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Supporting Information

A Facile and Green Synthesis of Colloidal Cu_2ZnSnS_4 Nanocrystals and Their Application in High Efficient Solar Water Splitting

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Experimental Details

Materials

Copper (II) acetate ($Cu(OAc)_2$, Aldrich, 99.99%), zinc acetate ($Zn(OAc)_2$, Aldrich, 99.90%), tin (II) chloride ($SnCl_2$, Aldrich), sulfur powder (S, Aldrich), and thioglycolic acid (TGA, Aldrich, 97 %) were purchased and used as received**.** Vegetable oil (KOREA Ottogi Soybean 100% Oil) was purchased from a commercial shop market. All chemicals were used without any additional treatments.

Synthesis of Cu_2ZnSnS_4 (CZTS) Nanocrystals (NCs)

In a typical synthesis, 0.5 mmol $Cu(OAc)_2$, 0.25 mmol $Zn(OAc)_2$, 0.25 mmol $SnCl_2$ and 10 ml vegetable oil were mixed in a three-neck flask at room temperature and cycled between vacuum and argon three times. Figure S1 shows the color evolution of a reaction mixture during the reaction. Afterward, the mixture was kept at 150 °C under vacuum for 30 min. During heating, the mixture solution turned from a deep sky blue (Figure S1 (a)) to a faint brown (Figure S1 (b)) color, indicating intermediate reaction complex formation. In a 10 ml scintillation vial, 1.0 mmol S powder and 2 ml vegetable oil was sonicated until the S dissolved and a red-orange (Figure S1 (c)) solution formed. The flask containing metal precursors solution is backfilled with argon, heated to desired reaction temperatures and S-vegetable oil mixture solution was swiftly injected into the flask under vigorous stirring. An instantaneous reaction solution color change from brown to black (Figure S1 (d)) takes place. After injection, the temperature of the reaction mixture dropped to below desired reaction temperatures, and it was allowed to recover to the pre-injection temperature. When mixture heated over 310 ^{o}C, it changed from aqueous solution to sticky and yield of product was quite small as compared to those of low reaction temperatures. The reaction time after injection was 30 min., after which the flask was cooled down to room temperature naturally to obtain NCs products. The NCs products were purified by precipitation with ethanol, and followed by centrifugation at 3000 rpm for 10 min. for three times. Finally, the obtained NCs product was dispersed in 5 mL of toluene to form stable colloidal ink.

Ligand exchange (LE) process for CZTS NCs

The ligand exchange of vegetable oil-capped CZTS NCs with thioglycolic acid (TGA) was carried out using hydrolysis method. More specifically, vegetable oil-capped CZTS NCs were dispersed in 5 ml of toluene and kept for stirring. In separate vial, 0.8 ml of TGA was mixed in 10 ml of ethanol. Both the prepared solutions were mixed together and kept for stirring for few hours. Then, 4 ml of deionized water (DI) was added into this mixture and formed under layer was collected directly. 5 ml of ethanol was again added to the remaining solution and stirring is continued for another few hours. Further, this mixture was allowed for centrifugation and the TGA-capped CZTS NCs precipitate was collected and was easily dispersed in DI water for use in next step.

Fabrication of water splitting device

In order to fabricate the PEC device, we designed earth abundant materials based CZTS NCs/Zn(O,S)/TNRs structure as a photoelectrode. TNRs were hydrothermally grown on FTO substrate at 150 °C for 9 h and then Zn(O,S) layer with 5 nm thick was deposited by atomic layer deposition technique at 120 °C on TNRs. Finally, Zn(O,S)/TNRs were immersed into a TGA capped CZTS NCs disperse in DI water for 6 h at room temperature under dark condition.

