Electronic Supplementary Information

Integrating $CuInSe_2$ Nanocrystals with Polymeric Carbon Nitride Nanorods for Photocatalytic Water Splitting

Yun Zheng,[*a, b, c] Yilin Chen,[a] Lvting Wang,[a] Mingyue Tan,[a] Yingying Xiao,[a] Bifen Gao[a] and Bizhou Lin[a]

[a]*Fujian Key Laboratory of Photoelectric Functional Materials, College of Materials Science and Engineering, Huaqiao University, Xiamen, Fujian 361021, P. R. China.*
E-mail: zheng-yun@hqu.edu.cn
[b]*Institute of Luminescent Materials and Information Display, College of Materials Science and Engineering, Huaqiao University, Xiamen, 361021, P. R. China.*
[c]*State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou, Fujian 350116, P. R. China*

Experimental section

Chemicals and regents

L-alanine (BR), NaOH (AR), NH_4HF_2 (AR), Copper iodide (CuI, 99.998%), chloroplatinic acid (99.9%), and Na_2SO_4 (AR) were purchased from the China Sinopharm Chemical reagent Co. Ltd. oleylamine (OAm, C18: 80-90%) and 1-octadecene (ODE, 90%) were supplied by Aladdin-reagent. Tetradecanoyl chloride (97%), tetraethoxysilane (98%), Indium acetate ($In(OAc)_3$, 99.99%), and sulfur powder (99.99%) were purchased from Sigma Aldrich Company. 3-aminopropyl triethoxysilane (98%) were purchased from J&K Chemical Ltd. Cyanamide (98%), and 3-mercaptopropionic acid (MPA, 97%) were obtained from Alfa Aesar Company. The solvents, including HCl (37%), acetone (AR), chloroform (AR), petroleum ether (AR), and triethanolamine (AR) were purchased from China Sinopharm Chemical reagent Co. Ltd. All chemicals were used as received without further processing. Deionized water with a resistance of 18.3 M Ω cm was used in the experiment. Ar gas (super grade purity, 99.999%) was supplied by Fuzhou Lianzhong Industrial Gases Co. Ltd.

Synthesis of N-myristoylalanine (C_{14}-L-Ala)

C_{14}-L-Ala was synthesized according to ref. [1] . L-alanine (0.24 mol, 21.4 g) was mixed with deionized water (140 mL), NaOH (19.2 g) and acetone (120 mL). Under vigorous stirring at 0^{o}C, the mixture was dropwise added with tetradecanoyl chloride (0.2 mol, 49.3 g). Meanwhile, 20mL 0.2M NaOH solution was injected to maintain the pH at ~12. After reaction for 1 hour, a certain amount of HCl solution was added to adjust

the pH at 1. The solids were washed with deionized water till neutral, cleaned with petroleum ether for several times, and vacuum dried at 50 ^{o}C. The yield of C_{14}-L-Ala is 30~35g.

Synthesis of chiral mesoporous silica (CMS)

CMS was synthesized according to ref.[2]. C_{14}-L-Ala (0.321 g, 1.0 mmol) was dissolved in deionized water (22.1 g), and added with 0.01 M HCl (10 g, 0.1 mmol) under vigorous stirring at room temperature. After 1 h, a mixture of tetraethoxysilane (1.40 g, 6.7 mmol) and 3-aminopropyl triethoxysilane (0.23 g, 1.0 mmol) was added to the mixture with stirring at 400 rpm for 10min. Then the mixture reacted at room temperature under static conditions for 24 h. The products were collected by filtration and dried at 80 ^{o}C, and calcined at 550 ^{o}C for 6 h under air to remove the surfactants. The yield of CMS is 0.1~0.2g.

