Supporting information for

“$Cu_xAg_yIn_zZn_kS_m$ solid solutions customized with RuO_2 or $Rh_{1.32}Cr_{0.66}O_3$ co-catalyst display visible light driven catalytic activity for CO_2 reduction to CH_3OH”

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Contents:

Experimental

Preparation of photocatalysts

For a specific example, the preparation of $Cu_{0.37}Ag_{0.15}In_{0.80}Zn_{0.54}S_2$ will be described here. To a well stirred solution of water was added NH_4OH (100 ml, 33%), $AgNO_3$ (0.2775 gm, 1.6 mmol), $In(NO_3)_3$ (0.9820 gm, 3.3 mmol), $Zn(NO_3)_2.6H_2O$ (1.9423 gm, 6.5 mmol) and CuCl (0.1616 gm, 1.6 mmol; freshly prepared by the reduction of $CuCl_2.2H_2O$ {0.1364 gm, 0.8 mmol} with metallic Cu {0.0508 gm, 0.8 mmol} in boiling dilute hydrochloric acid {10 ml, 0.01 M}) was added one after the other. The stirring was continued for further 30 min at room temperature. To this solution thioacetamide (3.4733 gm, 45.7 mmol) in small portion was added to when grayish precipitate of a metal sulfide hybrid photocatalyst was immediately formed in reaction mixture. After centrifugation for 15 min, the catalyst separated from water was dried in an oven at 100°C for two days. The completely dried sample of catalyst was grinded and stored in vacuum desiccators before further use.

The co-catalyst loadings were made by dispersing the bare catalysts in a reactant solution, containing an appropriate amount of $(NH_4)_2$-$[RuCl_6]$ (29.9 % as Ru; 1 wt %) and irradiated to visible light for 1 minute. Alternatively, $Na_3RhCl_6.2H_2O$ (97 % as Rh; 1.32 wt %) and $Cr(NO_3)_3.9H_2O$ (99.9 % as Cr; 0.66 wt %) were used thermally as precursors for loading of RuO_2 or $Rh_{1.32}Cr_{0.66}O_3$ co-catalysts.[1]

Photocatalytic reduction of CO_2 to CH_3OH

The reduction of CO_2 was achieved in a Pyrex inner irradiation type reaction vessel connected to a closed glass gas circulation system. The catalysts (0.05 gm) with or without co-catalysts were dispersed in distilled water containing $NaHCO_3$ (0.21 gm, 2.5 mmol). The reaction mixture was irradiated under 1000 W high-pressure Xenon lamp at > 400 nm via a Pyrex glass tube, filled with aqueous solution of $NaNO_2$ (50 ml, 2M) in order to prevent the exposure of ultraviolet radiation. We found that the ~ 436 nm emission from high-pressure mercury lamp is primarily accountable for driving the reaction. The evolved product, CH_3OH was analyzed by GC-FID.

Determination of CH_3OH concentration

The analysis of methanol formation was performed by GC-FID. In particular, the retention time of each of the components was compared with those of known standards, having the same compounds. The concentration of methanol was determined from calibration curves (**Figure S1**) which in turn were obtained from the analysis of standard solutions.

The GC-FID standard calibration solutions were prepared by serial dilution of stock solutions. The concentrated solutions of more than 40 mg/L were diluted within the calibration range (1 to 40 mg/L) and calculated. The response of each analyte versus concentration was measured and plotted. Specifically, if the value of correlation coefficient of graph is greater than 0.99, the calibration is acceptable and thus equation of the line can be used in all subsequent calculations.[2]

Proposed Mechanism

$$CO_2 + H^\bullet \rightarrow O = C^\bullet - OH$$

$$O = C^\bullet - OH + H^\bullet \rightarrow HCOOH$$

$$HCOOH + 2H^\bullet \rightarrow H_2C(OH)_2 \rightarrow H_2O + HCOH$$

$$HCOH + 2H^\bullet \rightarrow CH_3OH$$

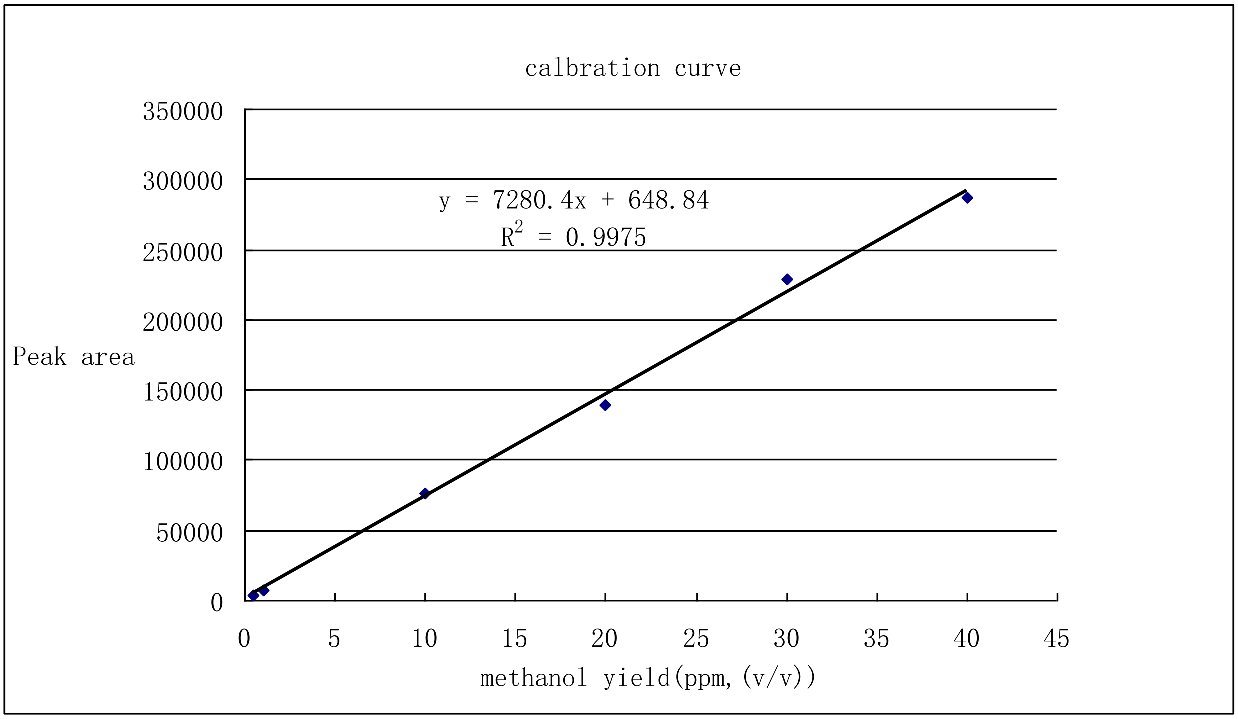


Figure S1 Calculation of the methanol yield (μmol g^{-1} h^{-1}) by standard methanol calibration curve using equation (1):

