# Electronic Supplimentary Information for

# Single source precursor driven phase selective synthesis of Au-$CuGaS_2$ heteronanostructures: an observation of plasmon enhanced photocurrent efficiency

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**Table S1** Crystallographic data for $[Ga(acda)_3]$ (**1**) and $[Ga(acda)_3Cu(PPh_3)_2]NO_3$ (**2**).

| | $[Ga(acda)_3]$(**1**) | $[Ga(acda)_3Cu(PPh_3)_2]NO_3$(**2**) |
|---|---|---|
| Empirical formula | $C_{18}H_{24}GaN_3S_6$ | $C_{54}H_{54}CuGaN_4O_3P_2S_6$ |
| Formula weight | 544.48 | 1194.57 |
| *T*, K | 150(2) | 296(2) |
| Crystal system | Monoclinic | Triclinic |
| Space group | *P2(1)/c* | *P-1* |
| *a* /Å | 12.6050(17) | 13.2940(11) |
| *b* /Å | 10.5038(15) | 14.7257(12) |
| *c* /Å | 17.814(2) | 15.9249(13) |
| $\alpha$ / deg | 90.00 | 64.196(2) |
| $\beta$ / deg | 98.654(3) | 80.020(2) |
| $\gamma$ / deg | 90.00 | 78.737(3) |
| *V* / Å$^3$ | 2331.7(6) | 2738.8(4) |
| *Z* | 4 | 2 |
| $\mu$, mm$^{-1}$ | 1.728 | 1.214 |
| $\lambda$, *Å* | 0.71073 | 0.71073 |
| *F*(000) | 1120 | 1232 |
| Crystal size, mm$^3$ | 0.13× 0.06 × 0.04 | 0.20× 0.18 × 0.16 |
| $D_{calc}$ / g cm$^{-3}$ | 1.551 | 1.449 |
| No. of data/ restraints /params | 10411/ 0 / 253 | 32361/ 0 / 664 |
| No. of reflns [$I > 2\sigma(I)$] | 4474 | 10019 |
| GOF on $F^2$ | 1.092 | 1.008 |
| Final *R* indices[$I > 2\sigma(I)$] | R1[a] = 0.0779, wR2[b] = 0.1318 | R1[a] = 0.0429, wR2[b] = 0.0876 |
| *R* indices (all data) | R1[a] = 0.1189, wR2[b] = 0.1454 | R1[a] = 0.0695, wR2[b] = 0.1002 |

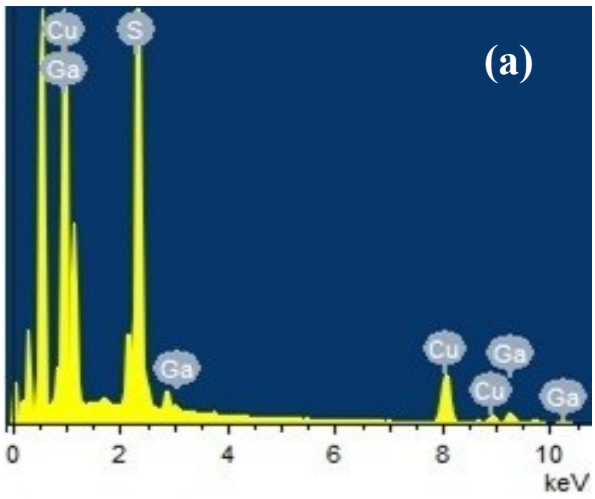
$R1(F) = \sum||F_o|-|F_c|| / \sum|F_o|$. [b] $wR2(F^2) = [\sum w(F_o^2-F_c^2)^2 / \sum w(F_o^2)^2]^{½}$.

**Table S2** Selected interatomic distances (Å) for the complex $[Ga(acda)_3]$ (**1**) and $[Ga(acda)_3Cu(PPh_3)_2]NO_3$ (**2**).

