Supplementary Information:

An Unconventional Outer-to-Inner Synthesis Strategy for Core (Au)-Shell Nanostructures with Photoelectrochemical Enhancement

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1. TEM image of Au-Bi_2S_3 core-shell NPs with low magnification

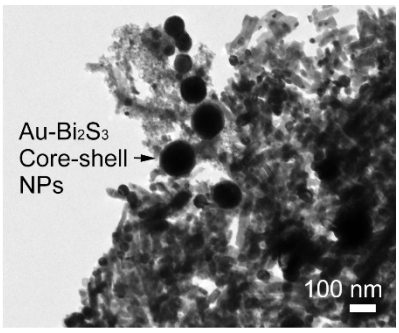

Fig. S1 TEM image of Au-Bi_2S_3 core-shell NPs with scale bar of 100nm.

2. SEM and TEM images of Au-Bi_2S_3/ZnO, Au-CdS/ZnO and Au-CdSe/ZnO layered hetero-nanostructures (HNSs)

For all the layered structures, Bi_2S_3, CdS and CdSe nanoparticles (NPs) are covered with Au layers (Fig. S2a). SEM images of the Au-Bi_2S_3/ZnO (Fig. S2b), Au-CdS/ZnO (Fig. S2c) and Au-CdSe/ZnO (Fig. S2e) layered HNSs show that high density hetero-nanorods (HNRs) with uniform diameters are evenly distributed on the substrate. TEM observations of Au-Bi_2S_3/ZnO layered HNSs have been exhibited in the main text. Here, TEM images of the Au-CdS/ZnO and Au-CdSe/ZnO layered HNSs are shown in Fig. S2d and f, respectively. CdS is wrapped outside the ZnO NRs with layered structure (Fig. S2d), while CdSe is decorated on the ZnO NRs with spherical shape and diameter about 300 nm (Fig. S2f). Enlarged view in the upper-right inset demonstrates that the thicknesses of CdS and Au layers are 15~20 and 5~10 nm, respectively. HRTEM images taken from different regions of upper-right inset confirm that Au (*1*), CdS (*2*) and ZnO (*3*) are highly crystalline structures with crystal faces (111), (101) and (002), respectively. For Au-CdSe/ZnO layered HNSs, the upper right inset of Fig S2f confirms that the Au layer is not crystalline and has a uniform thickness about 3 nm. HRTEM in the bottom of Fig S2f reveals (110) faces for crystalline CdSe.