Yield (μmol g^{-1} h^{-1}) =

$$\left[\frac{(Area-648.84)}{7280.4}\right]\times ppm\left(\frac{V}{V}\right)\times V_{rxn}(mL)\times D_{methanol}\left({}^{g}\!/_{mL}\right)\div M.W.(g)\div W_{catalyst}(g)\text{……….(1)}$$

$V_{rxn}(mL)$: reaction solution volume (mL)

$D_{methanol}$: density of methanol (g/mL)

$M.W.$: molecular weight of methanol (g)

$W_{catalyst}$: catalyst amount (g)

= [(Area-648.84)/ 7280.4] × 10^{-6} × 25 × 0.8/ 32/ 0.05…………………………………….(1)

Materials and Methods

All dried solvents, chemicals, and gases commercially available were used as received without further purification. NH_4OH was purchased from Fluka. $AgNO_3$ of 99.8% was purchased from Tanaka Kikinzoku and was stored in dried box before use. $In(NO_3)_3$ and $Na_3RhCl_6.2H_2O$ were purchased from Kojundo and Kanto Chemicals respectively. All other chemicals of analytical grade including $Zn(NO_3)_2.6H_2O$, $CuCl_2.2H_2O$, $(NH_4)_2$-$[RuCl_6]$, and $Cr(NO_3)_3.9H_2O$ were purchased from Wako Pure Chemicals.

The X-ray diffraction spectra were recorded on Shimadzu, XRD-6000 spectrophotometer at room temperature with the Cu K_a (α =1.5405 Å) radiation source, operating at 40 kV and 20 mA. The Diffuse reflection spectra were recorded on UV-visible NIR spectrometer (Shimadzu, UV-2450). Further, Kubelka-Munk method was used to convert reflection spectra to the corresponding absorbance spectra. The photocatalytic production of methanol was determined by gas chromatograph/ flame ionization detector (GC-FID; GC-8900, China Chromatography) using Poropack-QS column with helium as carrier gas. The size and morphology of photocatalysts were determined by scanning electron microscope (JEOL; JSM-6500 F). The sizes of co-catalysts were studied by transmission electron microscope (JEOL; JEM-2010 TEM).

Results

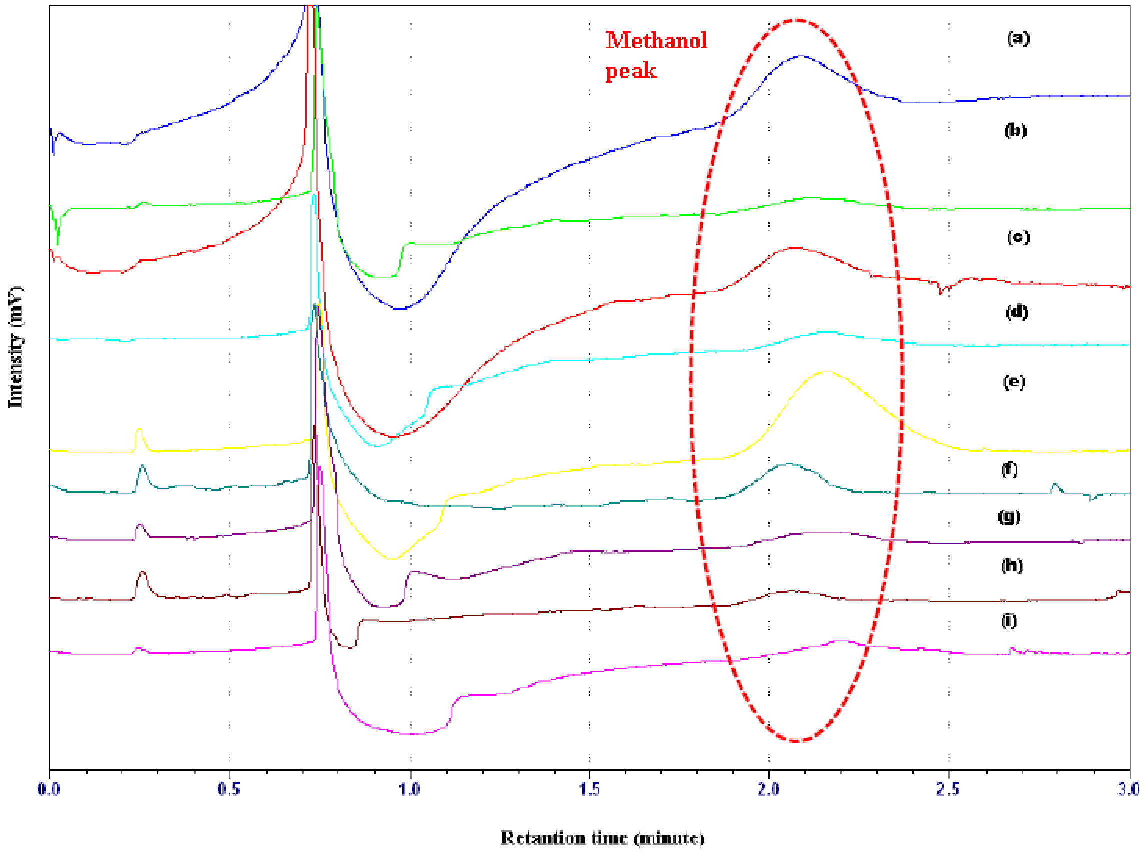


Figure S2. The Photocatalytic production of methanol: The GC-FID chromatogram in the presence of (a) $Cu_{0.00}Ag_{0.09}In_{0.23}Zn_{1.61}S_2$; (b) $Cu_{0.23}Ag_{0.21}In_{0.19}Zn_{1.50}S_2$; (c) $Cu_{0.30}Ag_{0.07}In_{0.34}Zn_{1.31}S_2$; (d) $Cu_{0.12}Ag_{0.30}In_{0.38}Zn_{1.22}S_2$; (e) $Cu_{0.45}Ag_{0.13}In_{0.24}Zn_{1.35}S_2$; (f) $Cu_{0.37}Ag_{0.15}In_{0.80}Zn_{0.54}S_2$; (g) $Cu_{0.05}Ag_{0.20}In_{0.06}Zn_{1.78}S_2$; (h) $Cu_{0.48}Ag_{0.34}In_{0.36}Zn_{1.05}S_2$ and (i) $Cu_{0.12}Ag_{0.13}In_{0.57}Zn_{1.02}S_2$.

