Electronic Supplementary Information

Colloid synthesis of $AgGa(S_{1-x}Se_x)_2$ solid solution nanocrystals with composition-dependent crystal phase for efficient photocatalytic degradation of methyl violet

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Photocatalytic evaluation.

The photocatalytic activity of five representative $AgGa(S_{1-x}Se_x)_2$ nanocrystals (NCs) with x = 1.00, 0.70, 0.50, 0.30 and 0.00 was evaluated for methyl violet (MV) degradation under visible light illumination, respectively. Firstly, 25 mg of NCs were suspended into 50 mL aqueous solution of MV (10 mg/L). Next, the suspensions were kept in the dark for 30 minutes with continuous stirring to establish an adsorption-desorption equilibrium. Thereafter, the photodegradation of MV was conducted by the irradiation of visible light using a 300 W Xe lamp with a cut-off filter (λ > 400 nm). At a given time interval, 2 mL of the suspensions was taken and centrifuged to remove the solid photocatalyst. Finally, UV-1000 spectrophotometer was used to monitor the Uv-vis absorbance of MV in the filtrate, and the degradation efficiency (E_{ff}) was estimated using the equation, E_{ff} (%) = $(1 - C/C_0) \times 100\%$, where C_0 and C are the absorbance of the MV solution at ~580 nm before and after irradiation. The photodegradation of methylene blue (MB) in the presence of $AgGa(S_{1-x}Se_x)_2$ NCs with x = 1.00, 0.50 and 0.00 was conducted under a similar procedure as above described.

Material characterization.

Powder X-ray diffraction (XRD) analysis was performed on a Rigaku D/max-2500 diffractometer with a graphite monochromator by using Cu-Kα radiation operating at 200 mA and 40 kV. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images were recorded on a FEI Tecnai G2 S-Twin with a field emission gun operating at 200 kV. Images were acquired digitally on a Gantan multiple CCD camera. Energy-dispersive X-ray (EDX) spectra were obtained using a JEOL JSM-6300 at 5 kV. The surface of the as-synthesized samples was characterized by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 X-ray photoelectron spectroscope, using Mg Kα X-ray as the excitation source. UV-vis absorption spectra were measured with a Shimadzu UV-3600 spectrophotometer.

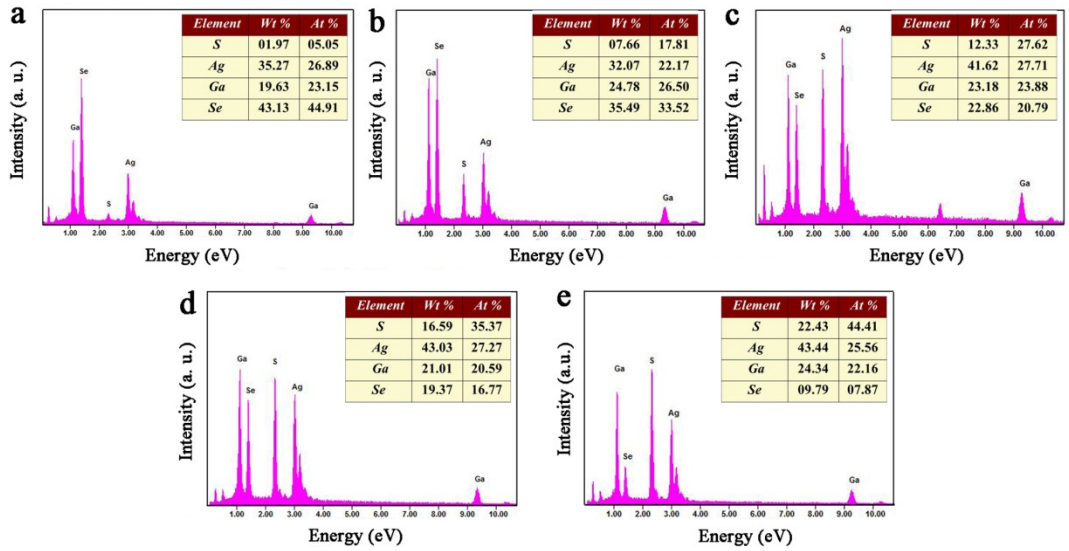

Fig. S1 EDX spectra of a field of AgGa$(S_{1-x}Se_x)_2$ NCs prepared with different molar ratios of S/Se reactants (a) 0.90:0.10, (b) 0.7.:0.30, (c) 0.50:0.50, (d) 0.30:0.70 and (e) 0.10:0.90.