Characterization

The scanning emission microscope (SEM) measurements were conducted using Hitachi SU-8010 and S4800 Field Emission Scanning Electron Microscope. Transmission electro microscopy (TEM) was obtained using a FEI TECNAI G2F20 instrument. X-ray diffraction (XRD) measurements were collected on a Bruker D8 Advance diffractometer with Cu Ka1 radiation (λ=1.5406 Å). Fourier transform infrared (FT-IR) spectra were collected with a thermo Nicolet Nexus 670 FTIR spectrometer, and the samples were mixed with KBr at a concentration of ca. 0.2 wt%. X-Ray photoelectron spectroscopy (XPS) data were obtained on a Thermo Scientific ESCALAB250 instrument with a monochromatized Al Kα line source (200

W). All binding energies were referenced to the C 1s peak at 284.8 eV of surface adventitious carbon. The UV-Vis diffuse reflectance spectra (DRS) were measured on a Cary 5000 Scan UV-Vis-NIR system of Agilent Technologies. Photoluminescence (PL) spectra were recorded on an Edinburgh FI/FSTCSPC 920 spectrophotometer under an excitation wavelength of 400 nm. Electrochemical measurements were conducted with a BAS Epsilon Electrochemical System in a conventional three electrode cell, using a Pt plate as the counter electrode and an Ag/AgCl electrode (3 M KCl) as the reference electrode, the active area is confined to 0.25 cm^2.

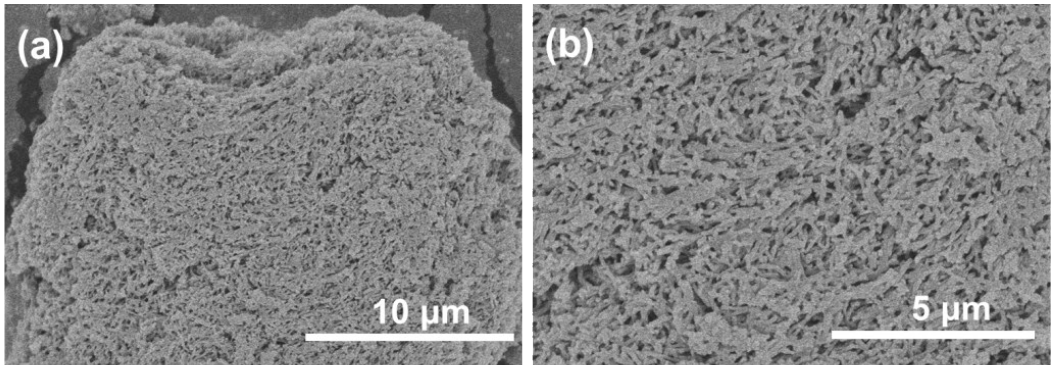

Fig. S1 SEM images of 3% $CuInSe_2$/CN.

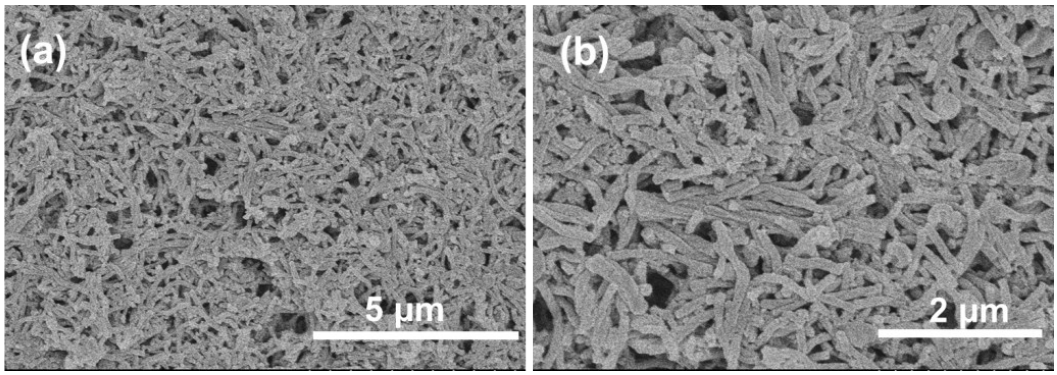

Fig. S2 SEM images of CN nanorods.