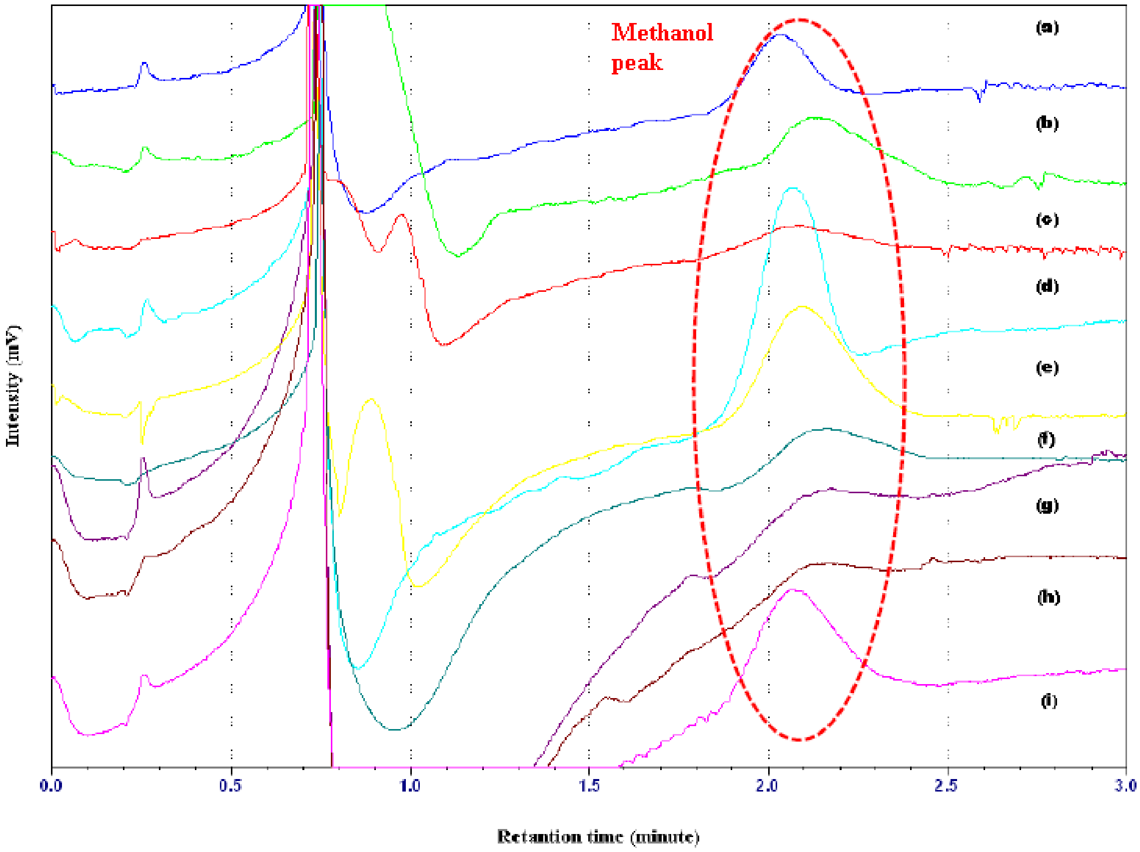


Figure S3. The Photocatalytic production of methanol: The GC-FID chromatogram in the presence of (a) $Cu_{0.00}Ag_{0.09}In_{0.23}Zn_{1.61}S_2$; (b) $Cu_{0.23}Ag_{0.21}In_{0.19}Zn_{1.50}S_2$; (c) $Cu_{0.30}Ag_{0.07}In_{0.34}Zn_{1.31}S_2$; (d) $Cu_{0.12}Ag_{0.30}In_{0.38}Zn_{1.22}S_2$; (e) $Cu_{0.45}Ag_{0.13}In_{0.24}Zn_{1.35}S_2$; (f) $Cu_{0.37}Ag_{0.15}In_{0.80}Zn_{0.54}S_2$; (g) $Cu_{0.05}Ag_{0.20}In_{0.06}Zn_{1.78}S_2$; (h) $Cu_{0.48}Ag_{0.34}In_{0.36}Zn_{1.05}S_2$ and (i) $Cu_{0.12}Ag_{0.13}In_{0.57}Zn_{1.02}S_2$.

