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Page 1 of 33

Observation of enhanced photocurrent response in M-CuInS₂ (M = Au, 1 2 Ag) heteronanostructures: phase selective synthesis and application † Abhisek Brata Ghosh,^a Namrata Saha,^a Arpita Sarkar,^a Amit Kumar Dutta,^a 3 Swarup Kumar Maji,^{*a*} and Bibhutosh Adhikary^{**a*} 4 5 6 ^aDepartment of Chemistry, Indian Institute of Engineering Science and Technology, 7 8 Shibpur, Howrah 711 103, West Bengal, India 9 *Corresponding author Tel: +91-3326684561 Ext. 512, Fax: +91-3326682916, 10 E-mail: bibhutoshadhikary@yahoo.in 11 *Electronic supplementary information (ESI) available: Fig S1 to S7 and Table S1 to S6. 12 CCDC reference numbers 940837 and 954069. For ESI and crystallographic data in CIF 13 format See DOI: 10.1039/ 14 The crystallographic data can also be obtained free of charge from the Cambridge 15 Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. 16 17 18 19 20 21 22 23 24 25 26 27

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28 Abstract

29 We report controlled synthesis of $CuInS_2$ in wurtzite and zinc blende phases by solution 30 based thermal decomposition of dual precursors $[In(acda)_3]$ (acda 2-31 (PPh₃ aminocyclopentene-1-dithiocarboxylic acid) and $[Cu(PPh_3)_2(acda)]$ = 32 triphenylphosphine) in the presence of appropriate surface-active agents. Furthermore, the preparation of M-CuInS₂ (M = Au and Ag) heteronanostructures on both the phases 33 34 has been achieved successfully by hot injection of respective gold and silver precursor 35 solution into the reaction mixture. The characterization of both pure and hybrid 36 nanostructures were carried out by X-ray diffraction (XRD), Uv-vis spectroscopy, 37 energy dispersive X-ray study (EDX) and transmission electron microscopy (TEM). 38 A detailed photovoltaic study has been performed with both pure materials and the 39 twin structures and their photocurrent and photoresponse behavior have been 40 compared. The study reveals that upon loading Au and Ag, the material exhibits high 41 photocurrent efficiency compared to pure CuInS₂. Appreciable increase in current density 42 ratio of light to dark confirms that these materials can be used in the fabrication of 43 promising photovoltaic devices.

44

52 Introduction

The decline of fossil fuel reserves along with simultaneous increase of global energy 53 54 consumption set a clear threat of energy crisis to the world. Consequently, much effort 55 has been focused to develop new functional materials with effective photo-induced carrier transport ability for using in inorganic photovoltaic cells.^{1,2} In the last few years, 56 57 nano-scaled ternary and multinary semiconductor sulfides of suitable band-gap have 58 drawn considerable attention for the fabrication of low cost high efficiency photovoltaic devices.³⁻⁵ Among them semiconductors of I-III-VI₂ class such as CuInS₂, CuInSe₂ 59 CuGaS₂, CuIn_xGa_{1-x}Se₂ have emerged as promising candidates for photovoltaic study as 60 their band gaps (1.4 - 2.2 eV) match well with the solar spectrum.⁶⁻¹¹ 61

62 In recent times, several successful colloidal synthetic methodologies have been developed for the synthesis of CuInS₂ of tunable size and shape.¹²⁻²⁰ In particular 63 64 synthesis based on solvothermal decomposition of suitable single-source or dual-source precursor complexes have turned out to be highly efficient.²¹⁻³⁰ The synthesis of CuInS₂ 65 66 by the thermal decomposition of sulfur bonded metal complex was first initiated by Hirpo et al. using (PPh₃)₂CuIn(SEt)₄.³¹ Later, the method was popularized by Vittal using 67 thiocarboxylate complexes of Cu(I) and In(III).^{23,26} Then after few years, Lu and his 68 69 coworkers have used dithiocarabamate complexes of In and Cu as dual source precursor to synthesize phase selective CuInS₂.²⁵ 70

71 More recently instead of pure semiconductor, metal-semiconductor 72 heteronanostructures have rapidly gained wide interest due to their exciting functional features.³²⁻³⁹ This type of coupled materials strongly influences the electron transport 73 74 property of the semiconductor and thereby improve their optoelectronic and photovoltaic performances.⁴⁰⁻⁴⁵ Significant attempts have been made to synthesize a heterostructure 75

with the semiconductors by coupling them with metallic silver, gold, palladium or
platinum. For example, studies have been made with hybrid materials like Au-Cu₂S, AuCdS, Au-CdSe, Au-SnS, Au-Cu₂ZnSnS₄, Pt-CuInS₂, Ag-AgInS₂ etc.⁴⁶⁻⁵⁴ However; in all
these cases the core issue that remained was to establish a proper synthetic strategy for
the formation of heteronanostructure.