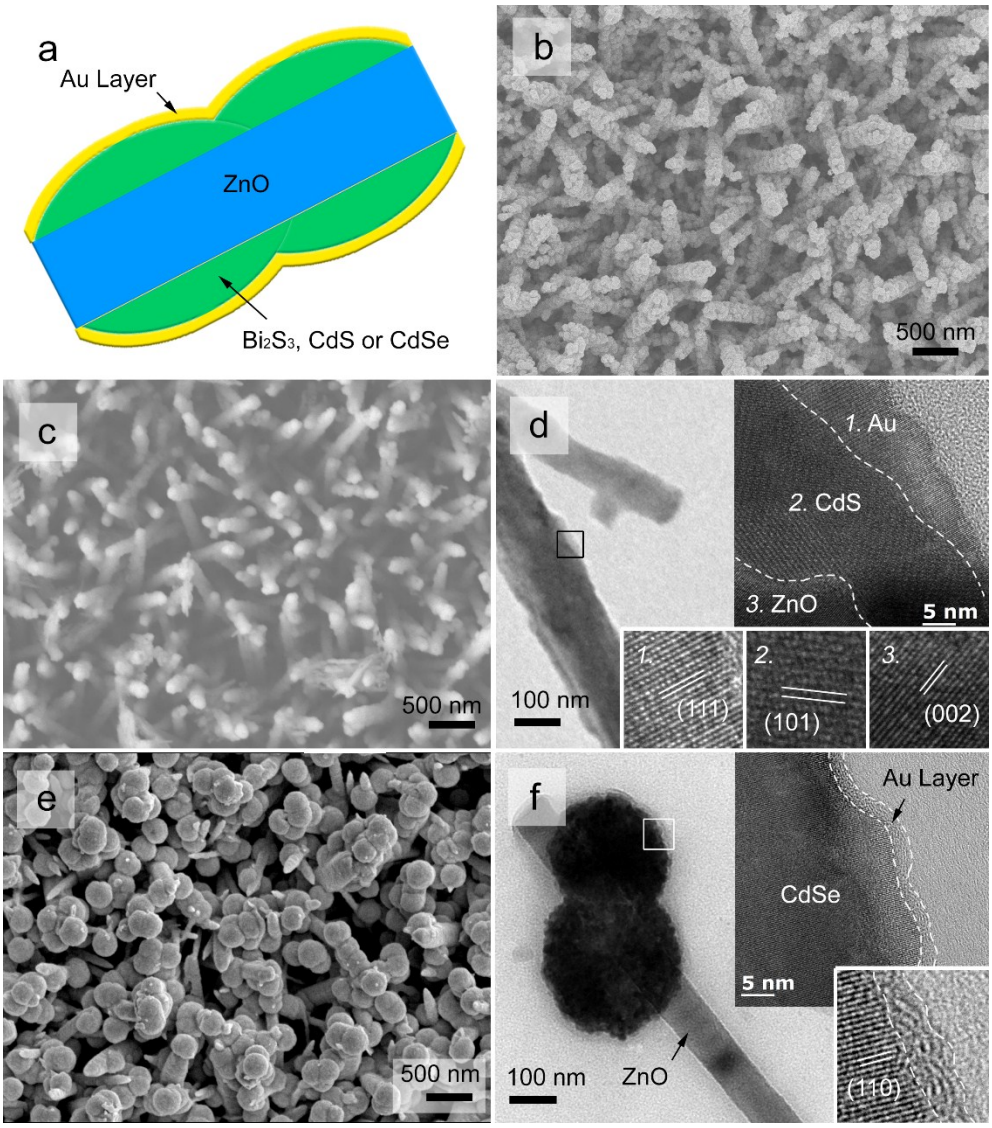

Fig. S2 a) Sketch of the Au-Bi_2S_3/ZnO, Au-CdS/ZnO and Au-CdSe/ZnO layered HNSs; b) SEM image of the Au-Bi_2S_3/ZnO layered HNSs; c-f) SEM (c, e) and TEM (d, f) images of the Au-CdS/ZnO (c, d) and Au-CdSe/ZnO (e, f) layered HNSs. The upper-right insets of Fig. S1d and f are HRTEM images taken from the squares in figure d and f, respectively. The bottom insets in figure d and f are the close-up views observed from different region in the corresponding upper-right images.

3. SEM images of Au-Bi_2S_3/ZnO, Au-CdS/ZnO and Au-CdSe/ZnO core-shell NP/NR hetero-nanostructures

SEM images with lower and higher magnifications of Au-Bi_2S_3/ZnO, Au-CdS/ZnO and Au-CdSe/ZnO core-shell NP/NR hetero-nanostructures (HNSs) are shown in the left and right columns of Fig. S3, respectively. From the left column we can see that all of the core-shell NP/NR HNSs with higher density are evenly distributed on the substrate. The right column demonstrates that the diameters of Au-Bi_2S_3/ZnO core-shell NPs are smaller and uniform (Fig. S3b), while those of Au-CdS/ZnO and Au-CdSe/ZnO core-shell NPs are larger and relatively non-uniform (Fig. S3d and e).

