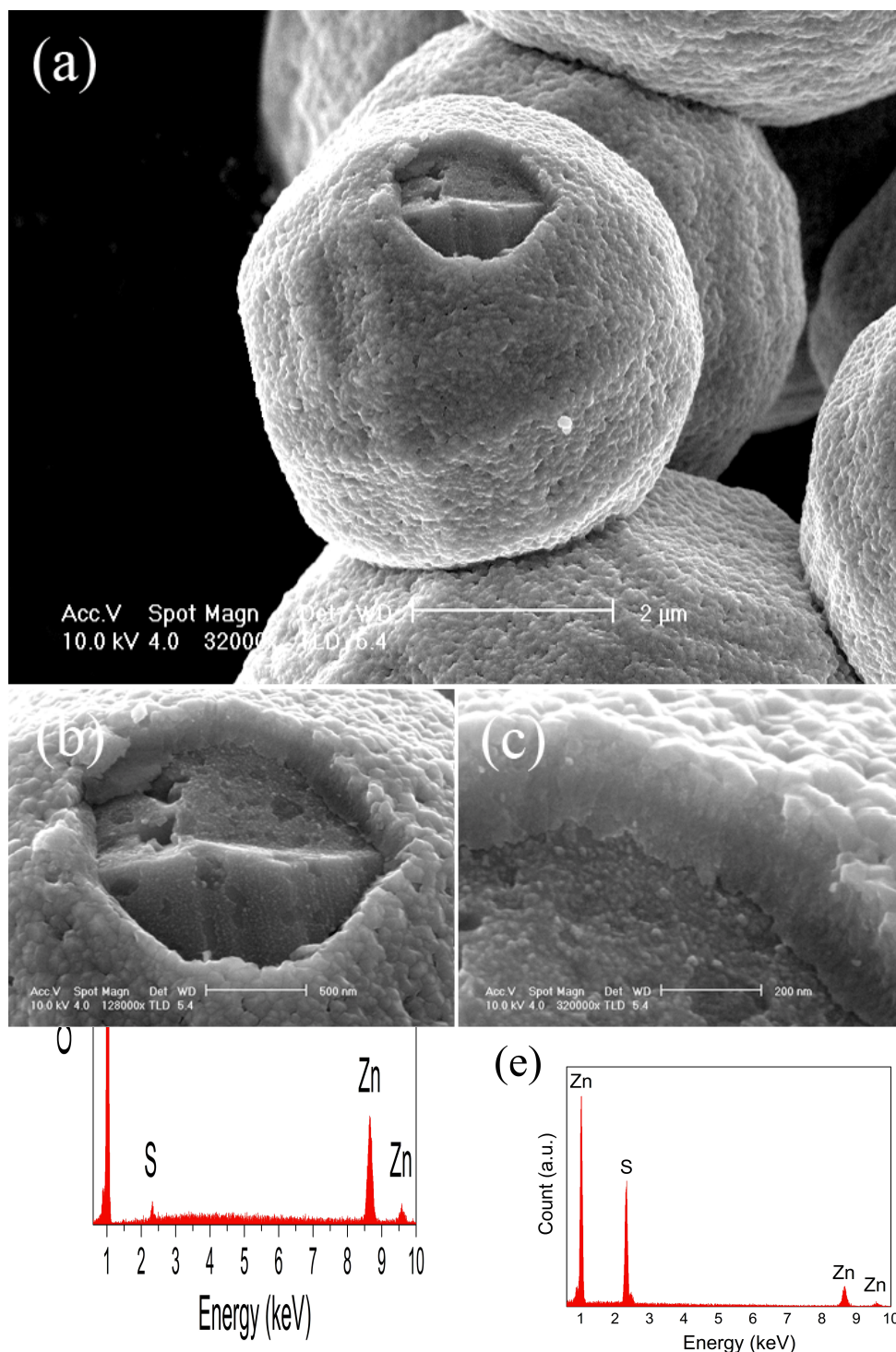


Figure SI-2. (a), (b), (c) SEM images at different magnifications of the Zn/zinc-blende ZnS compound core/shell microspheres obtained in the second step; (d) EDS spectrum of the core of the Zn/ZnS microsphere shown in the SEM images; (e) EDS spectrum of the shell of the Zn/ZnS microsphere shown in the SEM images.