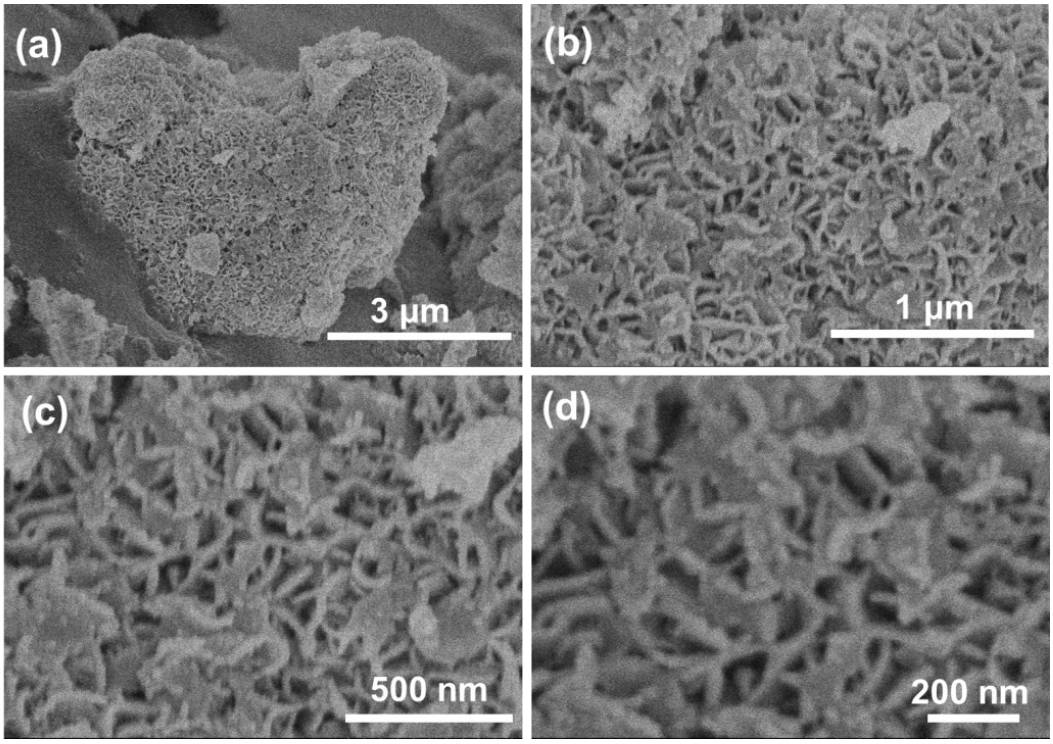

Fig. S3 SEM images of $CuInSe_2$ nanocrystals.