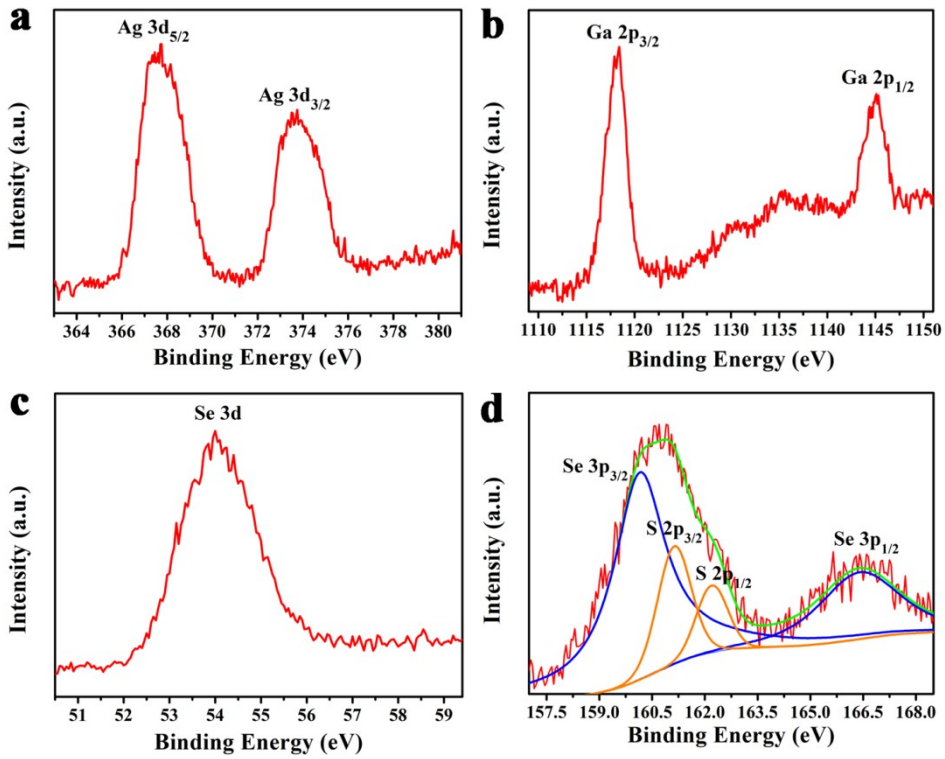

Fig. S2 XPS spectrum of the representative AgGa$(S_{0.3}Se_{0.7})_2$ NCs: (a) Ag 3d, (b) Ga 2p, (c) Se 3d and (d) S 2p and Se 3p core levels. The orange lines are contributed from the S 2p orbital, and the blue lines are Se 3p orbital, respectively.