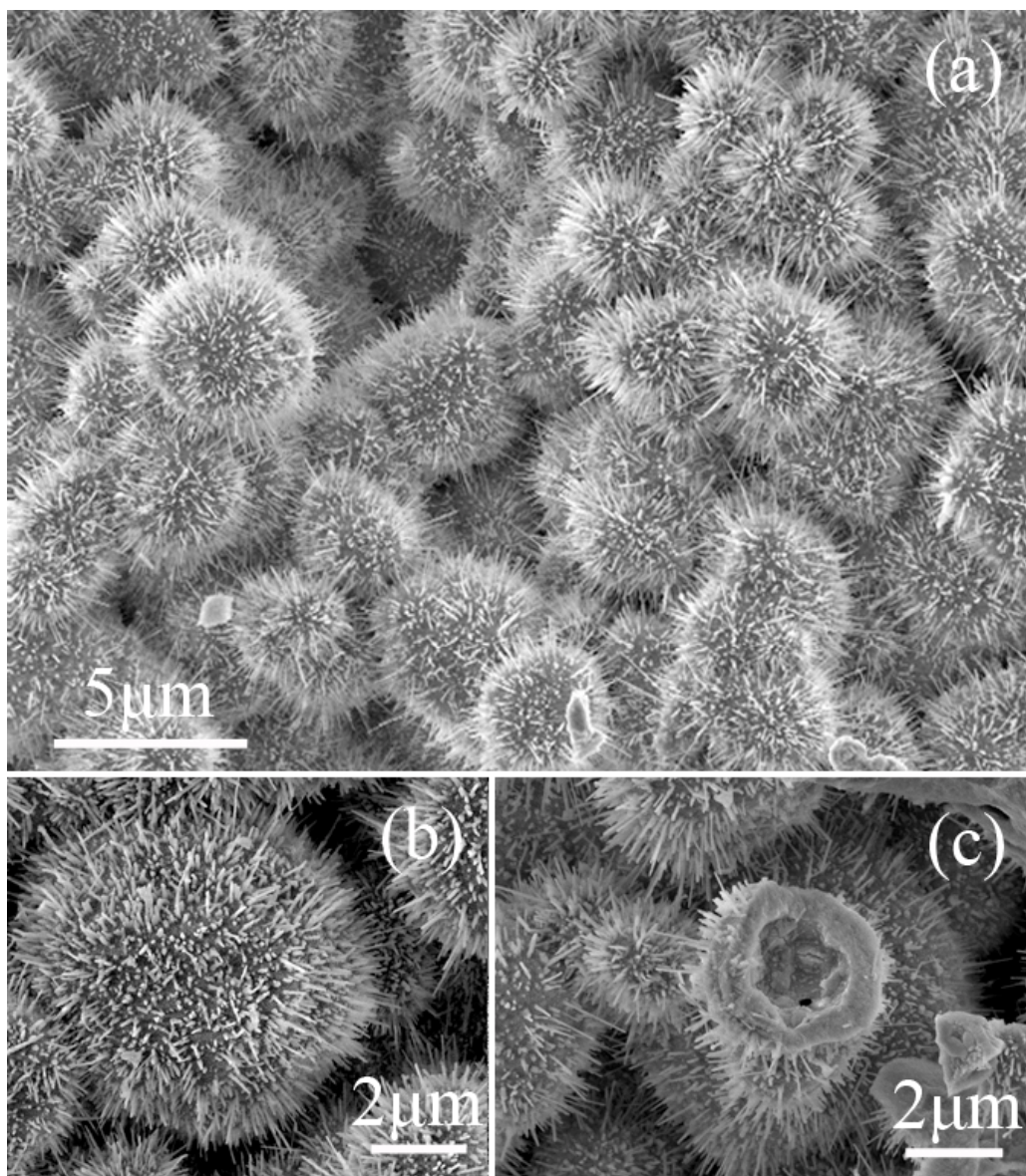


Figure SI-3. SEM images of the heterogeneous ZnS HUHNs obtained in the third step: (a) general image of ZnS HUHNs, (b) details of a single ZnS HUH, (c) image of broken ZnS HUH to show the internal structure.