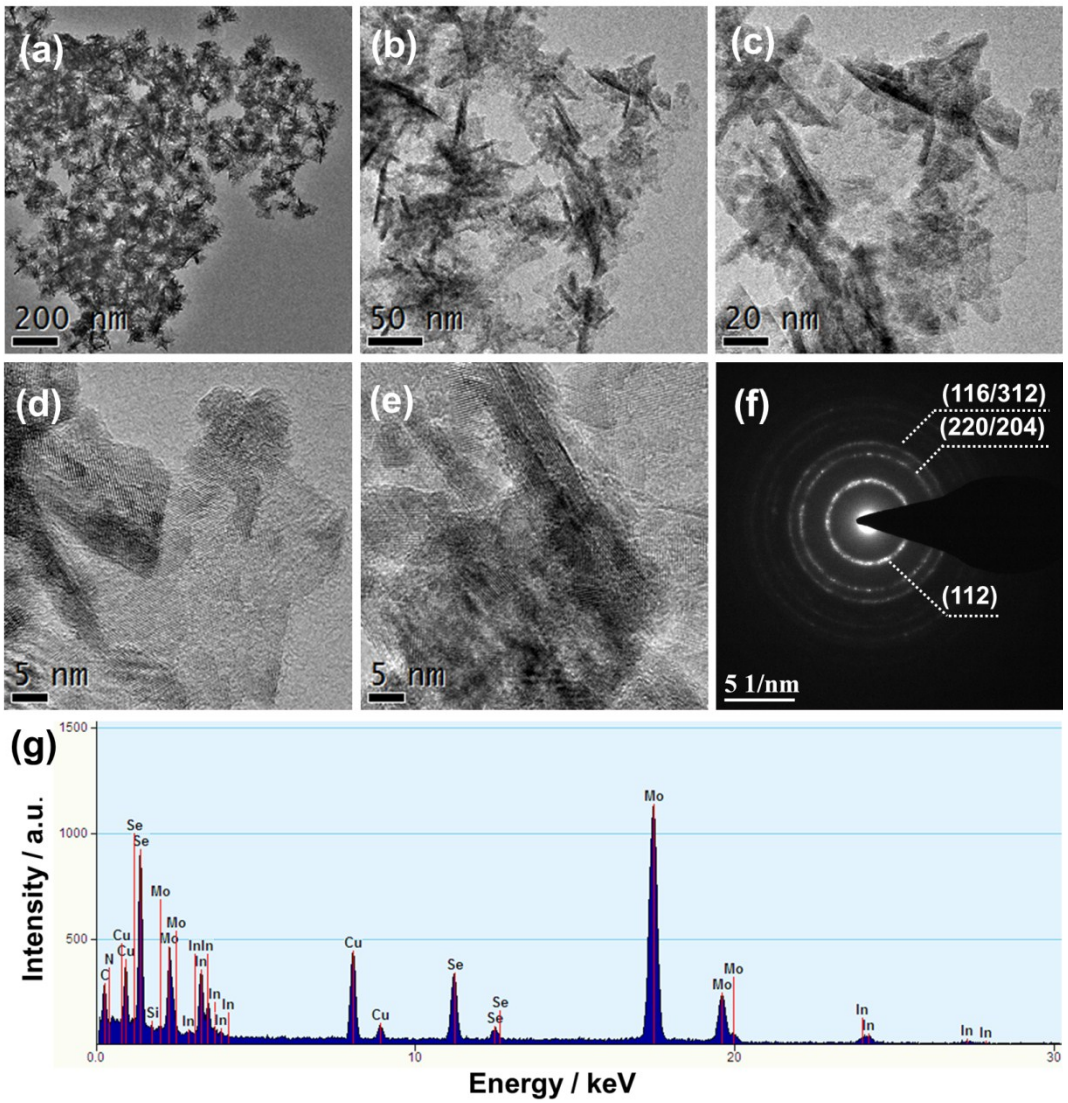

Fig. S4 (a-c) TEM, (d-e) HRTEM, (f) SAED, and (g) EDX images of $CuInSe_2$ nanocrystals on the grid of molybdenum mesh.

Fig. S4 shows the TEM and HRTEM images of the $CuInSe_2$ nanocrystals. The average size of the $CuInSe_2$ nanocrystals is about 20-50 nm. Moreover, corresponding selected area electrical diffraction (SAED) patterns also indicate the nanocrystal structure of the as-synthesized $CuInSe_2$. The three rings refer to the (112), (220)/(214), and (116)/(312) reflection direction. As demonstrated by the energy-dispersive X-ray spectroscopy (EDX) spectra, three elements of Cu, In and Se are detected for $CuInSe_2$ nanocrystals. It can be concluded that well crystallized tetragonal $CuInSe_2$ nanocrystals were prepared.

Table S1. Quantification results of $CuInSe_2$ nanocrystals on Mo sample holder by TEM-EDS.

Element	Weight (%)	Atomic (%)	Uncertainty (%)	Correction	k-Factor
C(K)	2.610	17.009	0.117	0.173	6.279
N(K)	0.000	0.000	100.000	0.259	4.045
Si(K)	0.000	0.000	100.000	0.977	1.000
Cu(K)	6.267	7.718	0.082	0.997	1.757
Se(K)	9.193	9.110	0.114	1.000	2.571
Mo(K)	77.017	62.815	0.435	0.998	4.581
In(K)	4.911	3.346	0.151	0.968	8.226