In the present work, we report a facile synthetic protocol for the formation of Au-81 82 CuInS₂ and Ag-CuInS₂ heterostructures. CuInS₂ in two different crystallographic phases 83 viz wurtzite and zinc blende has been synthesized by solvothermal decomposition of 84 dithiocarboxylate complexes of indium and copper followed by in-situ coupling of metallic Au and Ag by hot-injection technique. The crystallographic study of precursor 85 86 complexes as well as the phase orientation and the microscopic analysis of the pure and 87 the hybrid materials have been studied in detail. Finally, photo-induced carrier transport 88 properties and photocurrent behaviors of both pure and coupled materials have been 89 investigated systematically.

90

91 Experimental

92 Materials

All chemicals obtained from commercial sources were used without further purification.
Ammonia, cyclopentanone, carbon disulfide, Cu(NO₃)₂.3H₂O, triphenylphosphine
(PPh₃) were purchased from Spectrochem Pvt. Ltd. (India). Indium (III) chloride (98%),
gold (III) chloride hydrate (99.9%), silver (I) acetate (>99.0%), oleylamine (OAm,
tech., 70%), 1-dodecanethiol (1-DDT, 98%), oleic acid (OA, tech., 90%),
trioctylphosphine oxide (TOPO, 99%), 1-octadecene (ODE, tech., 90%) and indium tin

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99	oxide (ITO) coated glass slides were purchased from Sigma-Aldrich. Solvents were used
100	as received.
101	
102	Synthesis
103	The ligand 2-aminocyclopentene-1-dithiocarboxylic acid (Hacda) and the starting
104	material Cu ^I (PPh ₃) ₂ NO ₃ were prepared according to the literature method. ^{55,56}
105	
106	Synthesis of precursor complexes
107	Preparation of In(acda) ₃ (1)
108	To a methanol solution (10 mL) of $InCl_3$ (0.221 g, 1 mmol), a solution of Hacda (0.475
109	g, 3 mmol) in the same solvent (10 mL) was added in dropwise manner. Yellow
110	precipitate appeared immediately. The stirring was continued for 30 min. The
111	precipitate was collected by filtration, washed thoroughly with methanol, diethyl
112	ether and dried in vacuum. X-ray quality single crystals were obtained by
113	recrystallising the solid from acetonitrile at room temperature. Yield 0.46 g (78%).
114	Anal. Calcd for C ₁₈ H ₂₄ InN ₃ S ₆ : C, 36.64; H, 4.07; N, 7.13. Found: C, 36.42; H, 3.94; N,
115	7.03 %. IR data (KBr pellet, cm ⁻¹): 3286 (s,br), 3062 (w,br), 2900 (m), 1615 (s), 1474 (s),
116	1450 (s), 1410 (m), 1318 (m), 1288 (m), 1213 (m), 1041 (m), 971 (m), 876 (s), 776 (w),
117	610 (s) cm ⁻¹ . UV–Vis [in DMF, λ_{max} , nm (ε/M^{-1} cm ⁻¹)] 325 (23700), 398 (126900).
118	

119 Preparation of Cu(PPh₃)₂(acda) (2)

[Cu(PPh₃)₂NO₃] (1.95 g, 3 mmol) was dissolved in 15 mL of dichloromethane. To
this a methanol (10 mL) solution of Hacda (0.475 g, 3 mmol) was added in a stirring

122 condition. The solution became wine red and stirring was continued for 30 min 123 during which a deep orange microcrystalline product was deposited. The compound 124 was filtered, washed with methanol and diethyl ether and dried in air. The single 125 crystals suitable for X-ray analysis were collected from 2:1 acetonitrile - dichloromethane solution at room temperature. Yield 1.39 g (62%). Anal. Calcd for C₄₂CuH₃₈NP₂S₂: C, 126 127 67.56; H, 5.09; N,1.87. Found: C, 67.25; H, 5.16; N, 1.96. IR data (KBr pellet, cm⁻¹): 128 3445 (m, br), 3055 (m, br), 1599 (s), 1512 (m), 1426 (s), 1305 (m), 1083 (m), 1023 (m), 989 (m), 922 (m), 748 (m), 694 (m). UV-vis [in acetonitrile, λ_{max} , nm ($\varepsilon / M^{-1} cm^{-1}$)] 438 129 130 (102110), 315 (65886).