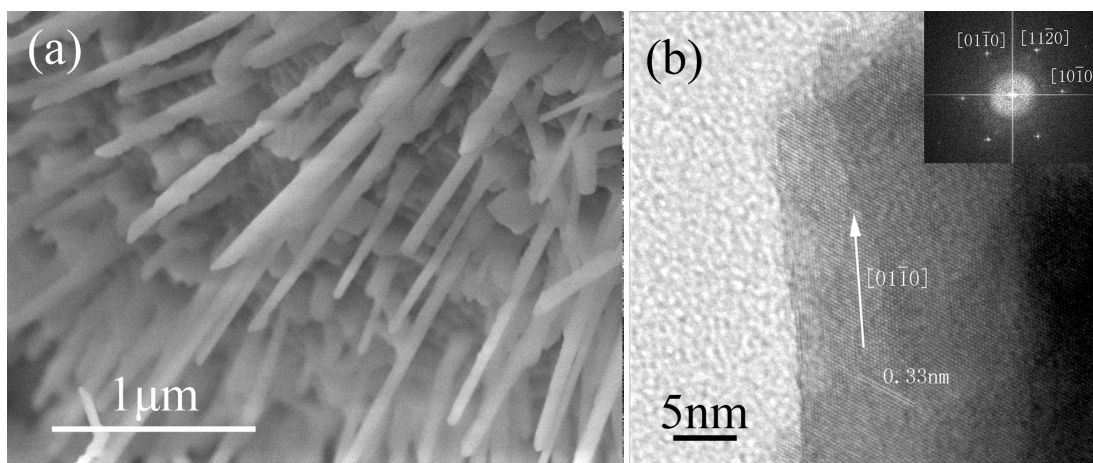


Figure SI-4. (a) SEM image of nanowire array on hollow sphere. (b) HRTEM image and corresponding electron diffraction pattern (inset) reveal that the nanowires are single crystals with hexagonal structure.

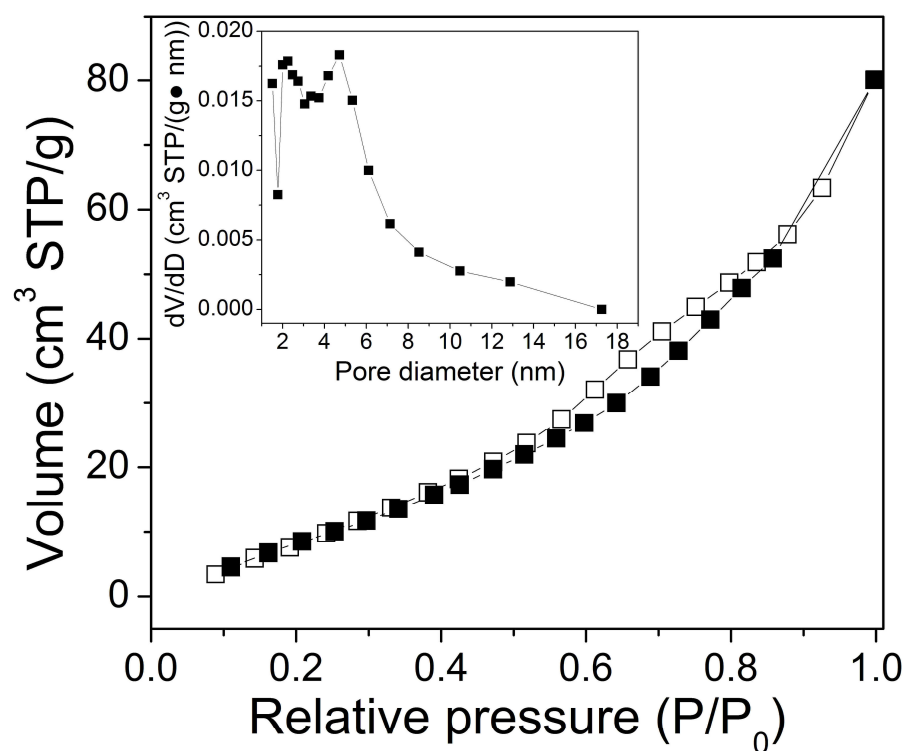


Figure SI-5. N₂ adsorption-desorption isotherms and pore size distribution (inset) of heterogeneous ZnS HUHNs at 77 K.