Growth of hydrothermally grown TiO_2 nanorod arrays (TNRs)

An FTO (Pilkington TEC GlassTM, sheet resistance 8 Ω sq^{-1}) substrate dimensions a size of 2 x 2 cm^2 was prepared and cleaned via ultra-sonication by sequentially immersing the substrate in DI water, ethanol, and acetone for 20 min. in each step to remove some of the organic contamination and dust. Briefly, equal 11.3 mL volumes of DI water and hydrochloric acid (35 % ~ 38 %) were mixed for 5 min., followed by the incorporation of 0.189 mL of titanium (IV) butoxide (97 %). The solution was subsequently transferred to a Teflon-lined stainless steel autoclave. Afterwards, 3 pieces of the cleaned FTO substrate were placed at an angle against the wall of the Teflon-liner. The hydrothermal treatment was performed at 150 °C for 9 h in a vacuum oven. After the reaction was finished, the autoclave was naturally cooled down to room temperature, and the sample was cleaned using DI water several times, finally dried using nitrogen gas. To enhance the crystallinity of the as-synthesized TNRs, a post-thermal treatment was carried out at 450 °C for 30 min. in an ambient air.

Deposition of Zn(O,S)/ TNRs

Zn(O,S) passivation layers were prepared on 1D TNRs using a laminar-flow thermal ALD reactor (Lucida D100, NCD, Korea). Diethylzinc (DEZ, EGChem., Korea), DI water, and 10 % hydrogen sulfide (mixed with N2, Gaschem., Korea) were used for Zn, O, and S sources, respectively. The deposition temperature was maintained at 120 °C. The oxygen-to-total anion ratio (O/(O+S)) of Zn(O,S) layer with

5 nm thick is measured to be 0.19 by XPS characterization. The band gap energy of 5 nm Zn(O,S) layer is 3.0 eV measured by ellipsometer. More details on ALD grown Zn(O,S) onto TNRs can be found in Ref. 1.

Sensitization of CZTS NCs on Zn(O,S)/ TNRs and TNRs.

TNRs and Zn(O,S)/TNRs were immersed into a TGA-capped CZTS NCs DI water solution for 6 h in dark condition and then rinsed with water and ethanol sequentially. After the deposition, the CZTS NCs-sensitized TNRs and Zn(O,S)/TNRs were dried under N_2 flow and directly used for PEC measurement without any additional treatments.

Characterization

The structural properties of the NCs and photoelectrodes were examined by X-ray diffraction (XRD), using a XRD, PANalytical, X'Pert-PRO Netherlands operated at 45 kV, 40 mA, and room temperature and the Raman spectroscopy recorded using Raman microscope (LabRam HR8000 UV, (Horiba Jobin-Yvon, France), KBSI, Gwangju center) with an Olympus microscope equipped with 100X magnification lends in the backscattering configuration. The excitation source was an Ar ion laser operating at wavelength of 514 nm and at 200 mW output power for identification and to assess the crystal structure. The size and shape of NCs and morphology of nanostructured photoelectrodes were performed by Field-emission Scanning Electron Microscopy (FE-SEM) and High-resolution Transmission electron microscopy (HR-TEM) using JEOL-3010 with an acceleration voltage of 300 kV. The compositional ratios of the NCs were investigated by energy dispersive X-ray spectroscopy (EDX, OXFORD INCA system) using A Tecnai G2 F30 installed in the scanning TEM (STEM) and high-angle annular dark-field imaging in the STEM (HAADF-STEM). TEM samples were prepared by drop casting technique using CZTS NCs dispersed in toluene and nanostructures powder in ethanol onto carbon meshed nickel TEM grids (200 meshes, Structure Probe, Inc.) The chemical binding energy of as synthesized NCs was examined using a high-resolution X-ray photoelectron spectroscope (HR-XPS, VG Multi lab 2000, Thermo VG Scientific, UK) at room temperature. The binding energies were calibrated using the carbon 1s line at 285.0 eV. The surface structures of the NCs were determined by ATR-FTIR on a spectrophotometer (PerkinElmer, Frontier-89063) at room temperature. All optical measurements of the NCs were performed in chloroform using a quartz or optical glass cuvette. The UV-Visible spectra for NCs and nanostructured photoelectrodes were obtained with Cary 100 (Varian, Mulgrave, Australia) spectrometer at room temperature. Visible static photoluminescence (PL) spectra were measured on a Horiba-Yvon Fluromax 4 with 345 nm excitation at room temperature. The high resolution ESI-MS experiments were performed with a SYNAPT G2 (Waters, UK) system, which uses an innovative multi-reflecting TOF system. The spectra of vegetable oil heat treated at different temperature ranging from room temperature to 330 oC were collected in the positive ion mode using a unit mass resolution microchannel plate (MCP) detector with equipped with a ESI sources assisted by compressed Ar and electrical pumping for the spray solvent. A thin droplet of the sample was dipped directly on brown Kraft envelope paper. The solvent (methanol) flow rate was 10 µL/min, Ar was used as a nebulizing gas at 1 L/min. Mass spectra were accumulated over 60 s and scanned over the m/z 50-1000 range. The scan speed was 20 spectra/sec and exact mass was 1 ppm RMS.

