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# The Synergistic Role of Double Vacancies within $AgGaS_2$ Nanocrystals on Charge Separation and Transfer for Efficient Photocatalytic Hydrogen Evolution

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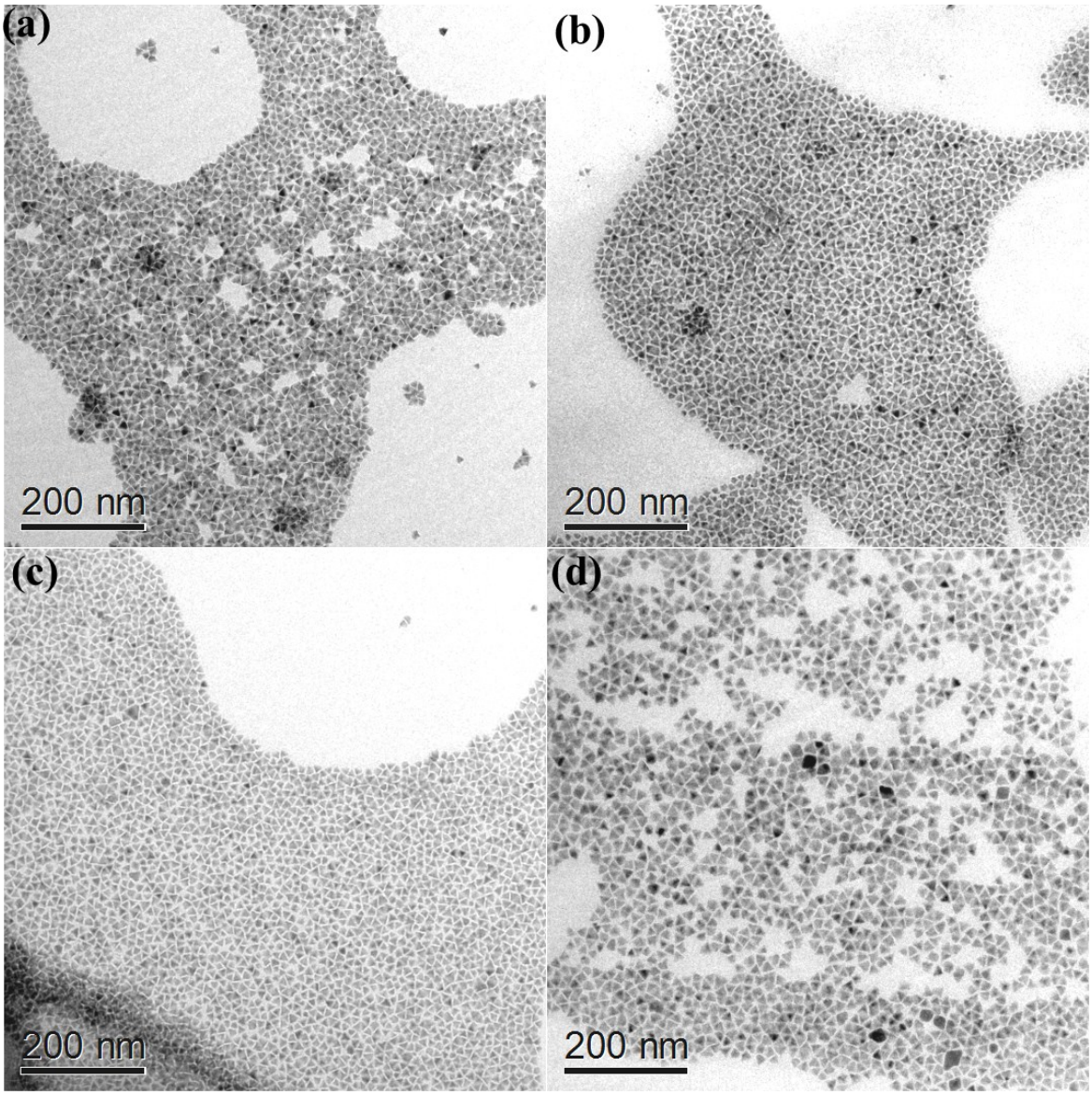


Fig. S1 TEM images of various AGS samples: (a) Ag-P/Ga-P=0.760; (b) Ag-P/Ga-P=0.634; (c) Ag-P/Ga-P=0.380; (d) Ag-P/Ga-P=0.253