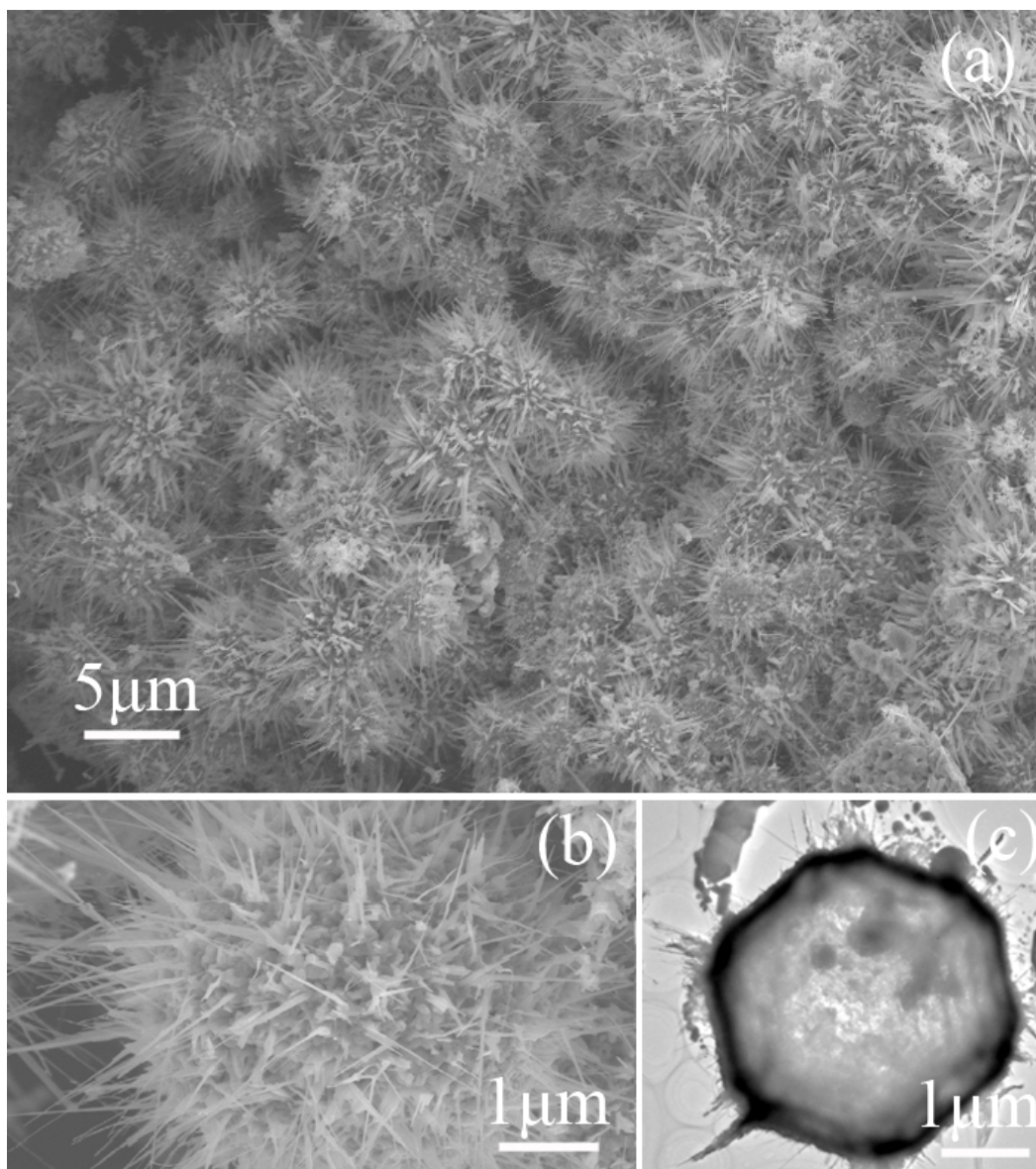


Figure SI-6. SEM and TEM images of the hollow ZnO urchin-like nanostructures synthesized by the effective three-step method: (a) general view of nanostructures, (b) higher magnification image of a single urchin-like nanostructure, and (c) TEM image of internal structure of nanostructure.