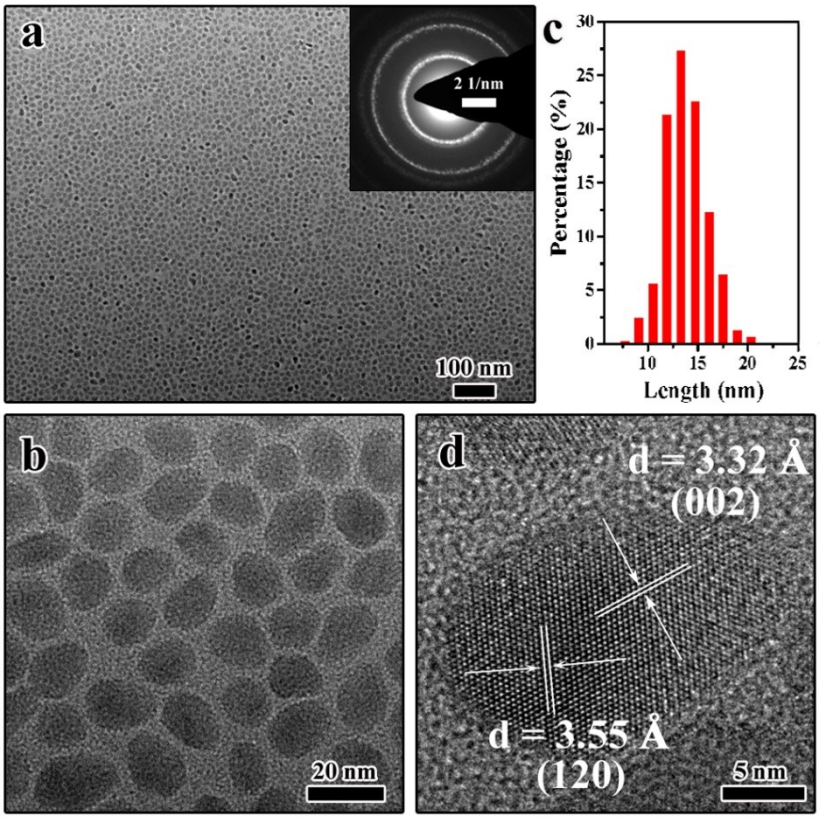

Fig. S3 (a)-(b) TEM and high-magnification images of $AgGaSe_2$ NCs. The inset in (a) is a selected-area SAED pattern. (c) Size distribution of the obtained NCs determined by (a). (d) HRTEM image of an individual $AgGaSe_2$ NC.[1]