131

132 Synthesis of nanoparticles by precursor decomposition

133 Wurtzite (Wz) CuInS₂ nanostructure

In a typical synthesis, In(acda)₃ (0.147 g, 0.25 mmol), Cu(PPh₃)₂(acda) (0.187 g, 0.25 134 135 mmol), 4.0 mL ODE, 1.0 mL OAm and TOPO (1 g, 2.58 mmol) were loaded in a two-136 necked round bottom flask. The solution was heated to 100 °C and degassed for ~ 20 min. 137 The temperature was raised to 260 °C under argon flow, kept it for 10 min and then 138 cooled to 210 °C. At this temperature 2 ml of DDT was swiftly injected into the reaction 139 vessel. The heating was further continued for 1 h. After cooling to room temperature, the 140 nanoparticles were precipitated by adding excess amount of dry ethanol. The product was 141 collected by centrifugation (8000 rpm, 10 min) and dispersed in toluene and again 142 reprecipitated with ethanol. The process was repeated several times for purification and then dried in vacuum. 143

144

145 Fcc Au - Wurtzite (Wz) CuInS₂ heterostructure

Initially, a stock solution of gold was prepared by dissolving HAuCl₄ (0.085 g, 0.25 mmol) in 3 ml OAm in a 25 ml two-necked round bottom flask. The solution was heated to 80 °C for 10 min under argon flow during which the light orange solution became colorless. The solution was cooled to room temperature and used as a gold source.

150 In(acda)₃ (0.147 g, 0.25 mmol), Cu(PPh₃)₂(acda) (0.187 g, 0.25 mmol), 4.0 mL 151 ODE, 1.0 mL OAm and TOPO (1 g, 2.58 mmol) were taken in a two-necked round 152 bottom flask and heated to 100 °C for ~20 min under vacuum. The mixture was heated to 260 °C under argon flow, maintained at this temperature for 15 min and then cooled to 153 154 210 °C. At this stage, 2 mL DDT was rapidly injected into the reaction flask and soon 155 after it the stock solution of gold was also injected. The reaction was continued for 156 another 1 h. After cooling to room temperature, the product was centrifuged and purified 157 using toluene as a solvent and ethanol as a nonsolvent.

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159 Fcc Ag - Wurtzite (Wz) CuInS₂ heterostructure

160 The stock solution of silver was prepared by dissolving AgOAc (0.042 g, 0.25 mmol) in 2 161 mL OAm and then heating the solution upto 120 °C for 10 min at inert condition. The 162 clear dark brown solution was used as a silver source.

163 The Ag - CuInS₂ was synthesized in the same way described above for Au 164 CuInS₂.

165

166 Zinc blende (Zb) CuInS₂ nanostructure

167 In a typical synthesis, In(acda)₃ (0.147 g, 0.25 mmol), Cu(PPh₃)₂(acda) (0.187 g, 0.25

168 mmol), 1 mL OA, 1 mL OAm and 2 mL ODE were taken in a two-necked flask and 169 heated to 100 °C under vacuum for 20 min. Then the temperature of the stirred mixture 170 was raised upto 260 °C under argon flow and kept at this condition for 1 h. Then the 171 mixture was cooled and the obtained product was collected and purified following the 172 same procedure described in case of wurtzite CuInS₂.

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174 Fcc Au – Zinc blende (Zb) CuInS₂ heterostructure

In(acda)₃ (0.147 g, 0.25 mmol), Cu(PPh₃)₂(acda) (0.187g, 0.25 mmol), 1 mL OA, 1 mL OAm and 2 mL ODE were loaded in a two-necked flask and degassed under vacuum at 100 °C for 20 min. Then the temperature was elevated to 260 °C at inert condition and previously prepared stock solution of gold was rapidly injected into the mixture. The temperature was lowered to 210 °C and kept at this condition for 1 h. After cooling the mixture to room temperature, the product was collected and washed thoroughly. The washing procedure was same as stated in the above cases.