Table S1 The content of the Ag and Ga in AGS nanocrystal samples as determined by ICP

| Products | Molar ratio of Ag-oleate and $Ga(AcAc)_3$ | Ag (Wt %) | Ga (Wt %) | Ag/Ga molar ratio |
|---|---|---|---|---|
| $AgGaS_2$ nanocrystal | 0.253 | 9.30% | 34.63% | 0.173 |
| | 0.507 | 16.27% | 29.52% | 0.357 |

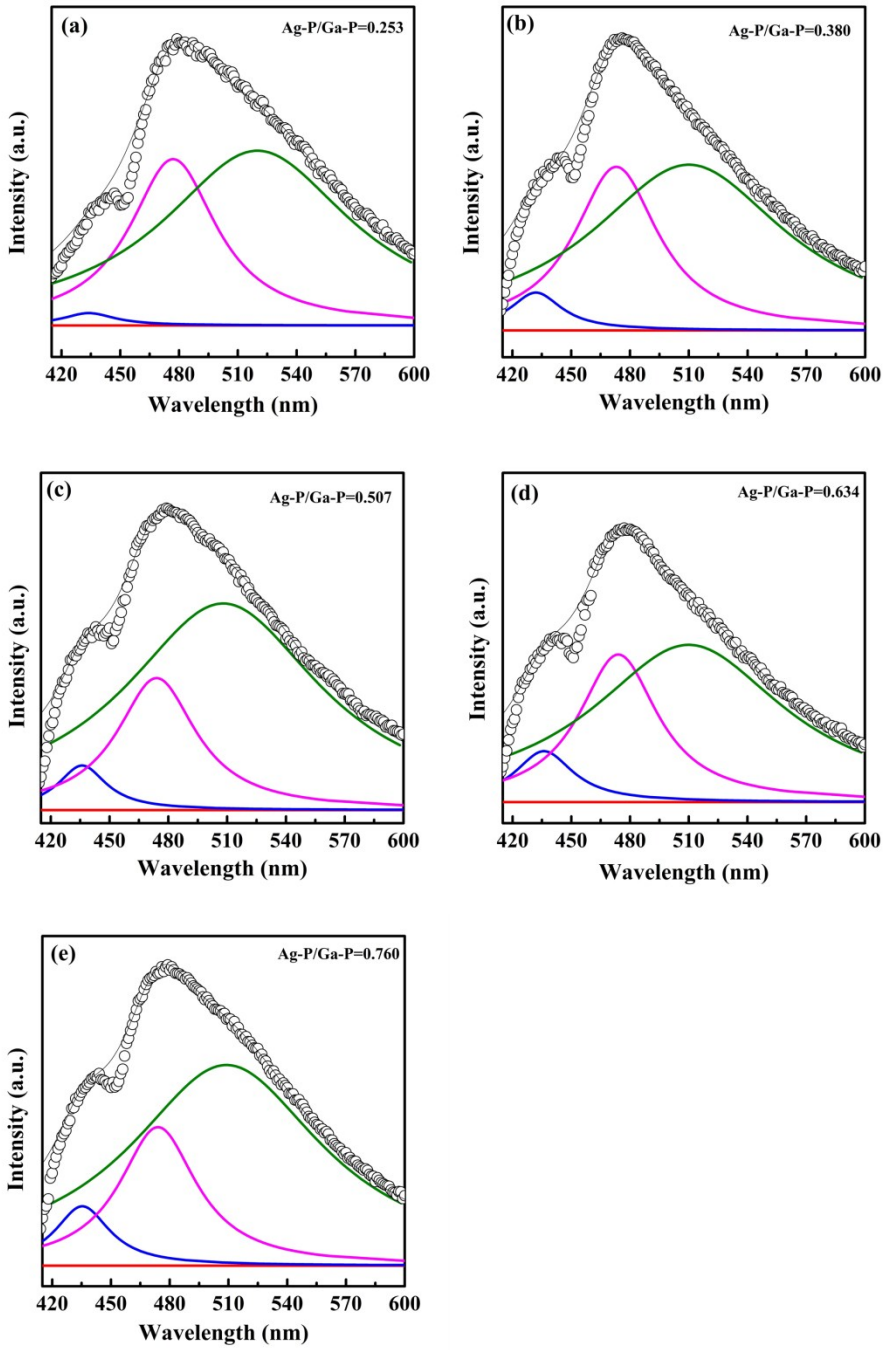


Fig. S2 Room-temperature photoluminescence spectra were performed for AGS nanocrystals with different Ag-P/Ga-P molar ratio: (a) Ag-P/Ga-P=0.253; (b) Ag-P/Ga-P=0.380; (c) Ag-P/Ga-P=0.507; (d) Ag-P/Ga-P=0.634; (d) Ag-P/Ga-P=0.760.