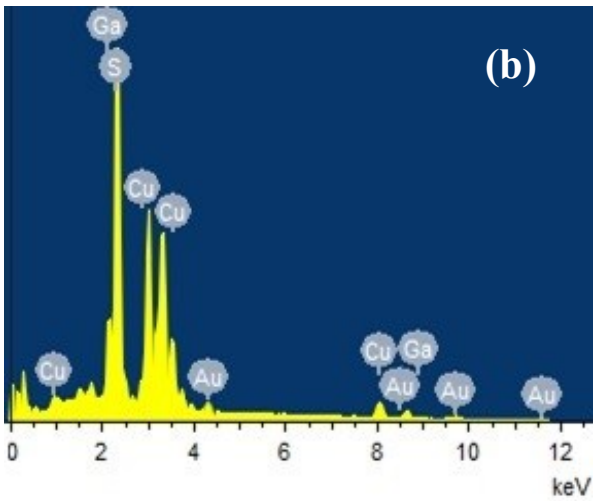
| $[Ga(acda)_3]$ (**1**) | | $[Ga(acda)_3Cu(PPh_3)_2]NO_3$ (**2**) | |
|---|---|---|---|
| Ga–S(1) | 2.264(2) | Cu–P(1) | 2.316(1) |
| Ga–S(2) | 2.669(2) | Cu–P(2) | 2.299(1) |
| Ga–S(3) | 2.482(1) | Cu–S(3) | 2.353(1) |
| Ga–S(4) | 2.302(1) | Cu–S(5) | 2.571(1) |
| Ga–S(5) | 2.266(2) | Ga–S(1) | 2.381(1) |
| | | Ga–S(2) | 2.372(1) |
| | | Ga–S(4) | 2.277(1) |
| | | Ga–S(5) | 2.343(1) |
| | | Ga–S(6) | 2.589(1) |

**Table S3** Selected bond angles (deg) for the complex $[Ga(acda)_3]$ (**1**) and $[Ga(acda)_3Cu(PPh_3)_2]NO_3$ (**2**).

| $[Ga(acda)_3]$ | | $[Ga(acda)_3Cu(PPh_3)_2]NO_3$ | |
|---|---|---|---|
| S(1)–Ga–S(2) | 71.89(6) | P(1)–Cu–P(2) | 123.36(4) |
| S(1)–Ga–S(3) | 101.74(6) | P(1)–Cu–S(3) | 102.55(4) |
| S(1)–Ga–S(4) | 121.34(7) | P(1)–Cu–S(5) | 103.73(4) |
| S(1)–Ga–S(5) | 127.71(4) | P(2)–Cu–S(3) | 112.97(4) |
| S(2)–Ga–S(3) | 154.59(6) | P(2)–Cu–S(5) | 113.11(4) |
| S(2)–Ga–S(4) | 87.58(6) | S(3)–Cu–S(5) | 97.57(4) |
| S(2)–Ga–S(5) | 96.98(6) | S(1)–Ga–S(2) | 74.97(4) |
| S(3)–Ga–S(4) | 74.66(6) | S(1)–Ga–S(4) | 113.08(4) |
| S(3)–Ga–S(5) | 105.74(6) | S(1)–Ga–S(5) | 100.67(4) |
| S(4)–Ga–S(5) | 108.53(7) | S(1)–Ga–S(6) | 151.05(4) |
| | | S(2)–Ga–S(4) | 106.75(4) |
| | | S(2)–Ga–S(5) | 135.16(4) |
| | | S(2)–Ga–S(6) | 90.09(4) |
| | | S(4)–Ga–S(5) | 115.44(4) |
| | | S(4)–Ga–S(6) | 94.80(4) |
| | | S(5)–Ga–S(6) | 72.46(4) |




| Element | Weight% | Atomic% |
|---|---|---|
| S | 31.61 | 49.00 |
| Cu | 33.44 | 26.17 |
| Ga | 34.95 | 24.83 |
| Totals | 100.00 | |




| Element | Weight% | Atomic% |
|---|---|---|
| S | 26.05 | 46.80 |
| Cu | 26.10 | 23.69 |
| Ga | 29.22 | 24.17 |
| Au | 18.63 | 5.34 |
| Totals | 100.00 | |

**Fig S1** EDX spectra of (a) $CuGaS_2$, (b) Au-Wz $CuGaS_2$ (left panel) and corresponding atomic percentage in tabular form (right panel).