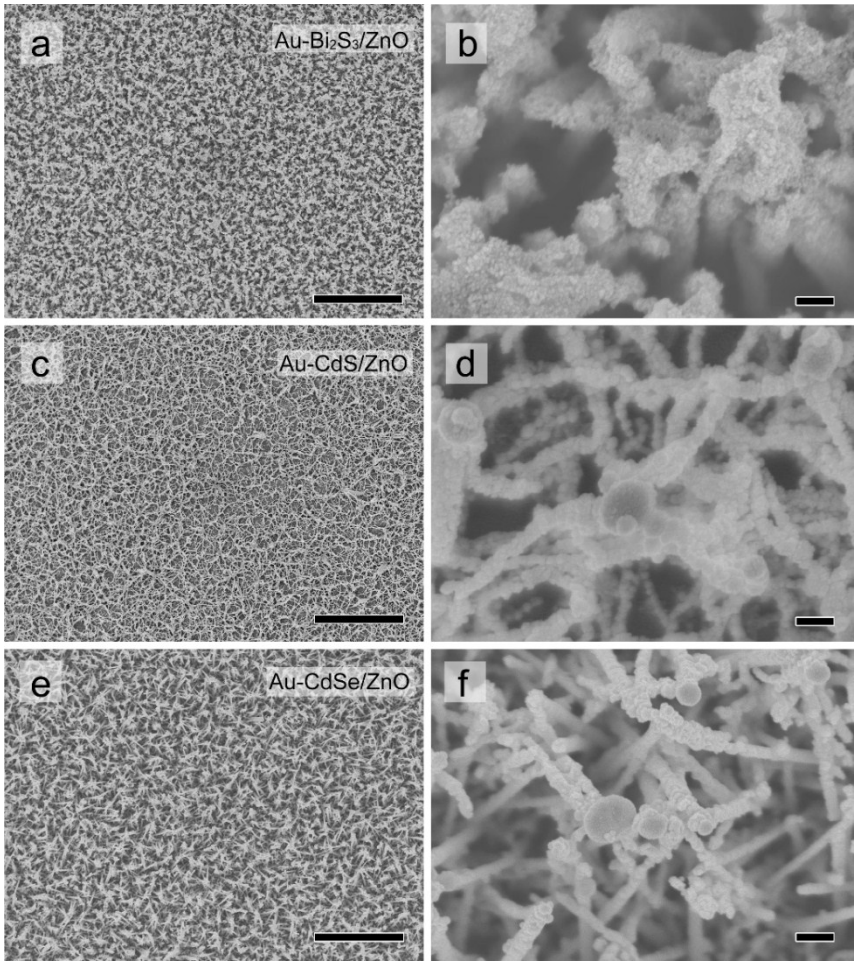

Fig. S3 a-f) SEM images with lower (a, c and e) and higher magnification (b, d and f) of Au-Bi_2S_3/ZnO (a, b), Au-CdS/ZnO (c, d) and Au-CdSe/ZnO (e, f) core-shell NP/NR HNSs. The scale bars of the left and right columns are 5 μm and 200 nm, respectively.

4. SEM images of Au-Bi_2S_3/ZnO, Au-CdS/ZnO and Au-CdSe/ZnO hetero-nanostructures fabricated via various temperatures

The annealing temperatures of Au-Bi_2S_3/ZnO, Au-CdS/ZnO and Au-CdSe/ZnO NP/NR HNSs used in current study are 520, 580 and 480 °C, respectively. To study the relationship between morphologies and annealing temperature of all the samples, SEM observations are performed. From Fig. S4a, e and i we can see that the Au-Bi_2S_3/ZnO, Au-CdS/ZnO and Au-CdSe/ZnO have almost no changes at 400, 500 and 400 °C comparing with their initial morphologies shown in Fig S2. When the annealing temperatures increases to 500, 560 and 460 °C, their morphologies have changes (Fig. S4b, f and j). Next, when the annealing temperatures increases to 520, 580 and 480 °C, the core-shell structures are formed on ZnO NRs (Fig. S4c, g and k). Finally, if annealing temperatures are increased to 540, 600 and 500 °C, the core-shell structures are removed from the surfaces of ZnO NRs (Fig. S4d, h and l), which might be due to evaporation.