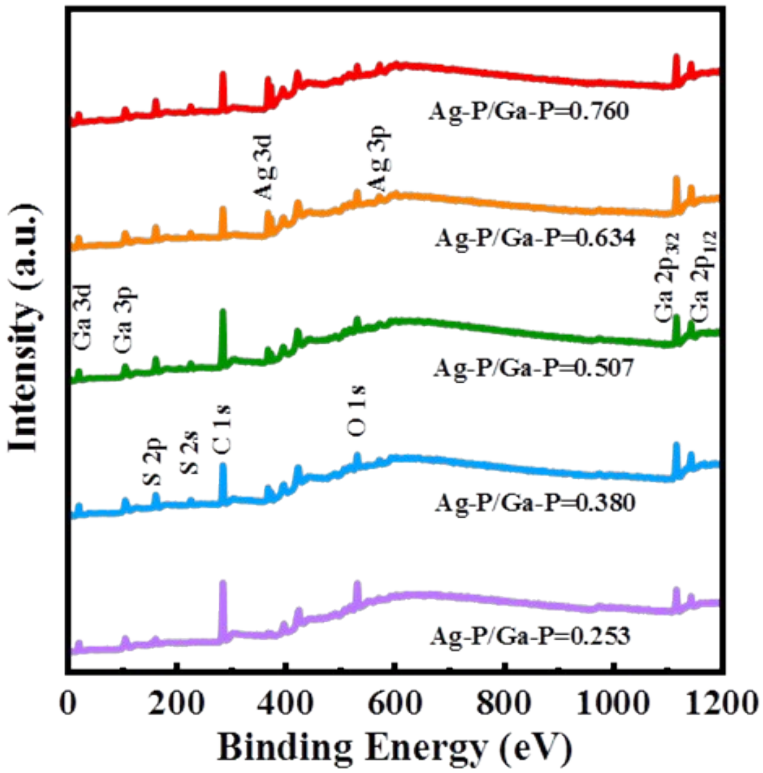


Fig. S3 Full-scale XPS spectra were carried out for AGS nanocrystals with different Ag-P/Ga-P molar ratio of 0.760, 0.507 and 0.253.

Table S2 The ratio of silver vacancies and $Ag^+$ to Ag 3d for AGS nanocrystals with Ag-P/Ga-P molar ratio of 0.76, 0.634, 0.507, 0.380 and 0.253.

| Ag-P/Ga-P | $V_{Ag}$ /Ag 3d | $Ag^+$/Ag 3d |
|---|---|---|
| 0.76 | 0.212 | 0.788 |
| 0.634 | 0.239 | 0.761 |
| 0.507 | 0.256 | 0.744 |
| 0.38 | 0.306 | 0.694 |
| 0.253 | 0.334 | 0.666 |

Table S3 The ratio of S 2p1/2 and S 2p3/2 to S 2p for AGS nanocrystals with Ag-P/Ga-P molar ratio of 0.76, 0.634, 0.507, 0.380 and 0.253.

| Ag-P/Ga-P | S $2p_{1/2}$/ S 2p | S $2p_{3/2}$/ S 2p |
|---|---|---|
| 0.76 | 0.618 | 0.382 |
| 0.634 | 0.65 | 0.35 |
| 0.507 | 0.682 | 0.318 |
| 0.38 | 0.711 | 0.289 |
| 0.253 | 0.756 | 0.244 |