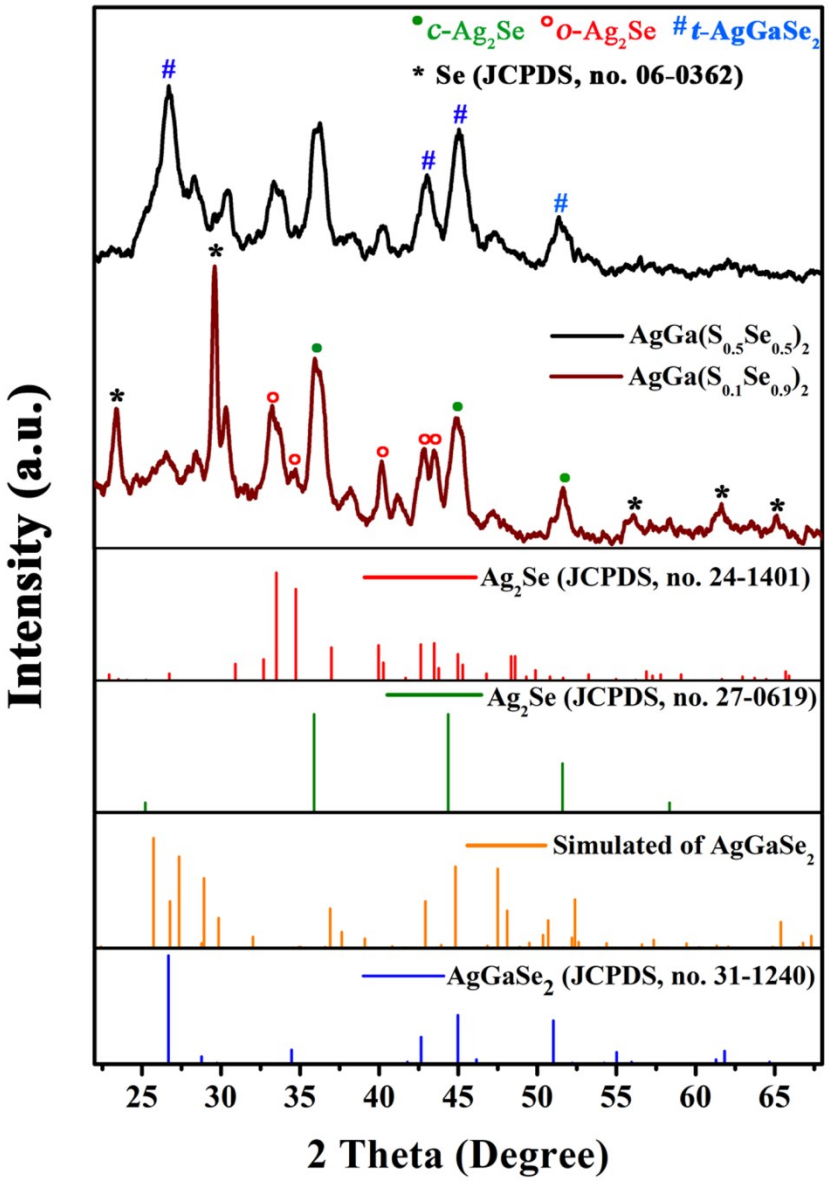

Fig. S4 The XRD patterns of the representative $AgGa(S_{0.5}Se_{0.5})_2$ (black line) and $AgGa(S_{0.1}Se_{0.9})_2$ NCs (wine line) that prepared at 280 °C for 1 minute, and standard orthorhombic Ag_2Se (red line, JCPDS, no. 24-1401), tetragonal Ag_2Se (green line, JCPDS, no. 2700619), tetragonal $AgGaSe_2$ (blue line, JCPDS, no. 31-1240), and the simulated orthorhombic $AgGaSe_2$ (orange line). *c*-Ag_2Se, *o*-Ag_2Se, and *t*-$AgGaSe_2$ representative cubic Ag_2Se, orthorhombic Ag_2Se and tetragonal $AgGaSe_2$, respectively.

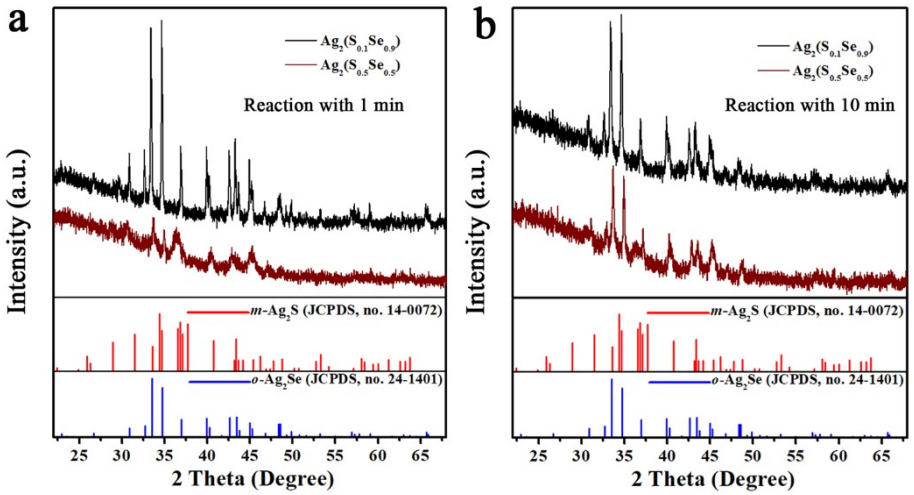

Fig. S5 The XRD patterns of the as-synthesized $Ag_2(S_{0.1}Se_{0.9})$ and $Ag_2(S_{0.5}Se_{0.5})$ NCs that taken by stopping the reaction at 1 min (a), and 10 min (b).