Experimental details for synthesis of ZnS nanobelts

ZnS nanobelts were synthesized by a simple Vapor-Solid route. An alumina boat with Zn (0.5 g) and S powders (1.5 g) was placed in the front of an alumina hollow tube with an inner diameter of 25 mm and a length of 22 cm. The alumina hollow tube together with the alumina boat was placed in the middle of a horizontal quartz tube furnace. The quartz tube was pumped and then filled with argon and re-pumped. After repeating the operation three times, the quartz tube was full of argon atmosphere. Then, the quartz tube was heated to 700°C in one hour under an argon flow of 50 standard cubic centimeters per minute (sccm). The temperature was kept at 700°C for half an hour, and the furnace was turned off and naturally cooled.

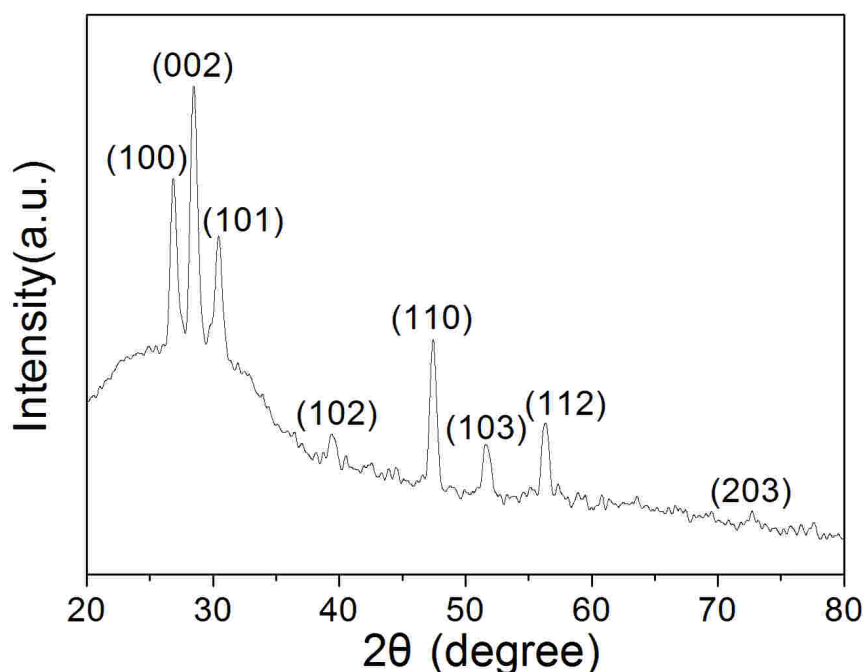


Figure SI-7. XRD pattern of the product shows that the product is ZnS in the hexagonal wurtzite structure.