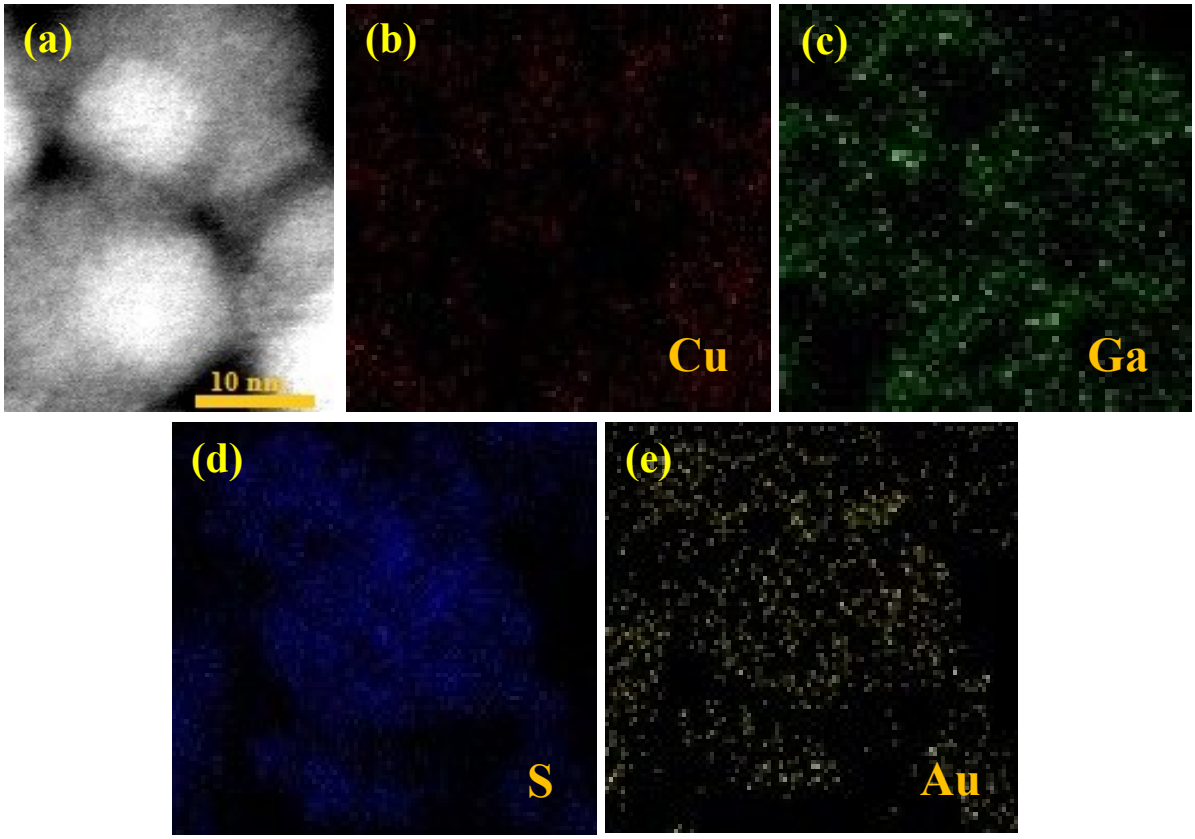



**Fig S2.** (a) Dark-field STEM image of Au-Wz $CuGaS_2$. Elemental mapping of (b) Cu, (c) Ga, (d) S and (e) Au in a single heterostructure of Au-Wz $CuGaS_2$.

**Preparation of colloidal solution of metallic Au nanoparticle for spectroscopic measurement:**

Au nanoparticle was prepared by following a modified method from the prior literature.[1,2] In a 25 mL two-necked round bottom flask gold (III) chloride (0.085 g, 0.25 mmol) was dissolved in 3 mL OAm. The mixture was then stirred and then heated to 80 °C for 10 min under argon flow during which the orange colored solution became colorless. Then the temperature was raised to 260 °C and kept at this condition for 1 h during which the color of the solution became dark purple. After cooling to room temperature, the product was centrifuged and dispersed in toluene. The Uv-vis absorption spectrum was recorded with the toluene dispersion of the nanoparticle.

[1. B. K. Patra, A. Shit, A. K. Guria, S. Sarkar, G. Prusty, N. Pradhan, *Chem Mater*., 2015, **27**, 650.
2. B. K. Patra, S. Khilari, D. Pradhan, N. Pradhan, *Chem. Mater*., 2016, **28**, 4358.]