182

183 Fcc Ag – Zinc blende (Zb) CuInS₂ heterostructure

184 The preparation was similar as that of Au - Zb CuInS₂.

185

186 **Physical mesurements**

187 Powder XRD patterns were obtained on a Philips PW 1140 parallel beam X-ray 188 diffractometer with monochromatic CuK α radiation (λ =1.540598 Å). Surface 189 morphologies were studied using a JEOL JEM-2100 transmission electron microscope 190 (TEM) working at 200 kV. Energy dispersed X-ray characterizations (EDX) were

191 performed in JEOL JSM-7100F. Infrared spectra were obtained in the range of 4000 -192 400 cm⁻¹ as pressed pellets in KBr on JASCO FT-IR-460 Plus. Absorption spectra and 193 were recorded on a JASCO V-530 UV-vis spectrophotometer. Impedance and I-V 194 measurements were carried out on μ -AUTOLAB III/FRA2 electrochemical workstation. 195 C, H and N elemental analyses were performed on a Perkin-Elmer model 2400 analyzer.

196

197 X-ray crystallography

198 The diffraction experiments were carried out at 120 K on a Bruker–APEX II SMART 199 CCD diffractometer using graphite–monochromated Mo–K α radiation ($\lambda = 0.71073$ Å). 200 The data were processed with SAINT, and absorption corrections were made with 201 SADABS.⁵⁷ The structures were solved by direct methods, expanded using Fourier 202 techniques and refined by full–matrix least–squares methods based on F² using SHELX– 203 97.^{58,59} The relevant crystallographic data for both the complexes are given in Table S1.

204

205 Photoelectrochemical measurements

206 The device for photo electrochemical measurement has been fabricated by the dropcasting method reported by Wang and his group.⁶⁰ Initially, the ITO coated glass slide 207 208 was washed thoroughly using water-acetone-isopropanol. Then the conducting side of an 209 ITO coated glass was drop coated with a concentrated solution of sample nanoparticles. 210 The film was then dried in air and annealed at 200 °C for 1 h to use it as a working 211 electrode. The photovoltaic characteristics and photo current response was measured 212 using linear sweep voltammetry within a potential range -1.0 to 1.0 V at a scan rate of 0.05 Vs⁻¹ using a 300 W Xe lamp. The photo sensitivity of the materials was investigated 213

by measuring the current in dark and under illumination chronoamperometrically by light
on-off cycle at a steady voltage of -0.61 V vs Ag/AgCl (0 V vs RHE) in 25 s intervals.
The whole study was performed using Ag/AgCl as a reference and Pt as a counter
electrode and 0.1 M Na₂SO₄ solution as the electrolyte (pH 7). Electrochemical
impedance measurements were carried out under illumination within the frequency range
100 kHz to 1Hz using a sinusoidal perturbation potential of 10 mV.

Photoelectrochemical reduction of a "sacrificial reagent" methyl viologen (MVCl₂) was performed to identify the reductive splitting of water.⁶¹ The experiment was carried out in a solution containing 0.01 M MV^{2+} in 0.1 M Na₂SO₄ (pH 7) using the same three electrode system where Au-Wz CuInS₂ thin film was used as the photocathode. A steady potential of -0.61 V (vs Ag/AgCl) was applied under dark as well as illuminated condition and the consequent change in the color of the thin film surface was observed.

226

227 **Results and discussion**

228 Description of crystal structures

229 The structure of In(acda)₃ consists of two independent units which nominally differ in the 230 In-S bond distances and S-In-S bond angles. A perspective view of one of the In(acda)₃ 231 units is shown in Fig. 1a. Indium is bonded with six sulfur atoms of three bidentate acda 232 ligands leading to a InS₆ polyhedron where the donor atoms are located at an average 233 distance of 2.60 (2) Å from the metal center. Refinement of the structures was slightly 234 complicated by the fact that the atoms C3 and C16 are both disordered over two positions 235 sitting above and below the plane of the other three atoms in the five-membered rings. 236 Furthermore, the acda ligand containing S14 and S15 (in another unit of $In(acda)_3$) is 237 disordered such that the five membered ring has a minor component (of 0.29 occupancy)

238 related by a 180° rotation around the C25-C26 bond. Some restraints were used in order 239 to ensure a smooth refinement. Selected bond lengths and bond angles are listed in Table 240 S2 and S3 (in ESI[†]) respectively. The results clearly reveal that in both the units, the 241 trans angles are much lower than 180°, which indicates that the geometry of the complex 242 is highly distorted octahedral. The average In-S distance and the value of trans S-In-S 243 good angles obtained here are in agreement with those observed for $In \{S_2CN(CH_2CH_2)_2O\}_3$ by Kaim et al.⁶² 244

The crystal structure of Cu(PPh₃)₂(acda) (Fig. 1b) is triclinic with space group *P*-*I*. Cu(I) is bonded with the S atoms of one bidentate acda ligand and the P atoms of two monodentate triphenylphosphine ligands acquiring a distorted tetrahedral geometry. Selected bond lengths and bond angles are given in Table S2 and S3 (in ESI[†]) respectively. The average Cu(I)-S bond distance is found to be (2.412 Å) larger than that of Cu(I)-P distance (2.265 Å).