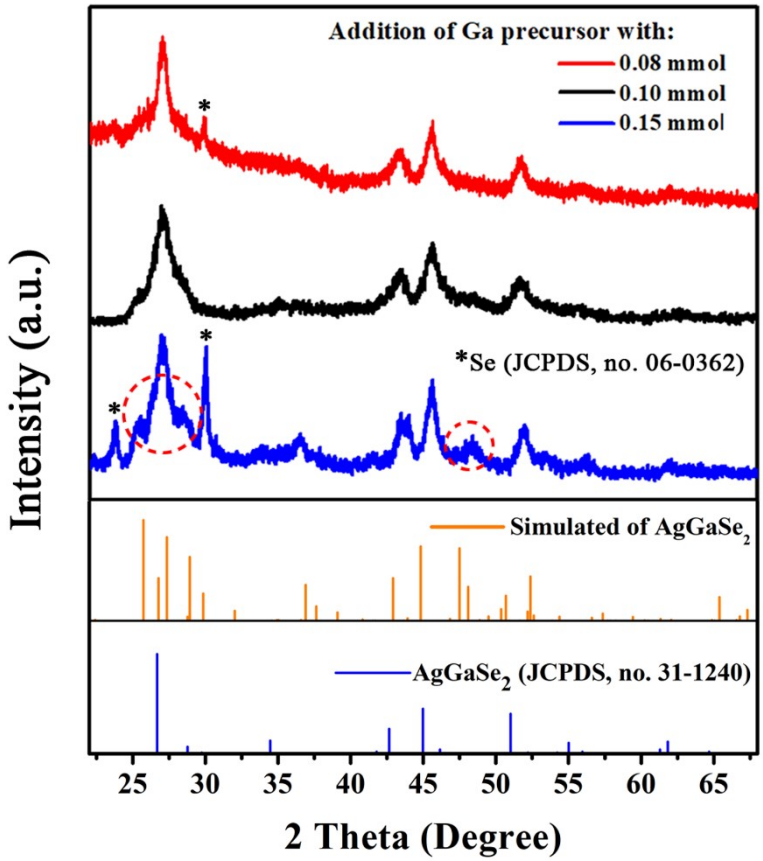

Fig. S6 The XRD patterns of the representative $AgGa(S_{0.5}Se_{0.5})_2$ prepared with the Ga^{3+} precursor addition of 0.08 mmol (red line), 0.10 mmol (black line) and 0.15 mmol (blue line) whose orthorhombic characteristics have been marked by the red dotted circles, and the standard tetragonal $AgGaSe_2$ (blue line, JCPDS, no. 31-1240), and the simulated orthorhombic $AgGaSe_2$ (orange line).

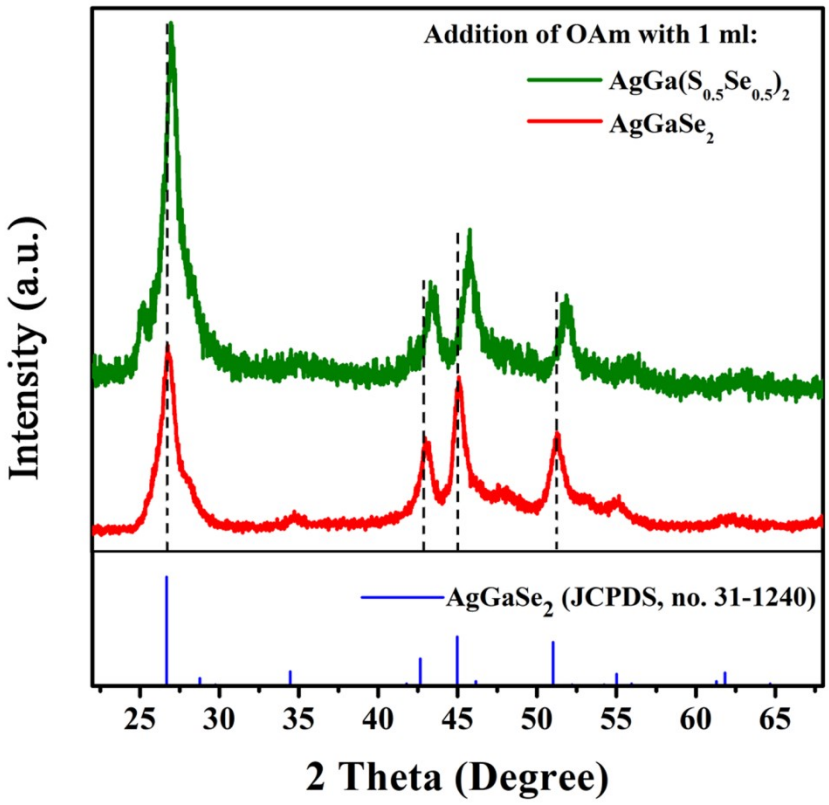

Fig. S7 The XRD patterns of the representative $AgGaSe_2$ (red line) and $AgGa(S_{0.5}Se_{0.5})_2$ (green line) prepared with the OAm addition of 1 mL, and the standard tetragonal $AgGaSe_2$ (blue line, JCPDS, no. 31-1240).

