## **Supporting Information**

## Synthesis of hollow ZnSe nanospheres with high photocatalytic activity: synergetic effect of cation exchange and selective Cu<sub>2-x</sub>Se

## template etching

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Fig. S1 TEM image (a) and XRD pattern (b) of the template  $Cu_{2-x}Se$  nanoparticles.



Fig. S2 Size comparision between hollow ZnSe nanospheres and original  $Cu_{2-x}Se$  templates.



**Fig. S3** The photograph of  $Cu_{2-x}Se$  methanol dispersion before (a) and after (b) addition of TBP in air.



Fig. S4. The UV-vis-NIR absorption spectrum of  $Cu_{2-x}Se$  nanospheres.



**Fig. S5** The time-dependent absorption spectra of MO solution containing P25 (a), bulk ZnSe (b) and hollow ZnSe (c) of the same weight under light irradiation produced by a 300 W Xe lamp with wavelength coverage from 320 nm to 780 nm.



Fig. S6 (a) Absorption spectra of ZnSe hollow nanospheres and  $TiO_2$  aqueous dispersion with the same optical density at 365 nm; (b) Comparision of photocatalytic degradation kinetics of methyl orange solution under 365 nm UV lamp excitation in presence of ZnSe hollow nanospheres and  $TiO_2$  with same optical density at 365 nm.



**Fig. S7** TEM image of the hollow ZnSe nanospheres after photocatalytic degradation of MO.