Fig. 1 A perspective view of the structures: (a) In(acda)₃ (1) and (b) Cu(PPh₃)₂(acda) (2).
Minor components of the disorder in (1) have been omitted for clarity.

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262 Synthesis and characterization of nanoparticles

According to the previous reports, several attempts have been made to synthesize CuInS₂ 263 till date.⁶³⁻⁶⁵ Most of them were involved in the reaction of different copper and indium 264 precursors with various sulfur sources.^{12-14,19,20} For example, Korgel and his group has 265 prepared CuInS₂ by the reaction of acetylacetonato complexes of In and Cu along with 266 sulfur powder at high temperature.¹³ Some other groups have used acetate salt of metals 267 (Cu and In) and alkylthiol mixture in a high boiling solvent to prepare CuInS₂.^{12,14} In one 268 of these cases, extra care was taken to remove Cu₂S from the surface of CuInS₂, 269 generated as a byproduct during synthesis.¹⁴ Recently, Tang *et al.* reported an interesting 270 observation where Cu and In precursors were allowed to react with DDT and ODE at 271 high temperature.²⁰ They obtained all three phases (wurtzite, zinc blende and 272 chalcopyrite) by the manipulation of anions of Cu and In sources and adjusting their 273 274 concentrations during synthesis. They have also synthesized CuInS₂ hexagonal nanoplate of different thickness and composition by varying reaction temperature and time.¹⁹ In our 275 276 work, as outlined in scheme 1, we have not only made a clear synthetic protocol of preparing CuInS₂ in two phases (Wz and Zb) but also introduced a facile route to 277 278 fabricate M-CuInS₂ (M = Ag, Au) hybrid nanostructure.

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- 283



Scheme 1 Scheme of the synthesis of CuInS₂ (Wz and Zb) and M-CuInS₂ (M = Au, Ag)
heteronanostructure.

295 Both wurtzite and zinc blende nanocrystals have been synthesized by the co-296 decomposition of $In(acda)_3$ and $Cu(PPh_3)_2(acda)$ in presence of appropriate surface active 297 stabilizers. In overall synthetic process ODE has been used as solvent and OAm has 298 served as activating agent which significantly lowers the decomposition temperature of 299 molecular precursor. In our experiment, we observed the surfactant-dependent phase 300 stabilization of $CuInS_2$ where surface active stabilizers play a crucial role in phase 301 selectivity. Pure wurtzite CuInS₂ was obtained when DDT was used as surfactant along 302 with TOPO during the decomposition of precursors. In our previous study, we explained the multipurpose use of DDT in nanopaticle synthesis.⁶⁶ However, in this case DDT is 303 probably acting as a stabilizer of wurtzite phase.^{25,26} On the other hand TOPO is acting as 304 305 a passivating agent as well as a stabilizer which can readily binds to the surface of the 306 growing nanoparticles to reduce the surface energy and to protect nanocrystals from





Fig. 2 Powder X-ray diffraction pattern of (a) Wz CuInS₂ (No. 186), (b) Zb CuInS₂
(JCPDS No. 75-0106).

331 It has already been established that the coupled structure formation occurs in three 332 different ways: 1) epitaxial growth of one material on another, 2) recrystallization of one 333 material on the other and 3) thermal fusion of a particular lattice plane of two previously formed materials.^{67,68} In our case, we have adopted the first approach of synthesis 334 335 (Scheme 1). The Au and Ag seeds were prepared separately by the reduction of 336 corresponding metal salts in OAm at inert condition and then rapidly injected into the 337 reaction system containing the Cu(I) and In(III) precursors. The formation of hybrid 338 growth was confirmed by the X-ray powder diffraction patterns shown in Fig. 3. The observed patterns ensured that growth of Au and Ag has been taken place on both 339 340 wurtzite (Fig. 3a and 3c) and zinc blende (Fig. 3b and 3d) CuInS₂ successfully. Apart 341 from the reflections of corresponding Wz and Zb CuInS₂ planes, the additional peaks obtained at 20 values of approximately 38.5°, 44.3°, 64.6° and 76.9° can be indexed to 342 343 the lattice planes (111), (200), (220) and (311) of fcc Au (JCPDS no. 04-0784, space 344 group = Fm3m and cell constant a = 4.078 Å) and Ag (JCPDS no. 03-0931, space group 345 = Fm3m and cell constant a = 4.074 Å).