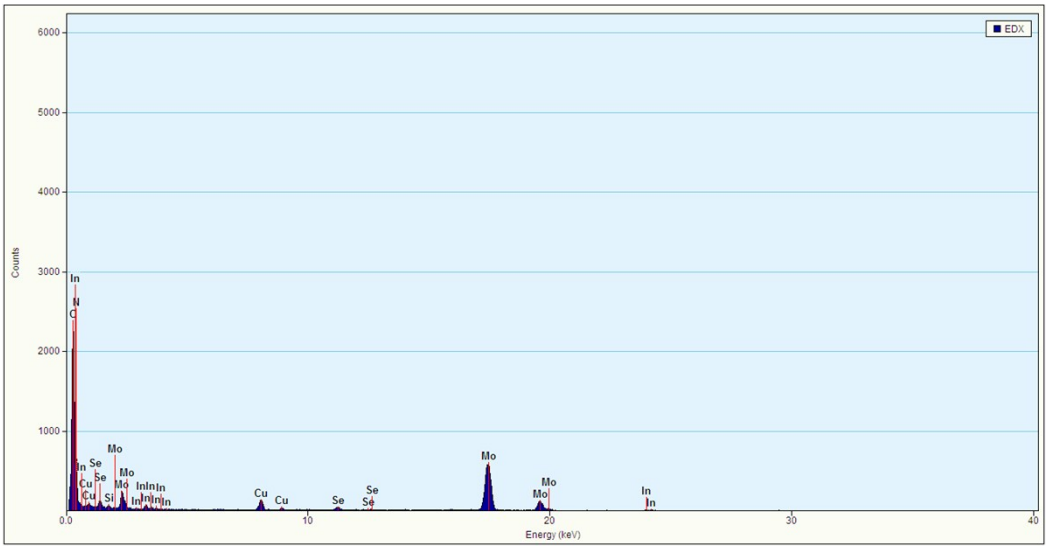

Fig. S5 EDX images of $CuInSe_2$/CN hybrid on the grid of molybdenum mesh.

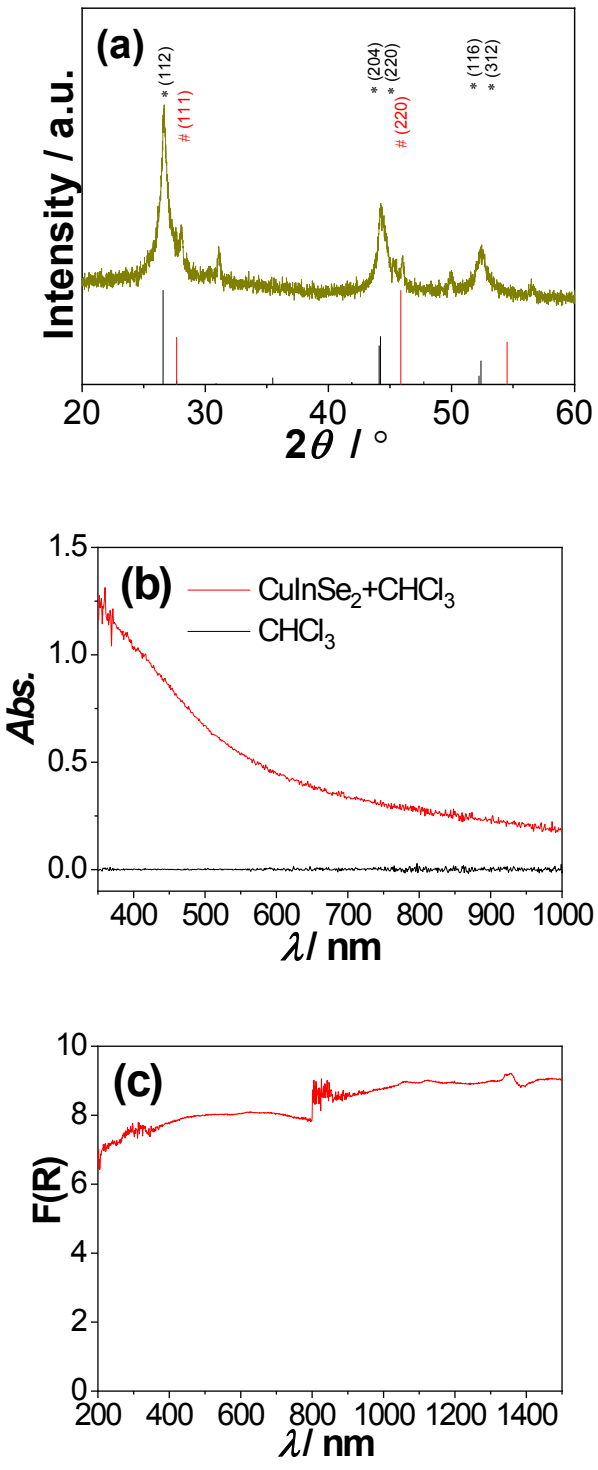

Fig. S6 (a) XRD pattern of $CuInSe_2$, (b) UV-Vis absorption spectra of $CuInSe_2$ and $CHCl_3$ solution, (c) UV-Vis DRS spectra of $CuInSe_2$ solids.