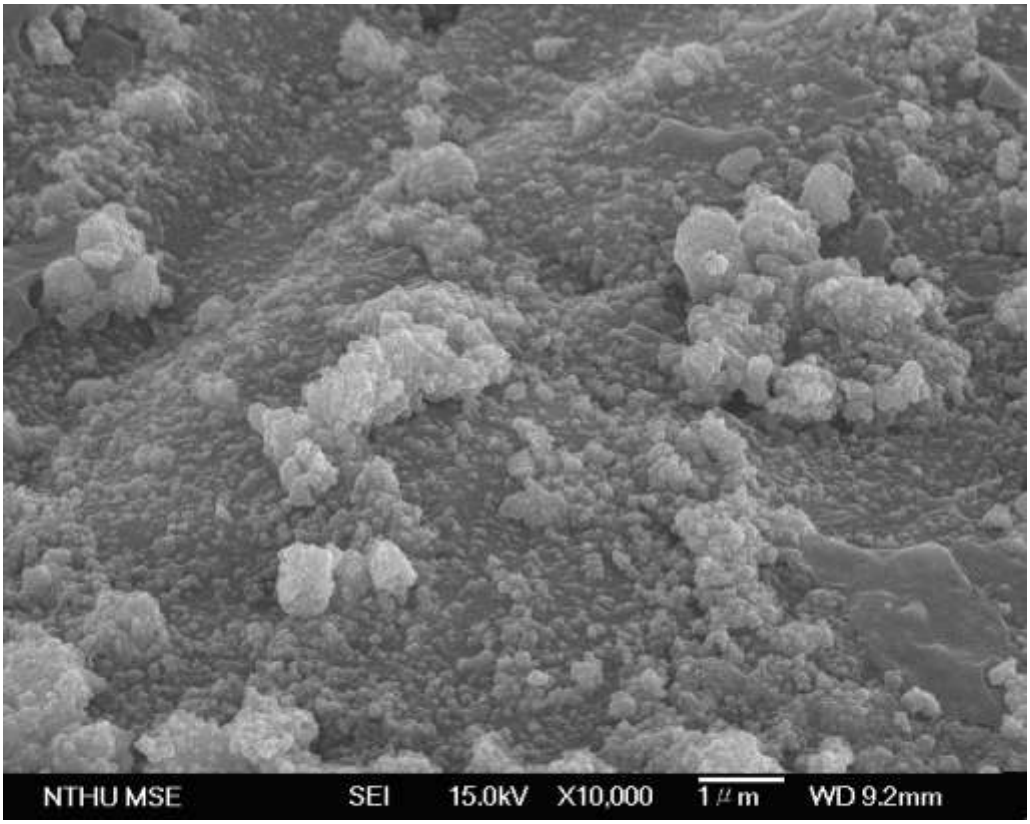


Figure S4. The SEM image of $Cu_{0.00}Ag_{0.09}In_{0.23}Zn_{1.61}S_2$ solid solution

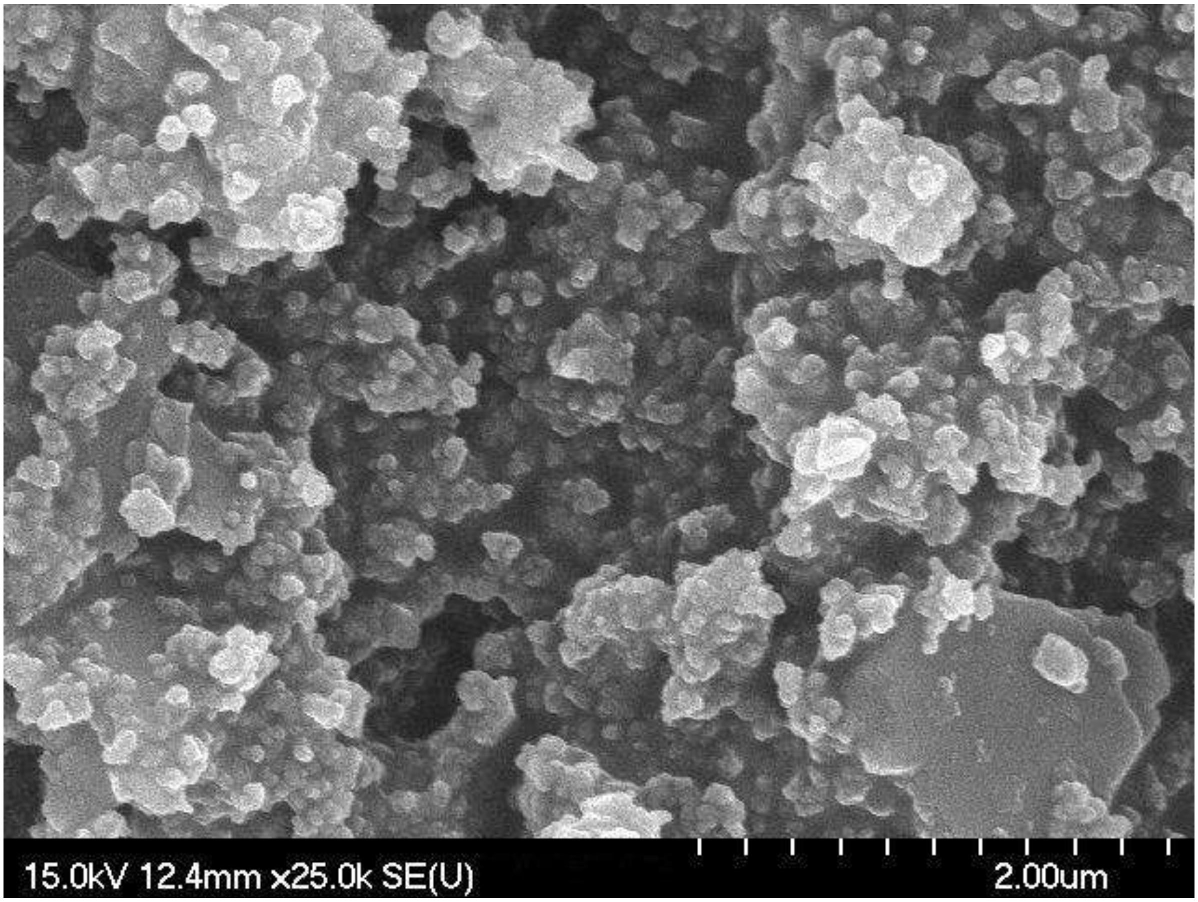


Figure S5. The SEM image of $Cu_{0.30}Ag_{0.07}In_{0.34}Zn_{1.31}S_2$ photocatalyst