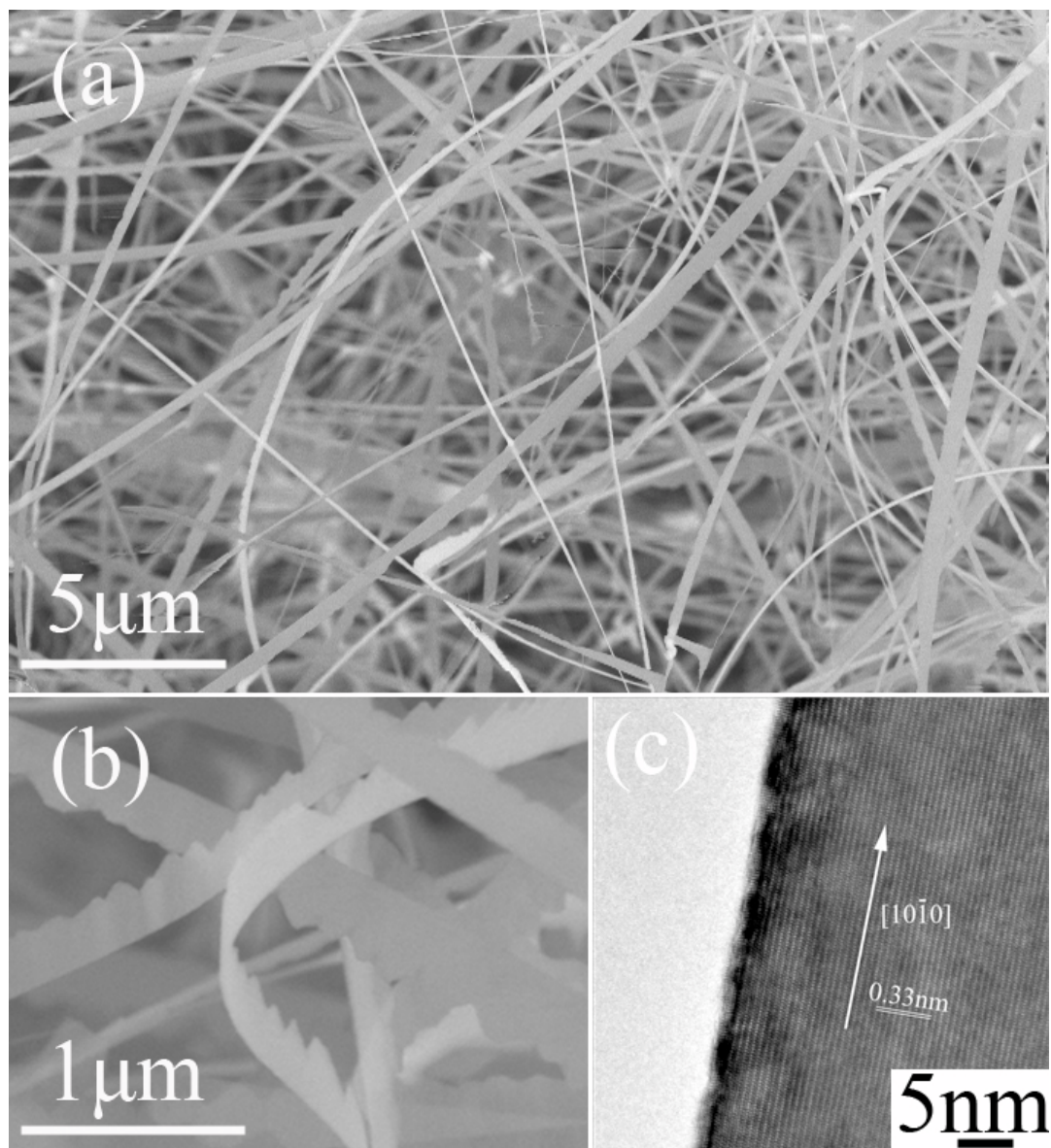


Figure SI-8. SEM images of the ZnS nanobelts synthesized by the vapor-solid method: (a) general view of ZnS nanobelts, (b) higher magnification image of the ZnS nanobelts, and (c) TEM image of a single ZnS nanobelt.

Experimental details of photocatalytic activity measurement

A cylindrical pyrex flask (capacity ~ 40 mL) was used as the photoreactor vessel. The reaction system containing rhodamine B (RhB, Sigma-Aldrich Chemical Co.; 5.0×10^{-5} M, 30 mL) and ZnS HUHNS catalyst (10 mg) was magnetically stirred in the dark for 15 min to reach the adsorption equilibrium of RhB with the catalyst, and then exposed to light from a 300 W xenon lamp with UV output wavelength (≤ 390 nm). After UV irradiation for 10 min, the reaction solution was filtered to measure the concentration change of RhB. After the RhB had been degraded out, the ZnS HUHNS were filtered out and tried them with a new batch of RhB. The photocatalytic activities of commercial TiO_2 (Degussa P25, Degussa Co.), as-prepared wurtzite ZnS nanobelts, and commercial ZnS powders were also measured as references under the same experimental conditions. Moreover, photocatalytic degradation of methylene blue (MB) was also measured as a test reaction under the same experimental conditions.

