## **Supporting Information**

Metal@I<sub>2</sub>-II-IV-VI<sub>4</sub> Core-Shell Nanocrystals: Controlled Synthesis by Aqueous Cation Exchange for Efficient Photoelectrochemical Hydrogen Generation

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Figure S1 TEM image of the spherical Au colloids.



**Figure S2** (a) TEM image, (b) HRTEM image and (c) XRD pattern of  $Ag@Ag_2S$  core-shell nanostructures. The characterization results of HRTEM and XRD suggested that the core is spatially confined by an amorphous matrix of the shell.<sup>1,2</sup>



**Figure S3** XRD pattern of the Au@AZTS core-shell NCs. Here the Au@AZTS core-shell NCs with Au core size of 13 nm and shell thickness of 6 nm were employed to generate discernable diffraction peaks assignable to AZTS.



**Figure S4** (a) XPS survey spectrum and (b-e) high-resolution XPS spectra of the Au@AZTS core-shell NCs.



Figure S5 TEM image of the rod-like Au colloids.



**Figure S6** Comparison of the high-resolution XPS spectra of Au@AZTS core-shell NCs before and after the PEC hydrogen evolution test.

## Reference

[1] J. T. Zhang, Y. Tang, K. Lee, M. Ouyang, *Science*, 2010, **327**, 1634-1638.
[2] J. Gui, M. W. Ji, J. J. Liu, M. Xu, J. T. Zhang, H. S. Zhu, *Angew. Chem. Int. Ed.*, 2015, **54**, 3683-3687.