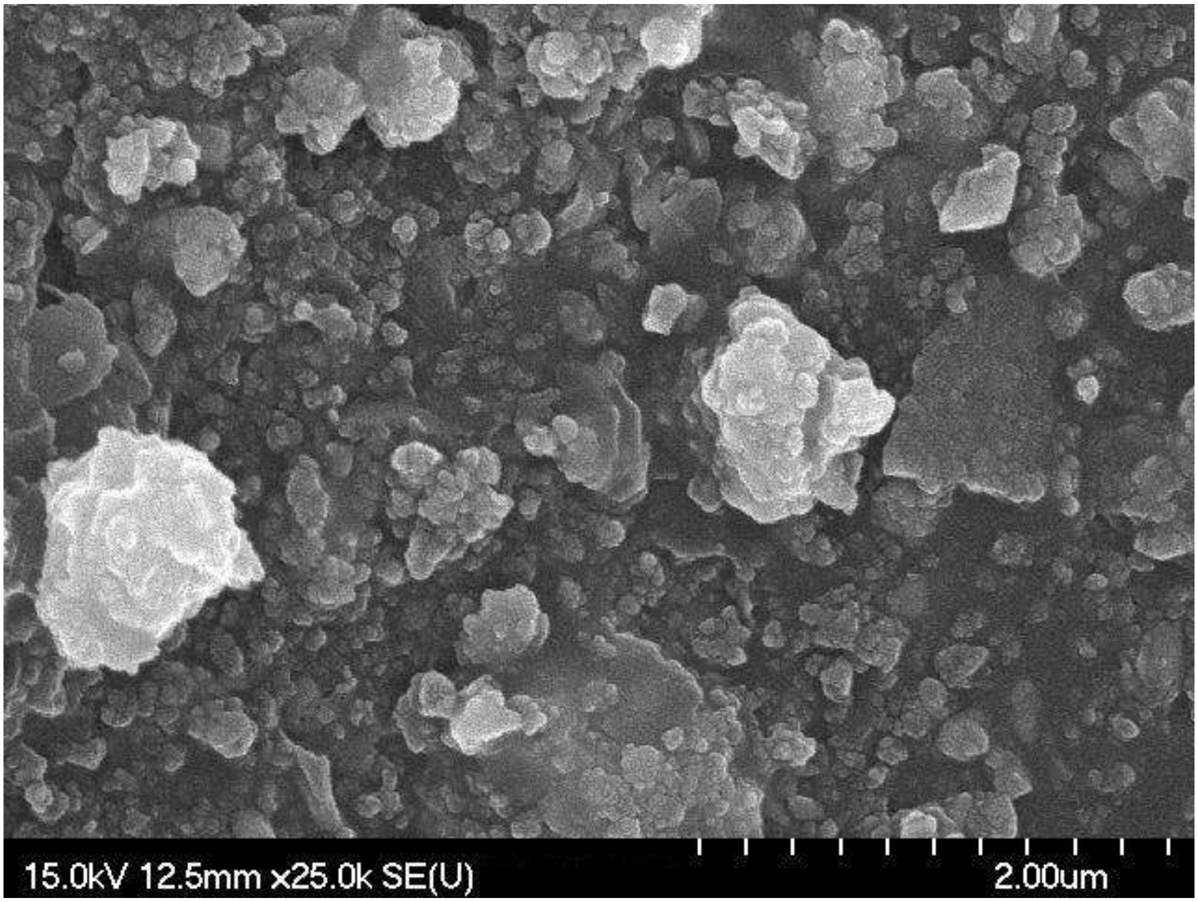


Figure S6. The SEM image of $Cu_{0.12}Ag_{0.30}In_{0.38}Zn_{1.22}S_2$ photocatalyst

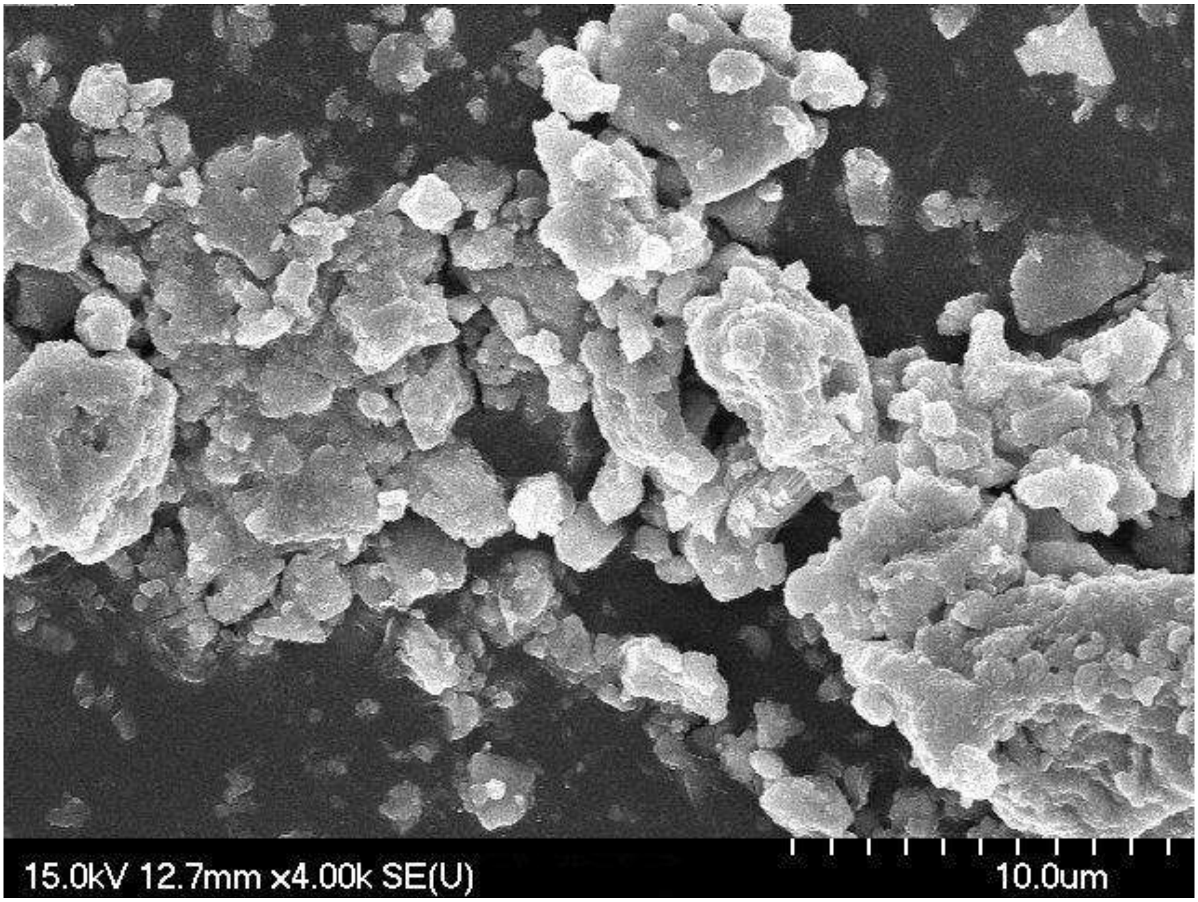


Figure S7. The SEM image of $Cu_{0.12}Ag_{0.13}In_{0.57}Zn_{1.02}S_2$ photocatalyst