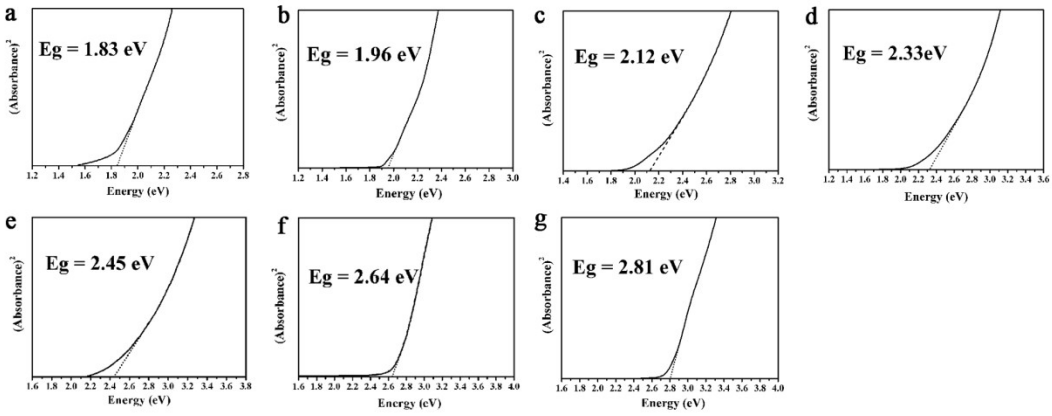

Fig. S8 The extrapolation of spectra to identify the E_g of $AgGa(S_{1-x}Se_x)_2$ NCs with x = (a) 1.00, (b) 0.90, (c) 0.70, (d) 0.50, (e) 0.30, (f) 0.10 and (g) 0.00.

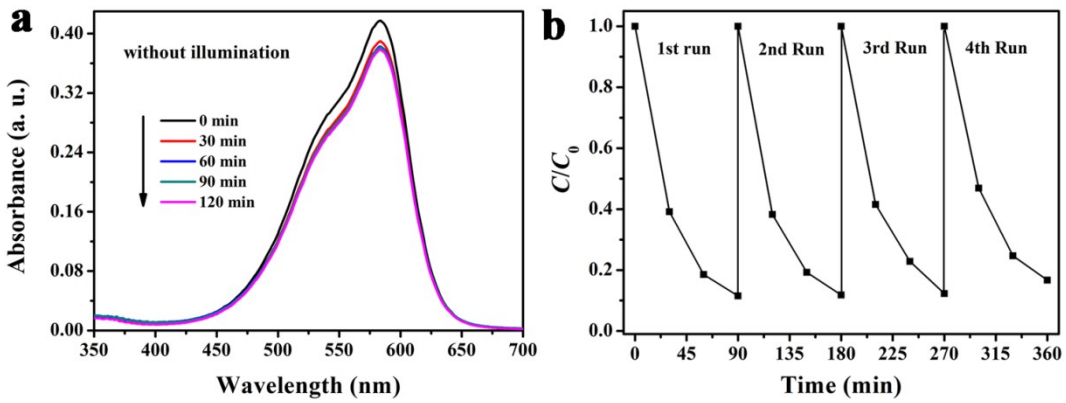

Fig. S9 (a) Temporal evolution of the absorption spectra of an aqueous MV solution in the presence of the representative $AgGa(S_{0.7}Se_{0.3})_2$ NCs without illumination (performed in the dark); (b) cycling four runs of the photodegradation of MV for the representative $AgGa(S_{0.7}Se_{0.3})_2$.

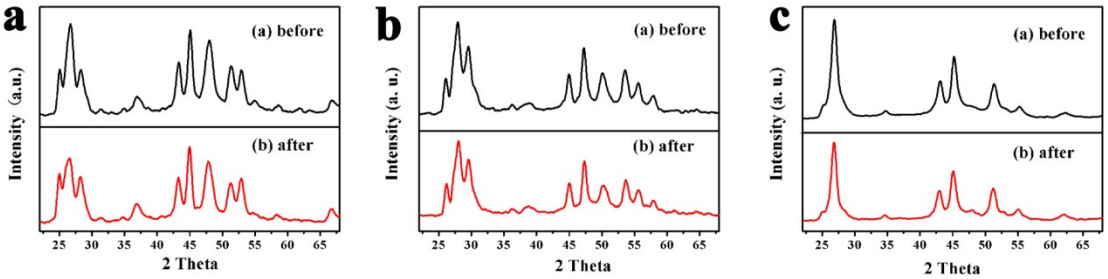

Fig. S10 XRD patterns of three random representative $AgGa(S_{1-x}Se_x)_2$ NCs with x = (a) 1.00, (b) 0.00 and (c) 0.70, before and after the photocatalytic experiment.