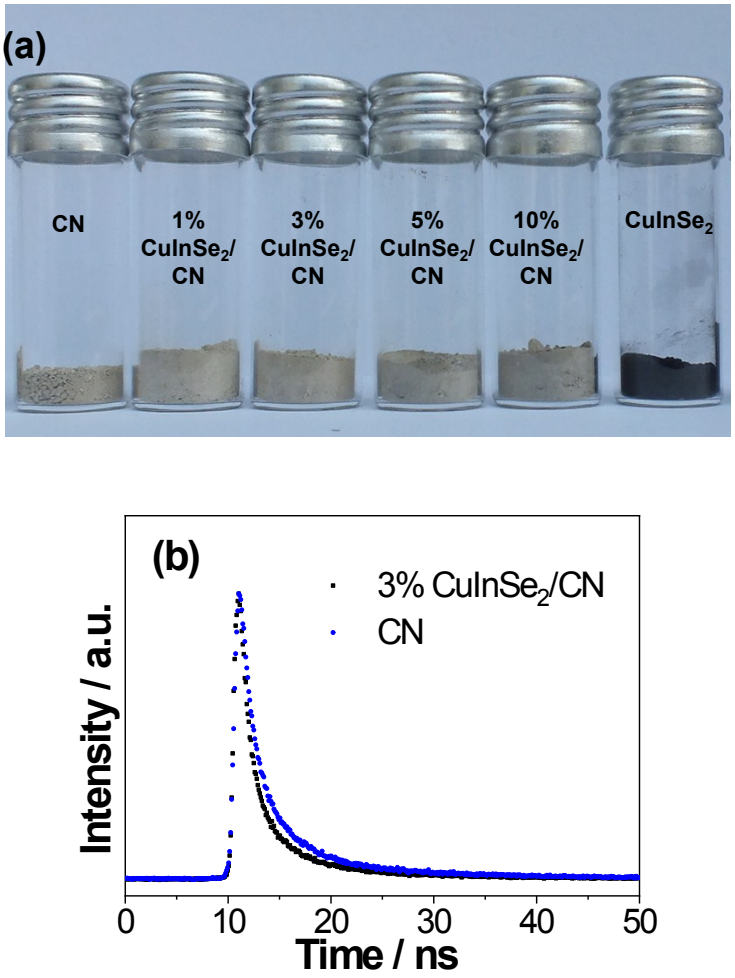

Fig. S7 (a) Digital photograph of $CuInSe_2$/CN hybrids, $CuInSe_2$ and CN, and (b) Time-resolved fluorescence spectra of CN and 3% $CuInSe_2$/CN excited by the incident light of 405 nm.

Table S2 The fitted fluorescence decay components of CN and 3% $CuInSe_2$/CN.

Sample	τ_1 (ns)	τ_2 (ns)	a_1 (%)	a_2 (%)	τ_{av} (ns)	X^2 (%)
CN	1.550	7.695	99.91	0.09	1.555	99.88
3% $CuInSe_2$/CTF	1.141	6.076	99.99	0.01	1.141	99.87