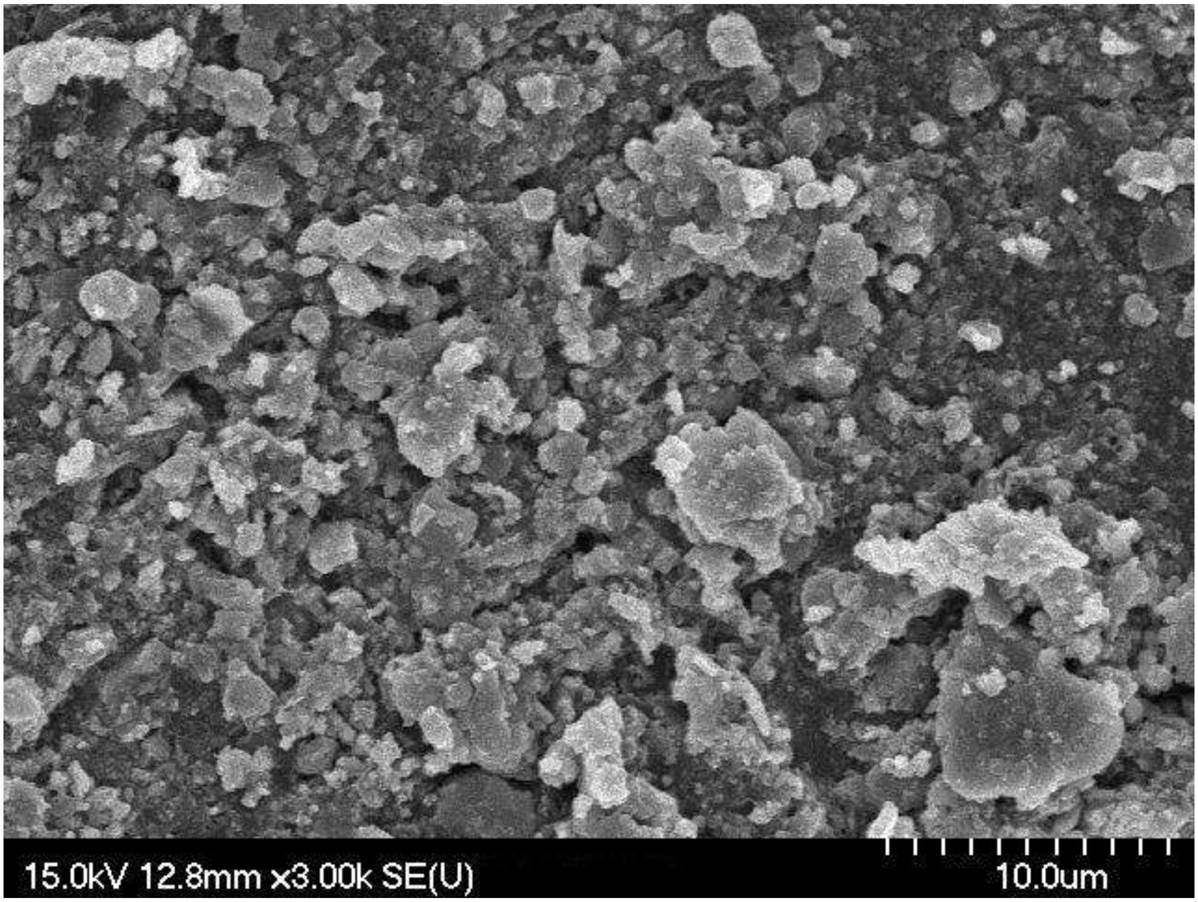


Figure S8. The SEM image of $Cu_{0.45}Ag_{0.13}In_{0.24}Zn_{1.35}S_2$ photocatalyst

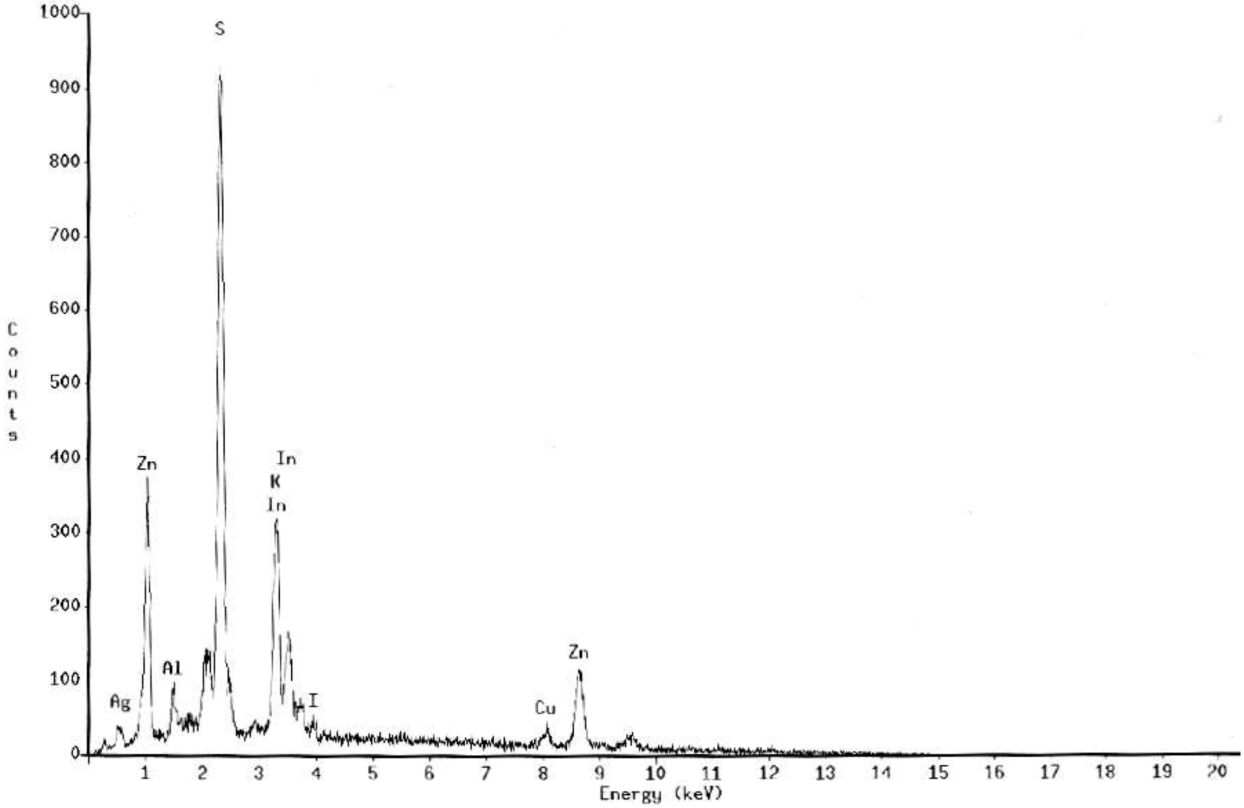


Figure S9. The energy dispersive X-ray spectrum of $Cu_{0.00}Ag_{0.09}In_{0.23}Zn_{1.61}S_2$ photocatalyst.