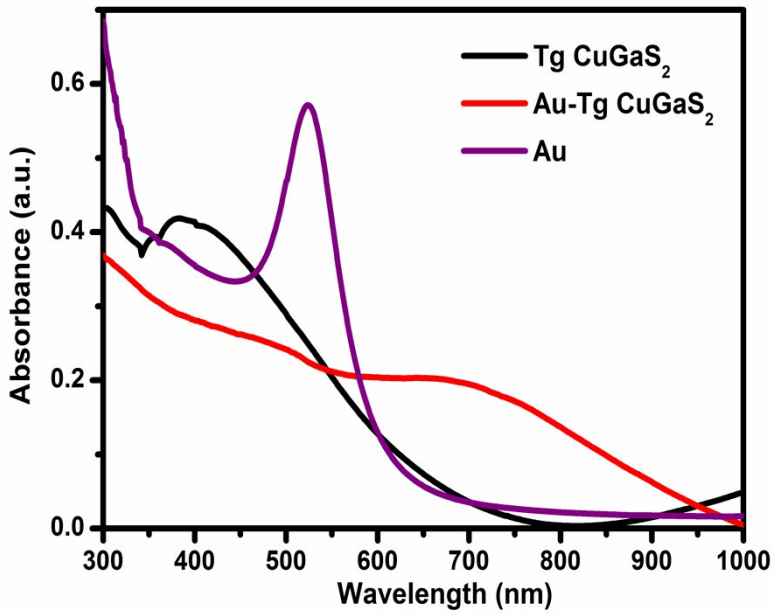



**Fig S3.** Absorption spectra of Au, Tg $CuGaS_2$ and Au-Tg $CuGaS_2$.

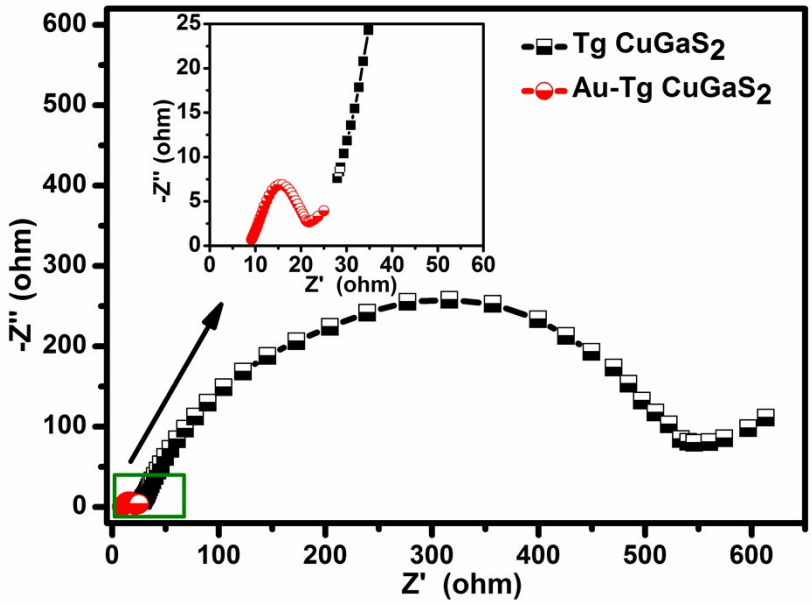



**Fig S4.** Nyquist plot of Tg $CuGaS_2$ and Au-Tg $CuGaS_2$ under illumination.

**Table S4** Variation of impedance parameters of $CuGaS_2$ and Au- $CuGaS_2$ in Wz and Tg phases obtained from the equivalent circuit fitting

| *Sample* | $R_s$ *(ohm)* | $R_{Ct}$ *(ohm)* | *CPE (μF)* |
|---|---|---|---|
| **Wz-$CuGaS_2$** | **29.2** | **313.7** | **0.7** |
| **Au-Wz-$CuGaS_2$** | **9.8** | **10.8** | **16.5** |
| **Tg-$CuGaS_2$** | **31.9** | **523.7** | **0.6** |
| **Au-Tg-$CuGaS_2$** | **9.9** | **18.4** | **15.3** |