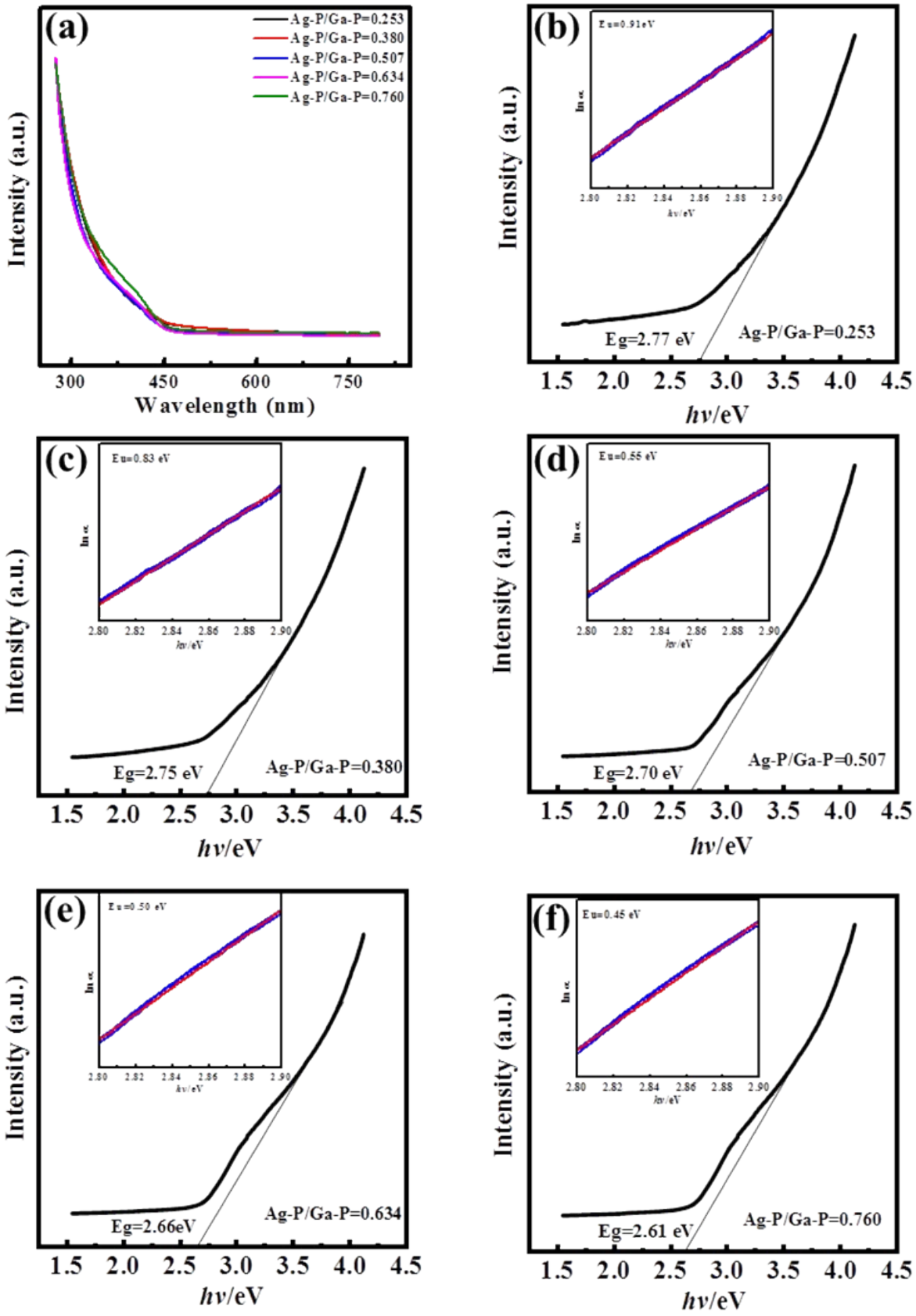
(a)
Ag-P/Ga-P=0.253
Ag-P/Ga-P=0.380
Ag-P/Ga-P=0.507
Ag-P/Ga-P=0.634
Ag-P/Ga-P=0.760
Intensity (a.u.)
300
450
600
750
Wavelength (nm)
(b)
Eu=0.91eV
ln α
hν/eV
Intensity (a.u.)
Eg=2.77 eV
Ag-P/Ga-P=0.253
1.5 2.0 2.5 3.0 3.5 4.0 4.5
hν/eV
(c)
Eu=0.83 eV
ln α
hν/eV
Intensity (a.u.)
Eg=2.75 eV
Ag-P/Ga-P=0.380
1.5 2.0 2.5 3.0 3.5 4.0 4.5
hν/eV
(d)
Eu=0.55 eV
ln α
hν/eV
Intensity (a.u.)
Eg=2.70 eV
Ag-P/Ga-P=0.507
1.5 2.0 2.5 3.0 3.5 4.0 4.5
hν/eV
(e)
Eu=0.50 eV
ln α
hν/eV
Intensity (a.u.)
Eg=2.66eV
Ag-P/Ga-P=0.634
1.5 2.0 2.5 3.0 3.5 4.0 4.5
hν/eV
(f)
Eu=0.45 eV
ln α
hν/eV
Intensity (a.u.)
Eg=2.61 eV
Ag-P/Ga-P=0.760
1.5 2.0 2.5 3.0 3.5 4.0 4.5
hν/eV