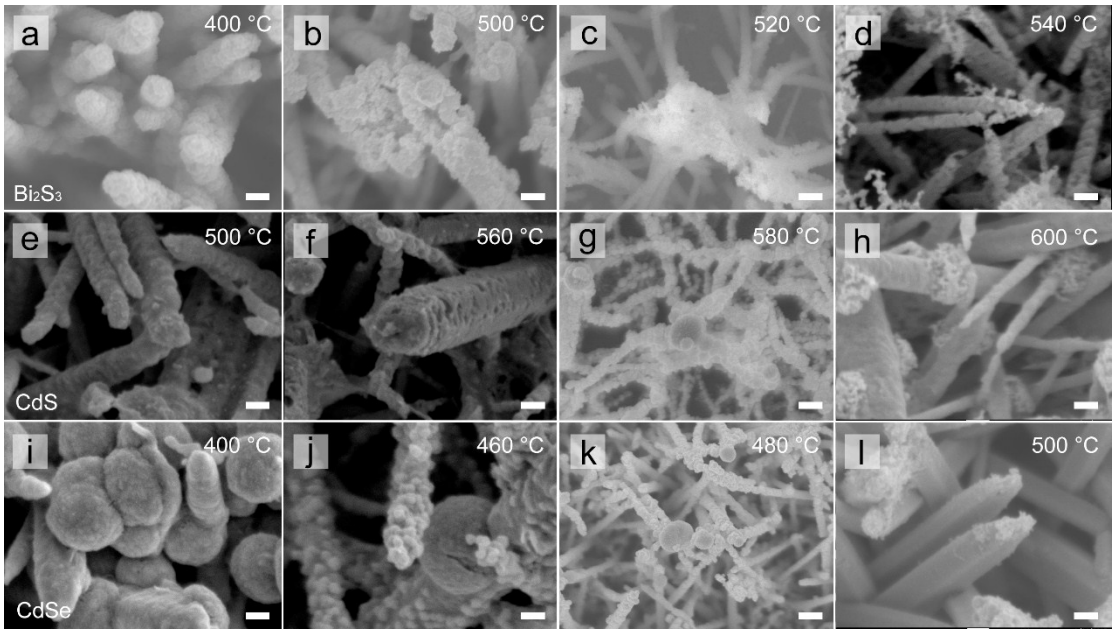

Fig. S4 a-d) SEM images of Au-Bi_2S_3/ZnO core-shell NP/NR HNSs annealed at 400 (a), 500 (b), 520 (c) and 540 (d) °C; e-h) SEM images of Au-CdS/ZnO core-shell NP/NR HNSs annealed at 500 (e), 560 (f), 580 (g) and 600 (h) °C; i-l) SEM images of Au-CdSe/ZnO core-shell NP/NR HNSs annealed at 400 (i), 460 (j), 480 (k) and 500 (l) °C. The scale bars are 100 nm for all images.

5. Synthesis process of Au-Bi_2S_3 and Au-CdS core-shell NPs on ZnO film

By using the same outer-to-inner strategy, the Au-Bi_2S_3 and Au-CdS core-shell NPs can also be fabricated on ZnO film. Firstly, ZnO film with the thickness about dozens of nanometers is deposited on the FTO glass by using magnetron sputtering. And then, a layer of Bi_2S_3 or CdS is covered on the ZnO film by using SILAR method. Next, an Au layer is coated on the surface of Bi_2S_3 or CdS layer. Finally, the Au-Bi_2S_3 or Au-CdS core-shell NPs are formed on ZnO film after annealing. It can be seen from the SEM images of Fig. S5 b-e that the diameters of Au-Bi_2S_3 NPs are smaller than those of Au-CdS core-shell NPs due to the higher melting point of Bi_2S_3 nanostructures.