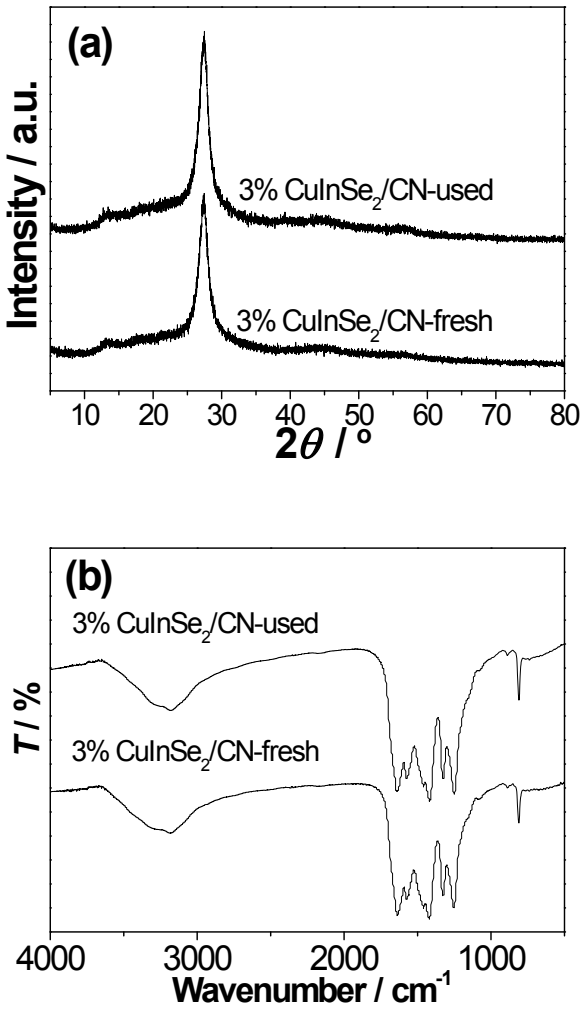

Fig. S8 (a) XRD patterns and (b) FT-IR spectra of 3% $CuInSe_2$/CN hybrid before and after photocatalytic water splitting reaction.

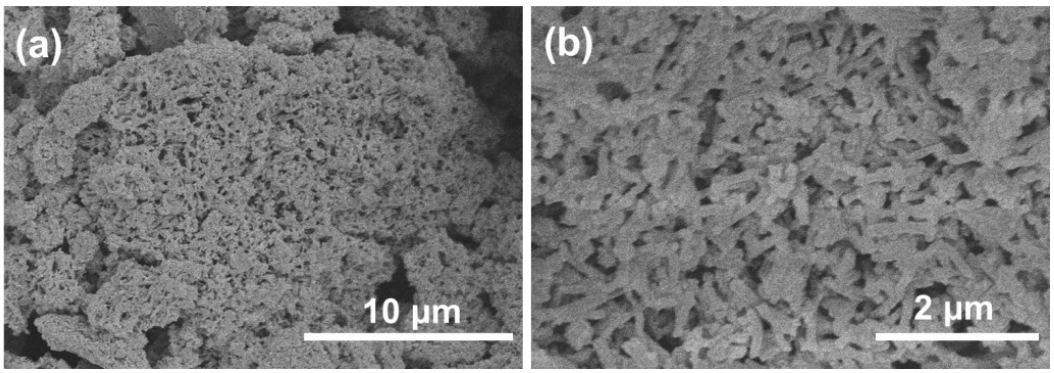

Fig. S9 SEM images of 3% $CuInSe_2$/CN after photocatalytic water splittting reaction.