Fig. S4 (a) UV-vis absorption spectrum for AGS with different Ag-P/Ga-P molar ratio; Curves of $(\alpha h\nu)^{1/2}$ versus hν fitted by $(\alpha h\nu)^{1/2} = A(Eg - h\nu)$ equation for different Ag-P/Ga-P: (b)Ag-P/Ga-P=0.76; (c) Ag-P/Ga-P=0.634; (d) Ag-P/Ga-P=0.507; (e) Ag-P/Ga-P=0.380; (f) Ag-P/Ga-P=0.253. The inset is The Urbach plots of various AGS nanocrystals from which the Urbach energy ($E_u$) can be obtained.

The band gap of the AGS nanocrystals are calculated by the transformed Kubelka-Munk function $(\alpha h\nu)^{1/2} = A(Eg - h\nu)$, as shown in Fig. S4 (b)-(f). These illustrate that the Ag-P/Ga-P decrease from 0.760 to 0.253 the bandgap of AGS nanocrystals exhibit a slightly broadening band gap from 2.61eV to 2.77 eV. The band gap broaden may be associated with weakened repulsion between Ag d and S p valence band states, which leads to lowering of the valence band maximum.[1]

The position of defect levels (acceptor level and donor level) in all AGS nanocrystals will be obtained, according to the equation: $\alpha = \alpha_0 \exp(h\nu / Eu)$, where α is absorption coefficient, $\alpha_0$ is a constant, $h\nu$ is the incident photon energy, and $Eu$ denotes the Urbach energy. And The $E_u$ values were calculated from the inverse of the slope of $Ln\ \alpha$ versus $(h\nu)$

Table S4 The bandgap ($E_g$) and Urbach energy ($E_u$) of all AGS samples.

| Ag-P/Ga-P | $E_g$ (eV) | $E_u$ (eV) |
|---|---|---|
| 0.760 | 2.61 | 0.45 |
| 0.634 | 2.66 | 0.50 |
| 0.507 | 2.70 | 0.55 |
| 0.380 | 2.75 | 0.83 |
| 0.253 | 2.77 | 0.91 |