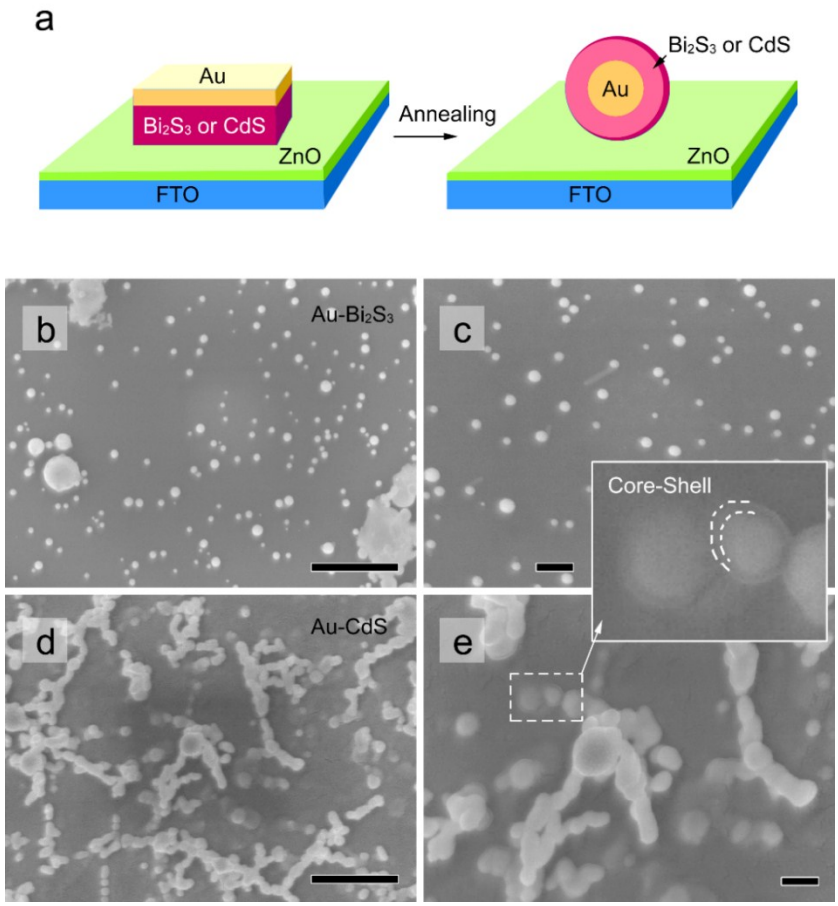

Fig. S5 a) Sketch of the synthetic process of Au-Bi_2S_3 and Au-CdS core-shell NPs on ZnO film; b-e) SEM images with lower (b, d) and higher (c, e) magnification of Au-Bi_2S_3 (a, b) and Au-CdS (d, e) core-shell NPs on ZnO film. The scale bars of the left and right columns are 1 μm and 200 nm, respectively.

From the enlarged view in the inset of Fig. S5e, a core-shell structure is clearly exhibited. Moreover, the densities of the Au-Bi_2S_3 and Au-CdS core-shell NPs on the ZnO film is lower than those on the ZnO NRs. This is because ZnO NRs have much larger surface area, providing higher nucleation sites of NPs. As a result, the loading amounts of Bi_2S_3 and CdS on ZnO NRs are higher than those on ZnO film. Here, one thing should be noticed that the CdSe layer cannot be uniformly fabricated on the ZnO thin film due to the corrosion of ZnO film in the ammonia solution, thus only Au-Bi_2S_3 or Au-CdS core-shell NPs are fabricated on ZnO film. The result demonstrates that the outer-to-inner strategy can also be applied to the fabrication of core-shell NPs on film structures.

6. Bi 4d peaks in XPS spectrum of the Au-Bi_2S_3/ZnO core-shell NP/NR hetero-nanostructures

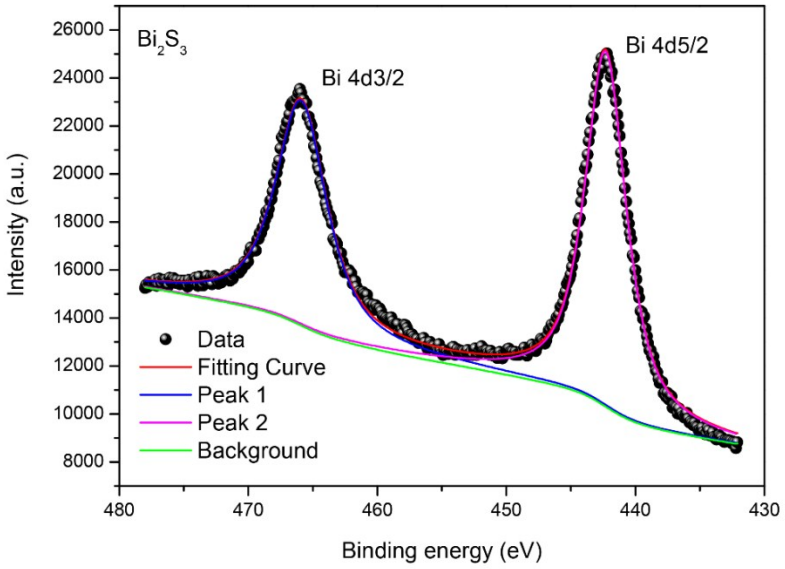

Fig. S6 Bi 4d peaks in XPS spectrum of the Au-Bi_2S_3 core-shell structures.