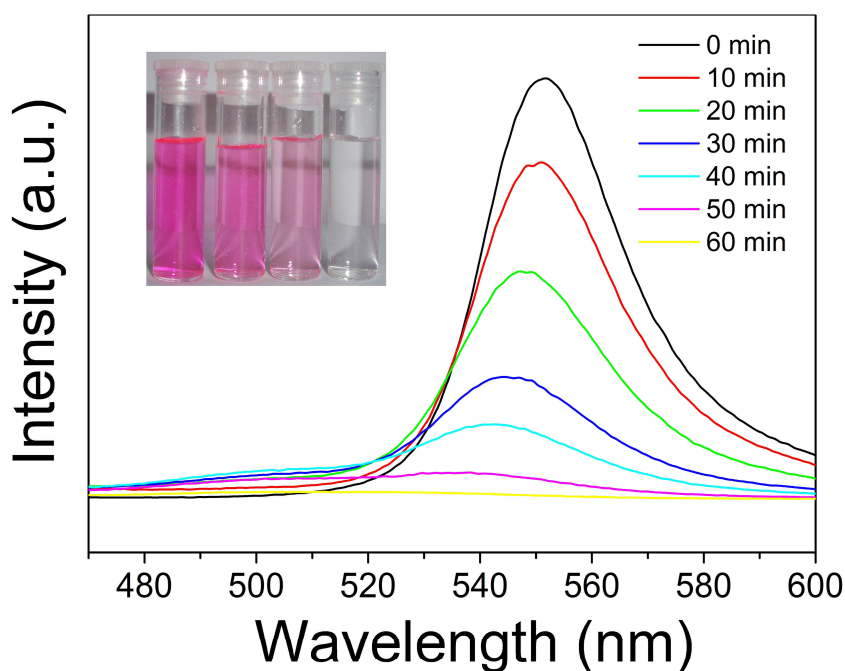


Figure SI-9. Absorption changes of an RhB aqueous solution at room temperature in the presence of heterogeneous ZnS HUHNS under UV irradiation for different reaction times, with the inset showing the color change of the reaction.