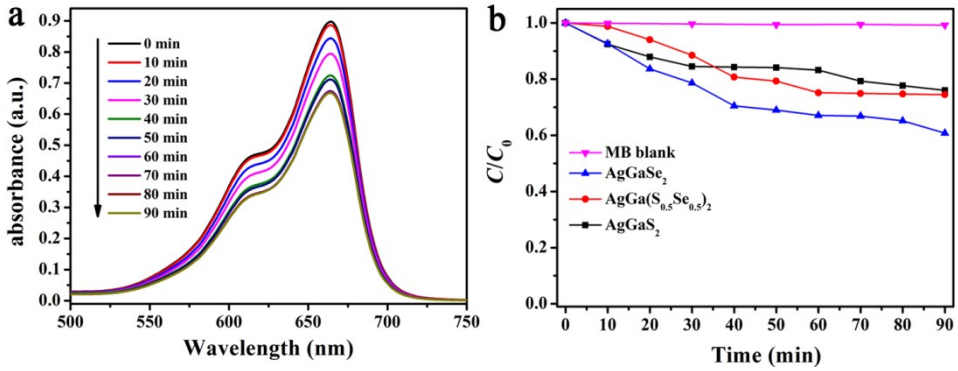

Fig. S11 (a) Temporal evolution of the absorption spectra of an aqueous MB solution in the presence of the representative $AgGa(S_{0.5}Se_{0.5})_2$ NCs under visible-light illumination; (b) photodegradation of MB solution by the use of the representative $AgGa(S_{1-x}Se_x)_2$ NCs with x = 1.0, 0.5 and 0.0.

The band position of $AgGa(S_{1-x}Se_x)_2$ NCs can be estimated based on the following formulas:[2]

$$E_{VB} = X - E^e + 0.5E_g \quad (1)$$

$$E_{CB} = E_{VB} - E_g \quad (2)$$

where E_{VB} and E_{CB} are the valence band (VB) and conduction band (CB) edge potential, respectively; E_g is the band gap energy of the as-synthesized $AgGa(S_{1-x}Se_x)_2$ NCs; X is the electronegativity of the as-synthesized $AgGa(S_{1-x}Se_x)_2$ NCs which is the geometric mean of the electronegativity of the constituent atoms;[3] E^e is the energy of free electrons on the hydrogen scale (4.5 eV). The values of the calculated data are listed in Table S1.

Table S1. Calculated values of X, E_{VB}, E_{CB} and E_g of the as-synthesized $AgGa(S_{1-x}Se_x)_2$ NCs

Compound	Electronegativity（eV）	E_{VB}（eV）	E_{CB}（eV）	E_g (eV)
$AgGaSe_2$	4.712	1.152	-0.678	1.83
$AgGa(S_{0.1}Se_{0.9})_2$	4.726	1.206	-0.745	1.96
$AgGa(S_{0.3}Se_{0.7})_2$	4.757	1.317	-0.803	2.12
$AgGa(S_{0.5}Se_{0.5})_2$	4.786	1.451	-0.879	2.33
$AgGa(S_{0.7}Se_{0.3})_2$	4.800	1.525	-0.925	2.45
$AgGa(S_{0.9}Se_{0.1})_2$	4.822	1.642	-0.998	2.64
$AgGaS_2$	4.842	1.747	-1.063	2.81

Additional References:

1) T. Bai, S. Xing, C. Li, Z. Shi and S. Feng, *Chem. Commun.*, 2016, **52**, 8581-8584.

2) M. Long, W. Cai, J. Cai, B. Zhou, X. Chai and Y. Wu, *J. Phys. Chem. B*, 2006, **110**, 20211-20216.

3) D. Ghosh and T. Chakraborty, *J. Mol. Struct.: THEOCHEM*, 2009, **906**, 87-93.