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- 349
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- 351



Fig. 3 Powder X-ray diffraction pattern of (a) fcc Au - Wz CuInS₂, (b) fcc Au - Zb
CuInS₂, (c) fcc Ag - Wz CuInS₂ and (d) fcc Ag - Zb CuInS₂.

The heterostructure formation was further indicated by Uv-vis absorption spectra of hybrid CuInS₂. The sharp plasmon resonance peak of pure metallic gold nanoparticle appeared at 523 nm (Fig. S1a in ESI[†]) was significantly broadened and red shifted to 730 nm on coupling with CuInS₂. This phenomenon was commonly observed in Au based heterostructures due to the delocalization of Au plasmon over the coupled semiconductors.⁶⁹⁻⁷⁰ The band gaps of the corresponding nanoparticles have been calculated from the Tauc's plot.⁷¹ CuInS₂ of both wurtzite and zinc blende phases exhibited the band gap of ~ 1.7 eV which was further dropped to ~1.4 eV on formation of twin structure (Fig. S1b in ESI[†]).

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383 Morphological investigation and TEM analysis

384 Fig. 4(a-d) shows low and high resolution TEM images of Wz and Zb CuInS₂. The Wz 385 material in Fig. 4a and 4b appears to be quasi-spherical of diameter ranging from 18-27 386 nm (particle size distribution is shown in Fig. S2 in ESI⁺). HRTEM image shown in Fig. 387 4b inset reveals clearly the lattice fringes with spacing $d = 0.318 \pm 0.002$ nm 388 corresponding to (002) lattice plane of Wz structure. Fig. 4c represents the TEM image of 389 Zb CuInS₂ with triangular shape of length 20 ± 3 nm. The lattice fringe of the material is 390 shown in Fig. 4c (inset). The calculated d spacing is 0.196 ± 0.004 nm and corresponds to 391 the (220) reflection plane of Zb phase. The SAED pattern shown in Fig. 4d reveals 392 crystalline nature of the material and the (112), (200) and (220) planes of Zb phase can be 393 labeled clearly. The average crystal size of the materials can be estimated on the basis of 394 Debye-Scherrer equation $D = 0.94\lambda/\beta\cos\theta$, where β is the peak width at half maxima. The strongest peak at $2\theta = 27.76^{\circ}$ for the Wz pattern and at 27.88° for the Zb pattern 395 396 respectively were used to calculate their grain size, which are nearly 28 and 27 nm 397 respectively.



413 Fig. 4 TEM images of (a) Wz CuInS₂ (low magnification), (b) Wz CuInS₂ (high
414 magnification) and (c) Zb CuInS₂ (low magnification). (d) SAED pattern of Zb CuInS₂.
415 4b inset) HRTEM image of Wz CuInS₂, 4c inset) HRTEM image Zb CuInS₂.

416

Fig. 5a shows a wide view of TEM image of Au-Wz CuInS₂ heteronanostructure. Fig. 5a inset represents the TEM image of single heterostructure where Au is attached to the corner of CuInS₂. The interface combination between Au and Wz CuInS₂ has been shown in Fig. 5b which clearly reveals that the epitaxy is formed by the matching of $5d_{(111)}$ of

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421 Au and 4d₍₁₁₁₎ Wz CuInS₂. The measured interplanar d spacings of 0.301 and 0.234 nm 422 can be assigned to (101) plane of Wz CuInS₂ and (111) plane of cubic Au(0), 423 respectively. The selected area electron diffraction (SAED) image at the interface area of 424 Au-Wz CuInS₂ shown in Fig. 5c supports the epitaxial junction formation as both Wz 425 $CuInS_2$ (101) and Au (111) planes are identified. In contrast, the situation of the epitaxy formation at the junction of Au-Zb CuInS₂ is quite different. Here the (111) plane of fcc Au is coupled with a different plane of Zb CuInS₂ than observed for Wz CuInS₂. Fig. 5d, e and f display the TEM and HRTEM images of the Au-Zb CuInS₂ heterostructure. Fig. 5e reveals the HRTEM image of single heterostructure where Au nanocrystal is located at the periphery of the Zb CuInS₂. As shown in Fig. 5f, the interface combination of Au and Zb CuInS₂ is observed between $4d_{(111)}$ of Au and $3d_{(112)}$ Zb CuInS₂. The lattice line spacing of 0.32 nm and 0.234 nm can be assigned to (112) plane of Zb CuInS₂ and (111) plane of fcc Au, respectively. The corresponding SAED pattern (Fig. S3 in ESI⁺) also supports the coexistence of both Zb CuInS₂ and gold.