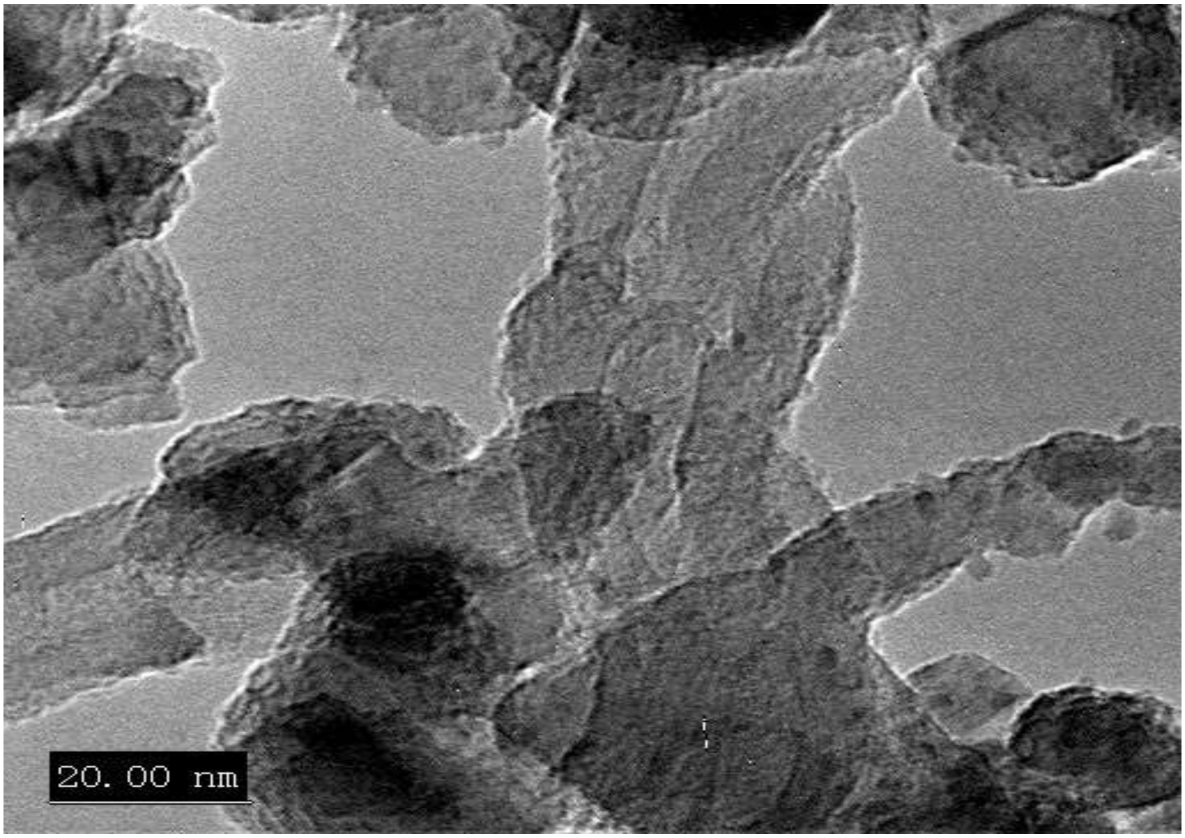


Figure S10. The TEM image of RuO_2 loaded $Cu_{0.00}Ag_{0.09}In_{0.23}Zn_{1.61}S_2$ photocatalyst showing < 5 nm size RuO_2 on the surface.