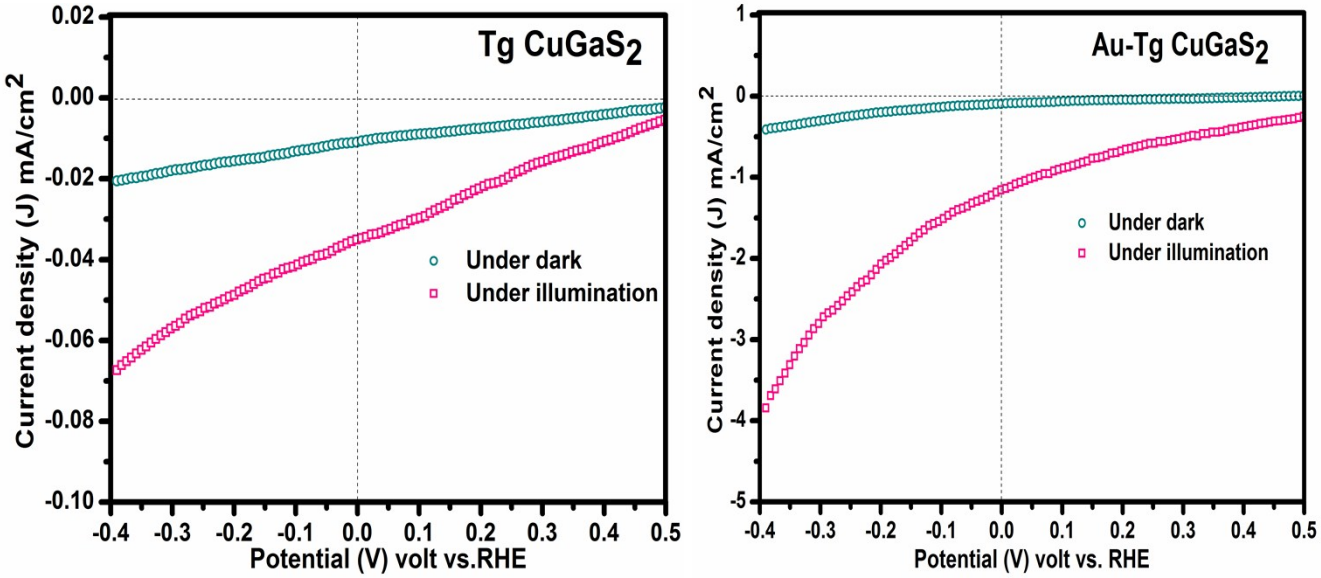



**Fig S5.** Current density versus voltage plots for (a) Tg $CuGaS_2$ and (b) Au-Tg $CuGaS_2$ and under dark and under illuminations.

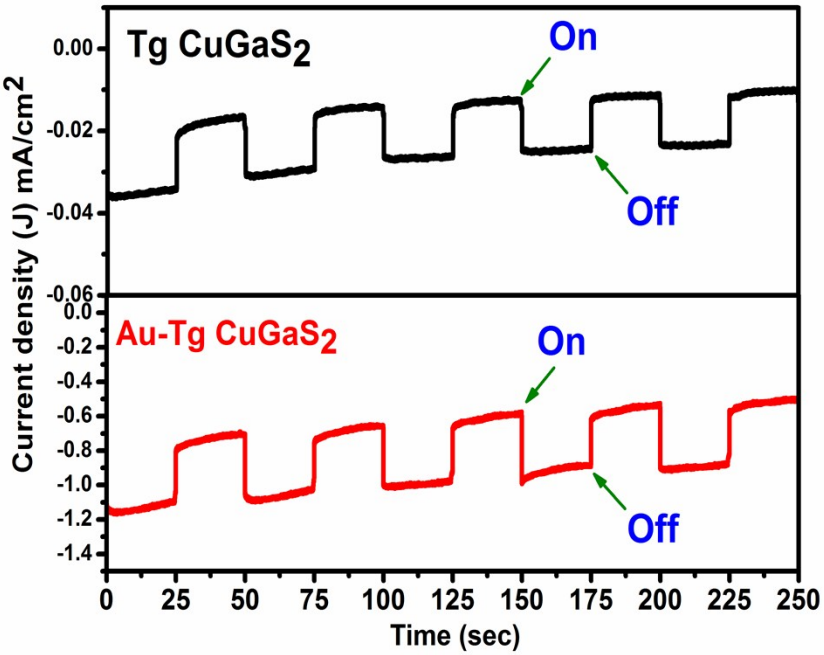



**Fig S6.** Current density versus time plots during successive on and off cycles of light for Tg $CuGaS_2$ and Au- Tg $CuGaS_2$ at 0 V vs RHE.

**Table S5** Summary of photocurrent data of pure and heterostructured $CuGaS_2$

| ***Sample*** | ***Current density under illumination at 0 V vs RHE (mA/cm²)*** | $I_{light}/I_{dark}$ |
|---|---|---|
| **Wz $CuGaS_2$** | **-0.043** | **4.8** |
| **Au-Wz $CuGaS_2$** | **-1.57** | **13.2** |
| **Tg $CuGaS_2$** | **-0.035** | **3.5** |
| **Au-Tg $CuGaS_2$** | **-1.16** | **12.2** |