Fig. 5 (a) TEM images of Au-Wz CuInS₂ (low magnification), inset (a) TEM image of a
single Au-Wz CuInS₂ hetrostructure, (b) HRTEM image indicating the interface
combination of Au and Wz CuInS₂, (c) SAED pattern of Au-Wz CuInS₂. (d) TEM image
of Au-Zb CuInS₂ (low magnification), (e) Zoomed view of a single Au-Zb CuInS₂
heterostructure and (f) HRTEM image of Au-Zb CuInS₂

462

463 The morphology of the Ag-CuInS₂ heterostructure is depicted in the high 464 magnification TEM images shown in Fig. S4 (in ESI⁺). The significant difference 465 observed in the growth pattern of Ag-CuInS₂ is that like gold, silver is not deposited 466 along a particular facet of CuInS₂. Fig. S4 (in ESI⁺) reveals that the silver decoration on

the surface of both Wz and Zb $CuInS_2$ is random and haphazard compared to that of gold and therefore it clearly rules out the chance of epitaxy formation. Moreover, when we tried to analyze the HRTEM images of the Ag-CuInS₂, no epitaxial junction along a specific facet was found. Hence, from the microscopic analysis it is evident that the growth of silver on semiconductor is non epitaxial.

To gain a better understanding of the elemental distribution in these nanomaterials EDX study was performed with the pure Wz CuInS₂ and M - Wz CuInS₂ (M = Au, Ag) heterostructure (Fig. S5 in ESI). The elemental ratio of Cu:In:S in bare CuInS₂ has been determined to be 1:1.07:1.98, which corroborates well with the required stoichiometric ratio of 1:1:2. In the case of coupled structure, the study clearly indicates the presence of Au and Ag along with Cu, In and S in Fig. S5b and c (in ESI[†]) respectively.

478

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479 Photovoltaic performances

480 To investigate the electron transfer ability of the materials the electrochemical impedance 481 measurements have been performed. Fig. S6 (in ESI⁺) shows typical Nyquist plots of 482 pure CuInS₂, Au-CuInS₂ and Ag-CuInS₂ of both Wz (Fig. S6a) and Zb (Fig. S6b in ESI⁺) 483 phases. A characteristic semicircle has been obtained in all the cases indicating a single 484 charge transfer process taking place between the working material and electrolyte. Hence, 485 it has been fitted on the basis of the Randles equivalent circuit model (Fig. S6c in ESI[†]) containing a solution resistance (R_s) , a charge transfer resistance (R_{Ct}) and a constant 486 phase element (Q).⁷² In the Nyquist plot, the high frequency limit of the semicircle 487 488 represents the solution resistance R_s whereas the low frequency limit indicates the sum of 489 solution resistance and charge transfer resistance (R_s+R_{Ct}) . The parameters associated

490 with electrochemical impedance measurement are given in Table S4 (in ESI⁺). From Fig. 491 S6 (in ESI⁺), it is clearly evident that in the cases of both phases, the Au-CuInS₂ 492 heterostructure display the smallest arc radius ($R_{\rm Cl}$) compared to that of Ag-CuInS₂ and Published on 09 December 2016. Downloaded by University of California - San Diego on 10/12/2016 06:51:37. 493 pure CuInS₂ indicating fastest charge transport ability of Au-CuInS₂ over the others. The 494 data given in Table S4 (ESI[†]) substantiate it. 495 0.15 Wz CulnS Under dark 0.10 496 Under illumination 0.05 497 0.00



Fig. 6 Current density versus voltage plots for (a) Wz CuInS₂, (b) Au-Wz CuInS₂ and (c) 508 509 Ag-Wz CuInS₂ under dark and under illuminations. (d) Current density versus time plots 510 during successive on and off cycles of light for Wz CuInS₂, Au-Wz CuInS₂ and Ag-Wz 511 CuInS₂ at -0.61 V vs Ag/AgCl.