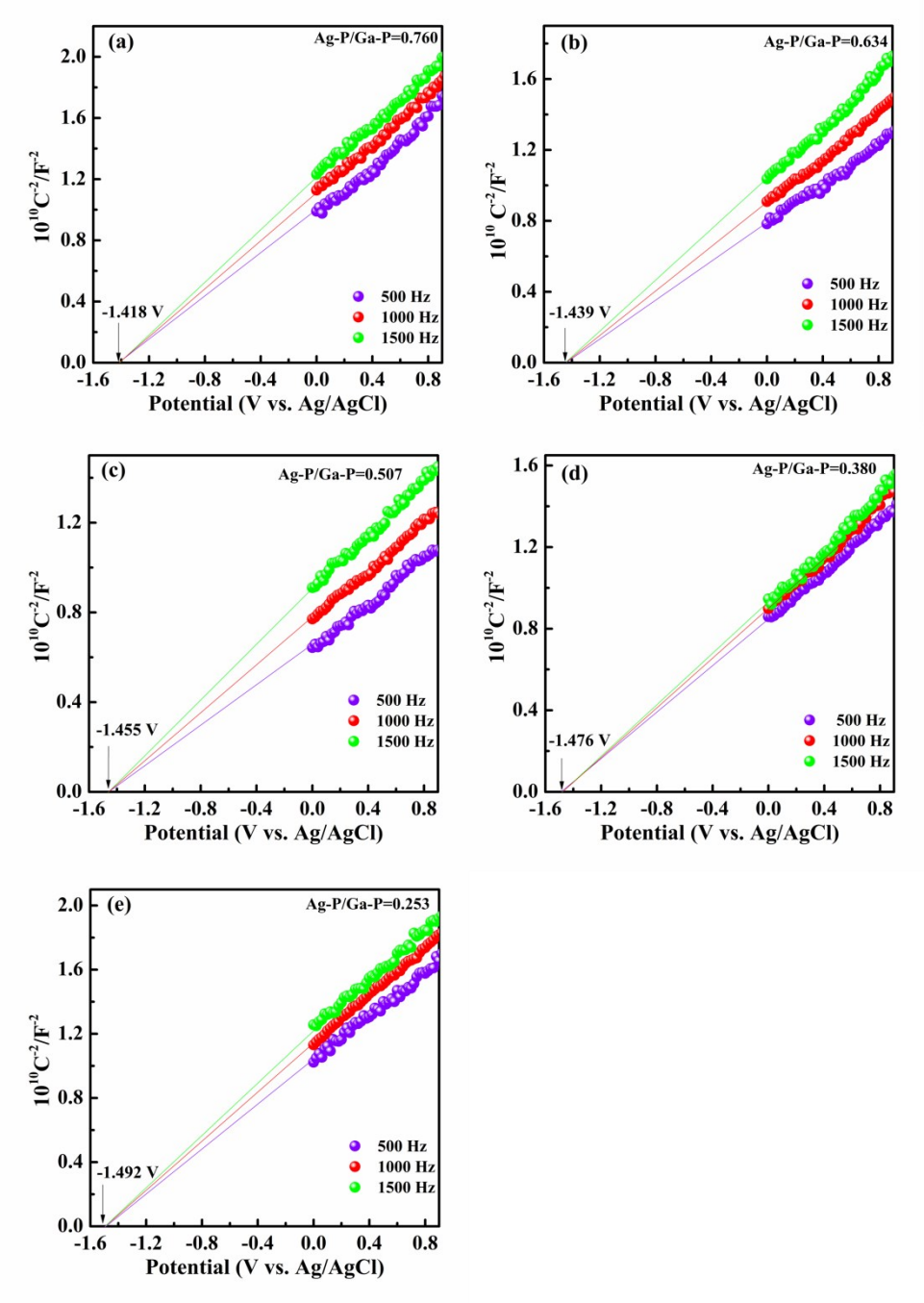


Fig. S5 Typical Mott-Schottky plots of AGS nanocrystals with different Ag-P/Ga-P molar ratio ((a) 0.760, (b) 0.634, (c) 0.507, (d) 0.380 and (e) 0.253) in 0.2 M $Na_2SO_4$ aqueous solution (PH=6.8).

The electrochemical flat-band potentials ($E_{fb}$) of the AGS nanocrystals can be obtained using Mott–Schottky plots (Fig. S5) which are estimated to be -1.418 , -1.439, -1.455, -1.476 and -1.492 V vs. Ag/AgCl at PH=6.8 for Ag-P/Ga-P molar ratio of 0.760, 0.634, 0.507, 0.380 and 0.253, respectively. The Ag/AgCl electrode can be converted into a normal hydrogen electrode, according to the formula: ψ (NHE) = ψ (Ag/AgCl) +0.059*PH+0.197[2-4]. As for n-type semiconductors which can be revealed by the positive slopes of the Mott-Schottky, the $E_{fb}$ value is ~0.3 V below the conduction band bottom ($E_{CB}$). Therefore, the conduction band bottoms of Ag-P/Ga-P molar ratio of 0.760, 0.634, 0.507, 0.380, and 0.253 are -1.112, -1.141, -1.157, -1.178, and -1.194 V vs NHE, respectively.