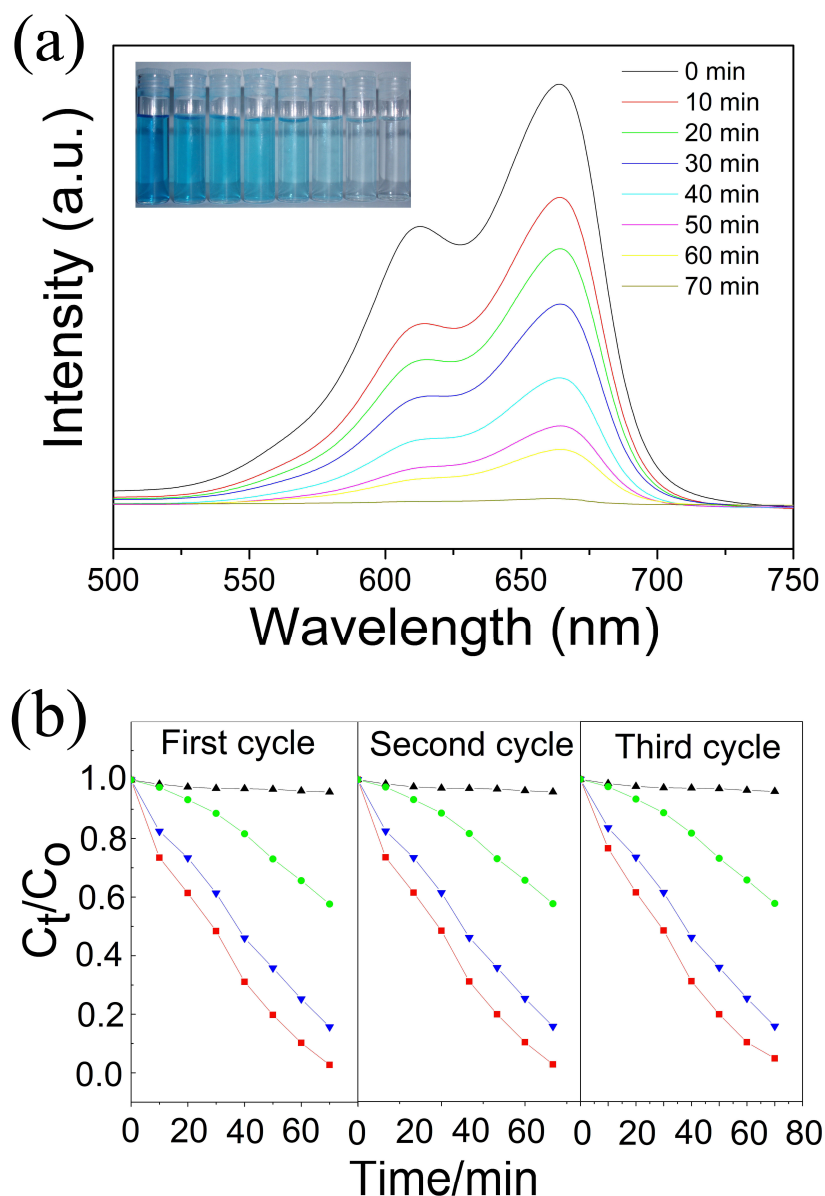


Figure SI-10. (a) Absorption changes of a MB aqueous solution at room temperature in the presence of heterogeneous ZnS HUHNs under UV irradiation for different reaction times, with the inset showing the color change of the reaction. (b) Three cycles of photocatalytic degradation of MB over commercial ZnS powders ($\blacktriangle$), as-prepared hexagonal wurtzite ZnS nanobelts ($\bullet$), the commercial photocatalyst P25 ($\blacktriangledown$), and the present heterogeneous ZnS HUHNs ($\blacksquare$). C_0 and C_t denote the initial concentration of MB and its concentration after reaction time t , respectively.

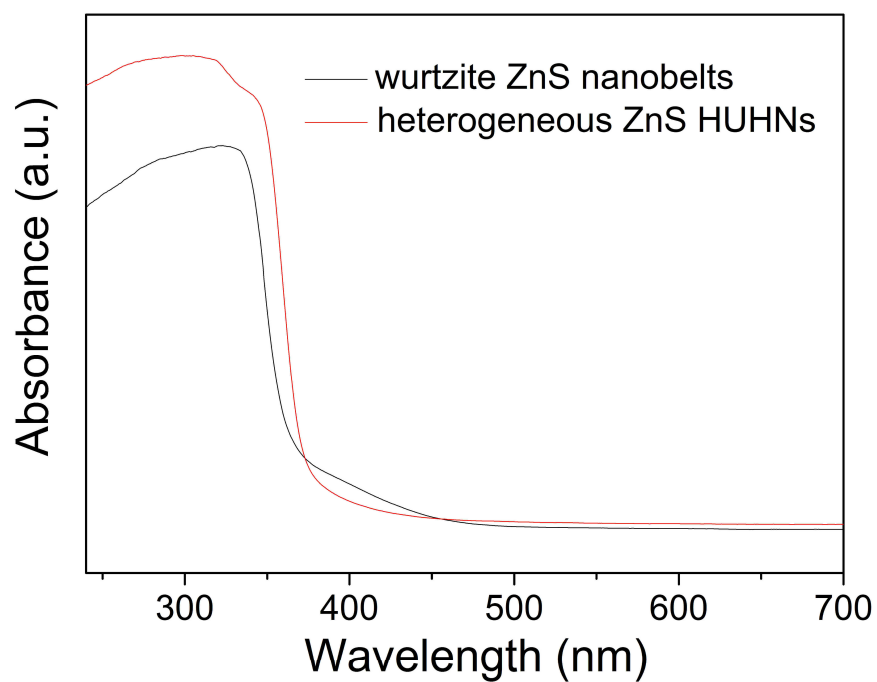


Figure SI-11. UV-Vis absorbance spectra of heterogeneous ZnS HUHNs and as-prepared hexagonal wurtzite ZnS nanobelts.