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513 In Fig. 6, the photovoltaic characteristics and the temporal photocurrent response 514 property has been shown. The photocurrent generated by the pure and the hybrid 515 materials was evaluated using linear sweep voltammetry and the choronoamperometric 516 measurements under chopped light illumination. Fig. 6a, b and c exhibit the current 517 density (J) versus voltage plots of Wz CuInS₂, Au-Wz CuInS₂ and Ag-Wz CuInS₂ 518 nanostructures respectively in dark and under light. In all the cases, the current density 519 under light and the photocurrent gain (Ilight/ Idark) is significantly higher for the coupled 520 structure than the pure one (Table S5 in ESI⁺). The photocurrent density value reported 521 here is also comparable with that of obtained for several CuInS₂ based heterstructures 522 (Table S6 in ESI⁺). In the case of pure Wz CuInS₂ at -0.61 V bias vs Ag/AgCl (0 V vs RHE), the value of Ilight/ Idark is 3.4, while for Au-Wz CuInS2 and for Ag-Wz CuInS2 the 523 524 values are 10.1 and 8.4 respectively. The higher photocurrent value of Au-CuInS₂ than 525 that of pure CuInS₂ and Ag-CuInS₂ is attributed to the effective exciton-plasmon coupling 526 (Fig. 7) taking place in Au-CuInS₂ which enhances the electron transfer behavior and hence the photocurrent density.⁵³ To investigate the photostability of the material the 527 528 current density versus time measurements have been carried out by consecutive light on 529 and off mode at 25 s intervals at a constant potential (-0.61 V vs Ag/AgCl). The plots of 530 current density versus time obtained for Wz CuInS₂, Au-Wz CuInS₂ and Ag-Wz CuInS₂ are shown in Fig. 6d. The study reveals that both the heterostructures have greater 531 532 stability with no loss of current density over a period of 250 s whereas the pure Wz 533 $CuInS_2$ shows a steady decrease of current density with time. The result indicates that the 534 coupling of metallic Au and Ag enhances the photocurrent sensitivity and photostability 535 of the semiconductor material. Similar feature has also been observed for CuInS₂, Au536 CuInS₂ and Ag-CuInS₂ of the Zb phase (Fig. S7 in ESI[†]). The superior carrier transport 537 phenomenon can be explained by the fact that both Ag and Au exhibit metallic character 538 to some extent in the heterostructures which efficiently restrain the recombination of 539 photogenerated electrons. This in turn helps easy transportation of charge carriers along 540 the semiconductor under illumination resulting high photocurrent efficiency.⁵³



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549 Fig. 7 Schematic representation of plasmon-exciton coupling occurs in Au-CuInS₂
550 heterostructure due to epitaxial growth.

In order to investigate the photoelectrochemical reduction performance of the material, we have performed the reduction of methyl viologen under a certain applied bias. On illumination, a deep blue color precipitate of methyl viologen cation radical (MV^{+*}) , which is the photoreduced product, was found to deposit on the working electrode surface $(MV^{2+}_{colorless} to MV^{+*}_{blue})$ indicating the reductive splitting of water.⁶¹

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560 Conclusion

In summary, we report a simple colloidal approach of synthesis of CuInS₂ in two phases 561 (Wz and Zb) from dual precursors In(acda)₃ and Cu(PPh₃)₂(acda). During synthesis the 562 563 surface active agents play a major role in the phase selectivity. Furthermore, we have also 564 developed a simple route to fabricate the Au-CuInS₂ and Ag-CuInS₂ heteronanostructure 565 on both wurtzite and zinc blende phases successfully. From HRTEM characterization, we 566 can conclude that the heterostructure between the metal and the semiconductor has been 567 formed epitaxially for gold in both the phases to a particular lattice plane. In addition, our 568 study confirms the generation of a new material with promising applications. The 569 photocurrent efficiency of both pure and hetero nanomaterials have been investigated and 570 the corresponding results revealed that the photocurrent sensitivity and photostability 571 follow the order of Au-CuInS₂ > Ag-CuInS₂ > CuInS₂ for both the phases. This improved 572 charge transport ability is definitely attributed to the incorporation of metal on the 573 semiconductor which helps to migrate the semiconductor electrons through the metal and 574 thus resulting the photocurrent hike. Finally we believe that our findings will not only 575 open up a broad area of research of metal-semiconductor heterostructure synthesis but 576 also provide a deep fundamental insight on designing new functional materials essential 577 for renewable energy conversion and storage.

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New Journal of Chemistry

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Table of Contents

We demonstrate the phase selective synthesis of M-CuInS₂ (M = Au and Ag) heteronanostructure and their enhanced photocurrent activity compared to pure CuInS₂.