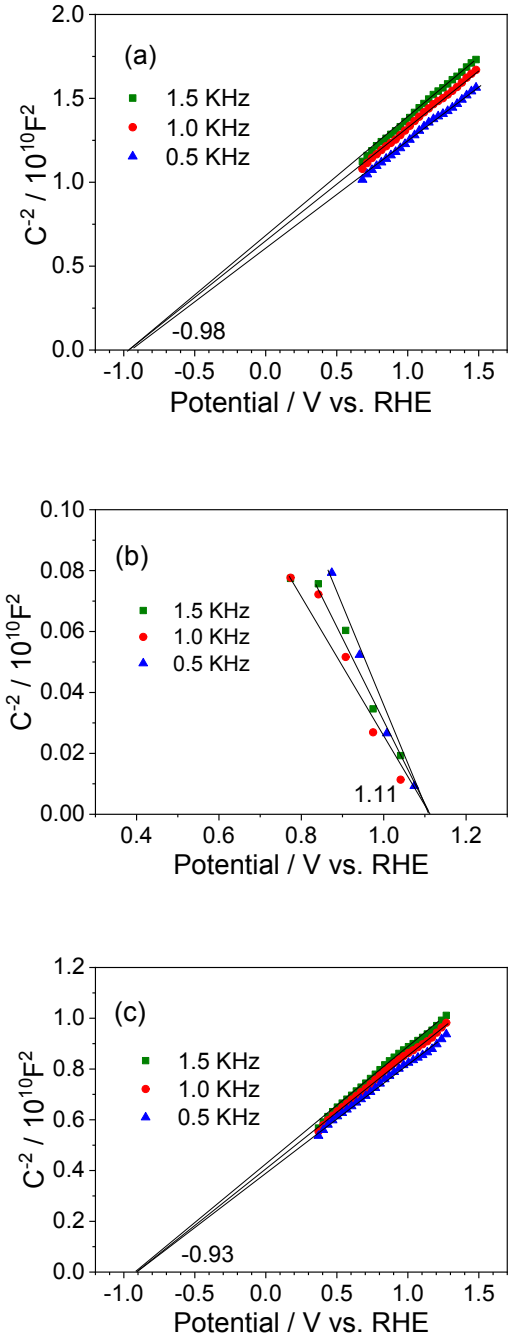

Fig. S10 Mott-Schottky plots of (a) CN, (b) $CuInSe_2$, and (c) 3% $CuInSe_2$/CN.

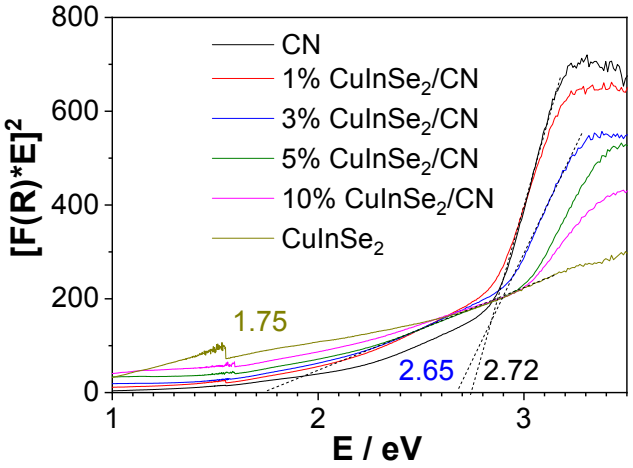

Fig. S11 The plots of $(\alpha hv)^2$ vs. photon energy (hv) for CN and $CuInSe_2$.

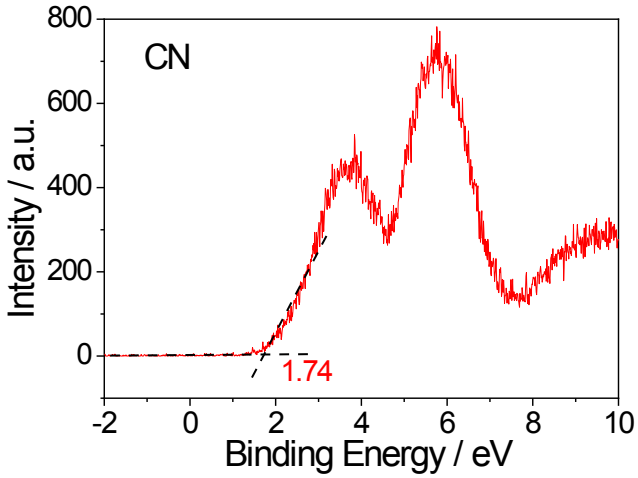

Fig. S12 XPS valence band spectra for CN nanorods.

References

1 M. Y. Takehara, I.; Takizawa, K.; Yoshida, R. , *J. Am. Oil Chem. Soc.*, 1972, **49**, 157-161.

2 (*a*) H. Jin, Z. Liu, T. Ohsuna, O. Terasaki, Y. Inoue, K. Sakamoto, T. Nakanishi, K. Ariga and S. Che, *Adv. Mater.*, 2006, **18**, 593-596; (*b*) H. Jin, H. Qiu, Y. Sakamoto, P. Shu, O. Terasaki and S. Che, *Chem. Eur. J.*, 2008, **14**, 6413-6420.