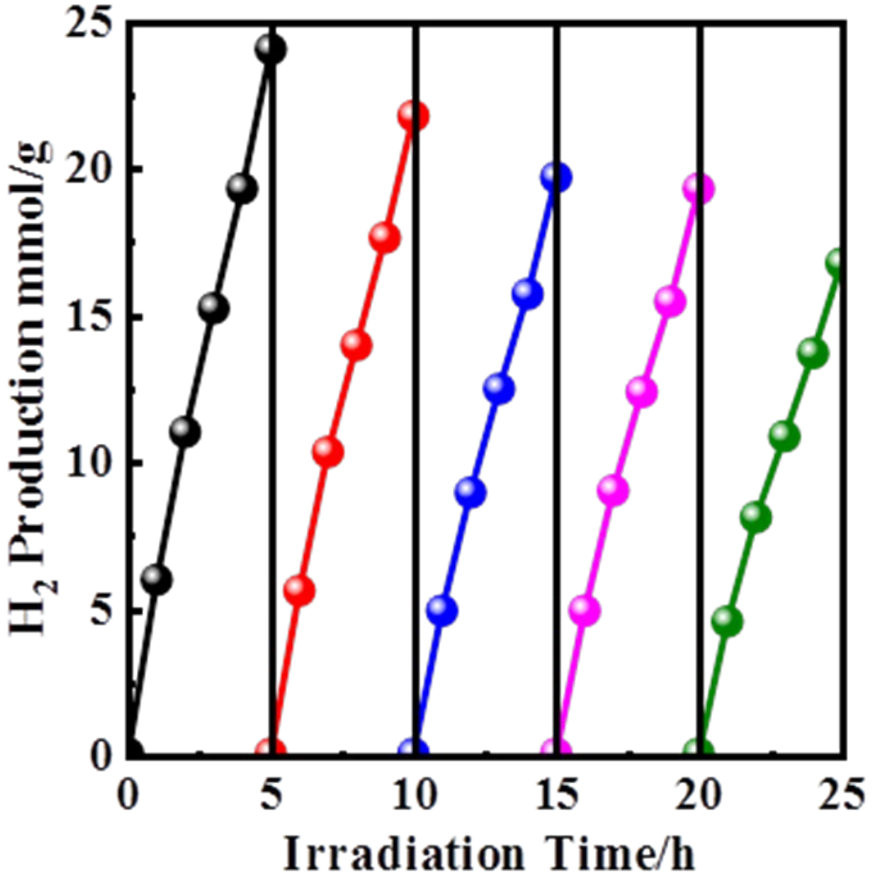


Fig. S6 Cycling tests of hydrogen production for non-stoichiometric AGS nanocrystals of Ag-P/Ga-P = 0.507.

The apparent quantum efficiencies (AQE) were obtained by performing hydrogen evolution with the same conditions, except that under monochromatic light (365, 400, 420, 450, 550 and 650nm). The light intensities were measured to be1.3, 8.5, 9.7, 11.4, 12.3 and 10.4 mW $cm^{-2}$, respectively, which using an optical power meter (PL-MW2000, Perfect light). The AQE was calculated on the basis of the following equation:

$$AQE = \frac{2 \times N_{H_2}}{N_p} \times 100\% = \frac{2 \times n_{H_2} \times N_A}{\frac{I \times A \times t}{h\upsilon}} \times 100\%$$

Where $N_p$ represent the number of incident photons and $N_{H2}$ represent the number of generated $H_2$ molecules, $n_{H2}$ represents the molar number of generated $H_2$, $N_A$ is Avogadro's constant, I represents the light intensity, A is irradiation area, t is reaction time, ν is incident light frequency and h is the Planck constant.

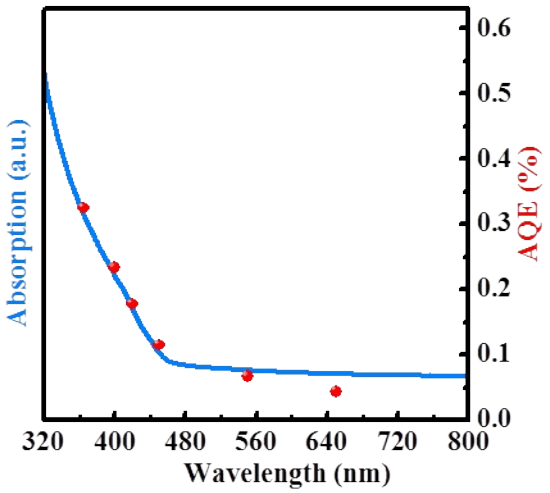


Fig. S7 The AQEs (red spheres) was calculated for hydrogen production over AGS nanocrystals of Ag-P/Ga-P=0.507 under various monochromatic light irradiations, in reference to its UV-vis absorption spectra (blue line)

To further certify that the reaction was driven by incident light, the wavelength-dependent apparent quantum efficiencies (AQE) of AGS nanocrystal with Ag-P/Ga-P=0.507 are determined by measuring the amount of generated hydrogen under various monochromatic light irradiation (Fig. 4(c)). The AQEs coincide well with the absorption spectra of AGS nanocrystals, which further verifies light-driven hydrogen production. The AQEs at 365nm, 400nm, 420nm, 450nm, 550nm and 650nm are determined to be 0.32%, 0.23%, 0.18%, 0.12%, 0.07%, 0.04%, respectively.

## References

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