7. XRD spectra of Au-Bi_2S_3/ZnO, Au-CdS/ZnO and Au-CdSe/ZnO core-shell NP/NR hetero-nanostructures

X-ray diffraction (XRD) spectra are shown in Fig. S7 to provide the crystallinity information of the Au-Bi_2S_3/ZnO, Au-CdS/ZnO and Au-CdSe/ZnO core-shell NP/NR HNSs. To clearly present the weaker peaks, some peaks with higher intensities are truncated, such as the (002) and (101) peaks of ZnO. The peaks of ZnO demonstrate the hexagonal wurtzite structure. Au comes from the cores, while Bi_2S_3, CdS and CdSe exhibit in three shell structures. Here it should be noticed that the peaks of Bi_2S_3 are weaker than those of CdS and CdSe, which demonstrates that the diameters of Bi_2S_3 NPs are smaller than those of CdS and CdSe NPs.

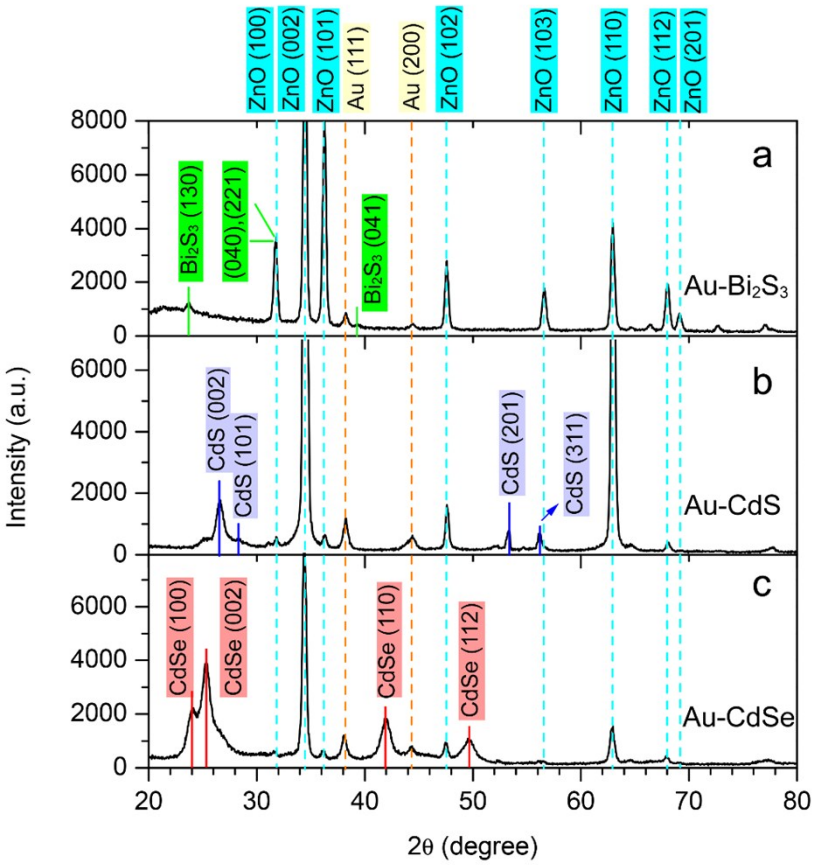

Fig. S7 a-c) XRD spectra of Au-Bi_2S_3/ZnO (a), Au-CdS/ZnO (b) and Au-CdSe/ZnO (c) core-shell NP/NR HNSs. The peaks of ZnO, Au, Bi_2S_3, CdS and CdSe are marked by light blue, yellow, green, purple and pink red, respectively.

8. Parameters deduced from EIS plots.

Table S1. Parameters deduced from EIS plots.

	Morphology	R_{ct} (Ω)	C_{dl} (F)	τ_{nc} (mS)
Au-Bi_2S_3/ZnO	Core-shell	2.577×10^{3}	3.866×10^{-7}	0.996
	Layered	3.299×10^{4}	1.241×10^{-8}	0.409
Au-CdS/ZnO	Core-shell	3.042×10^{5}	3.503×10^{-9}	1.066
	Layered	4.434×10^{5}	2.245×10^{-9}	0.995
Au-CdSe/ZnO	Core-shell	2.230×10^{4}	7.047×10^{-8}	1.572
	Layered	6.029×10^{4}	1.041×10^{-8}	0.628