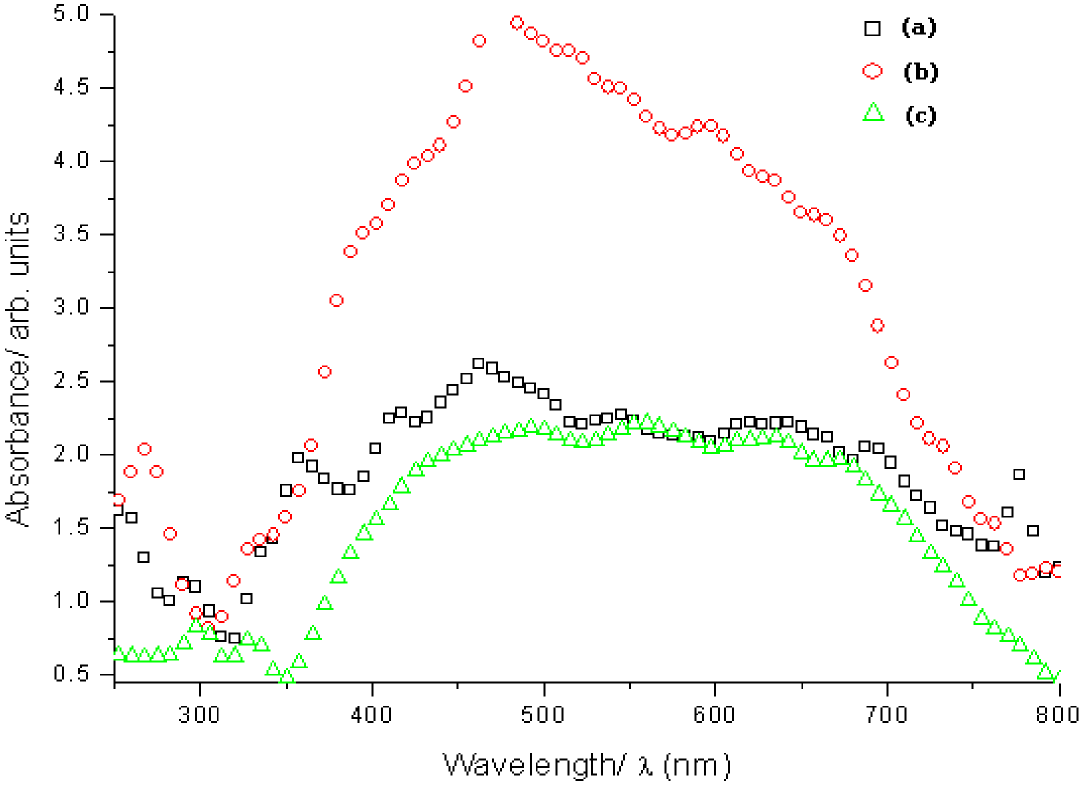
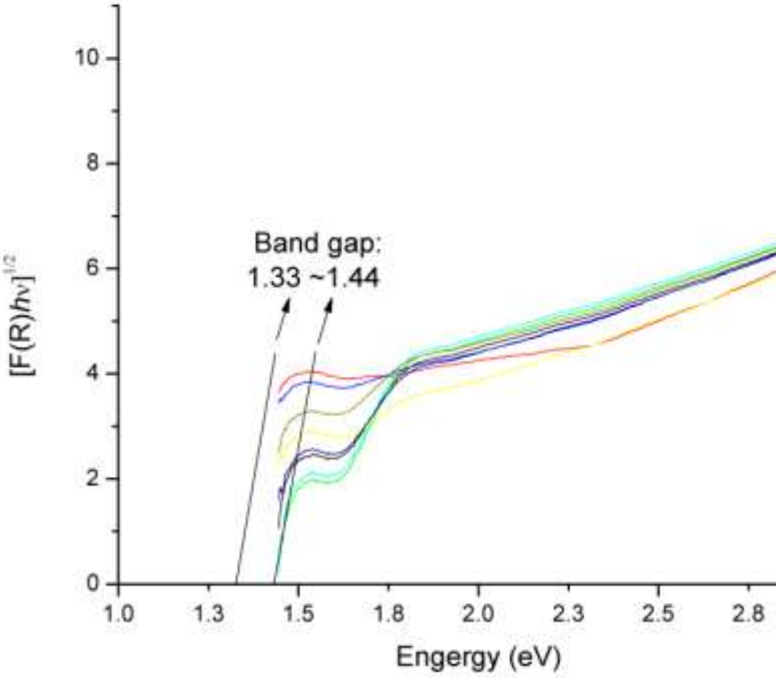


Figure S11. The diffuse reflectance UV–visible absorption spectra of (a) $Cu_{0.30}Ag_{0.07}In_{0.34}Zn_{1.31}S_2$, (b) $Cu_{0.12}Ag_{0.30}In_{0.38}Zn_{1.22}S_2$ and (c) $Cu_{0.45}Ag_{0.13}In_{0.24}Zn_{1.35}S_2$

ICP-MS analysis and electron neutrality: The ratios of different metals in the solid solution were precisely determined by ICP-MS analysis and are tabulated in table S1.

Entry	Cu	Ag	In	Zn	S	Electron Neutrality
1	0.00	0.09	0.23	1.61	2	0.00
2	0.23	0.21	0.19	1.50	2	0.01
3	0.30	0.07	0.34	1.31	2	0.01
4	0.12	0.30	0.38	1.22	2	0.00
5	0.45	0.13				
6	0.37	0.15				
7	0.05	0.20				
8	0.48	0.34				
9	0.12	0.13				

Entry 1 Example: 0.00x1 + 0.09x1 + 0.2



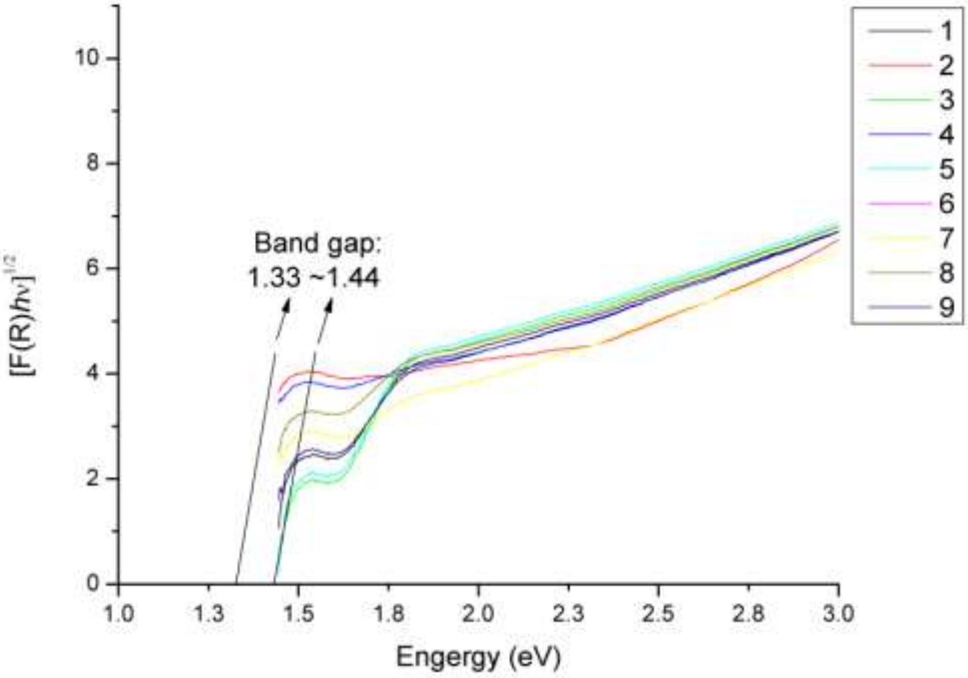
Surface Area determination of photocat

BET methylene blue adsorption method (J

9) 245, 221, 221, 222, 221, 223, 222, 2

deviation is 7.

The plot of the modified Kubelka–Munk function $[F(R1)h\nu]^{1/2}$ versus the energy of the absorbed light is as following. The value ranges from 1.33 to 1.44 eV.



References

1. I. Tsuji, H. Kato and A. Kudo, *Chem. Mater.*, 2006, **18**, 1969-1975.
2. M. A. Gunshefski, D. Word and J. Stainfield, *Method NCASI 99.01*, **1999**.