PEC measurement

The PEC measurements were conducted in a three-electrode configuration under light illumination using a potentiostat (CHI Instruments, USA). Samples were used as working electrodes with an active area of 0.2 cm^2. Pt and saturated (sat.) Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. The potential of the homemade sat. Ag/AgCl electrode (0.11 V vs. normal hydrogen electrode, NHE) was converted to be presented in this manuscript. An aqueous electrolyte containing 0.5 M Na_2SO_4 (pH 6.8) was used for the PEC test after nitrogen bubbling to remove the dissolved oxygen in the solution. A Xe lamp was used as a light source at 150 W with a light intensity of 100 mW/cm^2 with an AM 1.5 filter. The current-voltage (J-V) curves under the chopped light on/off illumination were performed at a scan rate of 20 mV/s during the potential sweep. The IPCE was measured in the wavelength range of 300 ~ 900 nm at a potential of 0.5 V versus the sat. Ag/AgCl electrode using a specially designed IPCE system for PEC water splitting. Herein, a 150 W Xenon lamp was used as the light source for generating the monochromatic beam. The calibration was performed using an NREL-certified silicon photodiode. Moreover, to evaluate cell resistance at photoelectrochemical working conditions, the electrochemical impedance spectroscopy (EIS) of the samples was measured in the same electrochemical configuration and electrolyte under the condition of 1 sun of illumination. The frequency ranged from 0.1 Hz to 10 kHz with amplitude of ±10 mV was adapted. The conduction band (CB) and valance band (VB) positions of all three CZTS, Zn(O,S) and TiO_2 compounds were determined from the previously reported literatures.[1-5] The CB and VB positions of Zn(O,S) and TiO_2 were determined with reference to our recently reported study, which suggest that the

CB position of Zn(O,S) is more negative than the TiO_2.[1] Furthermore, it is also revealed that the CB edge of CZTS is higher than the CB edge of TiO_2, while the VB edge of TiO_2 is more positive than the VB edge of CZTS.[2-5] Consequently, the energy band diagram of CZTS, Zn(O,S) and TiO_2 were proposed based on the available literatures and is graphically illustrated in Scheme 1(f) in the main manuscript.

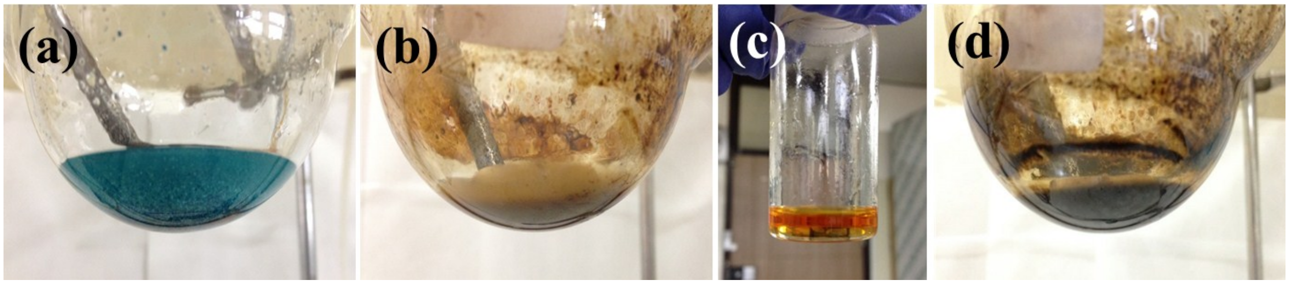


Figure S1. Photographs of reaction solution color evolution during the key intermediates steps of CZTS NCs formation reaction; (a) mixture of metal salts in vegetable oil at room temperature, (b) mixture of metal salts in vegetable oil heated at 150 °C for 30 min., (c) S powder dissolved in vegetable oil, (d) after injecting S precursor solution into the mixture of metal salts in vegetable oil.

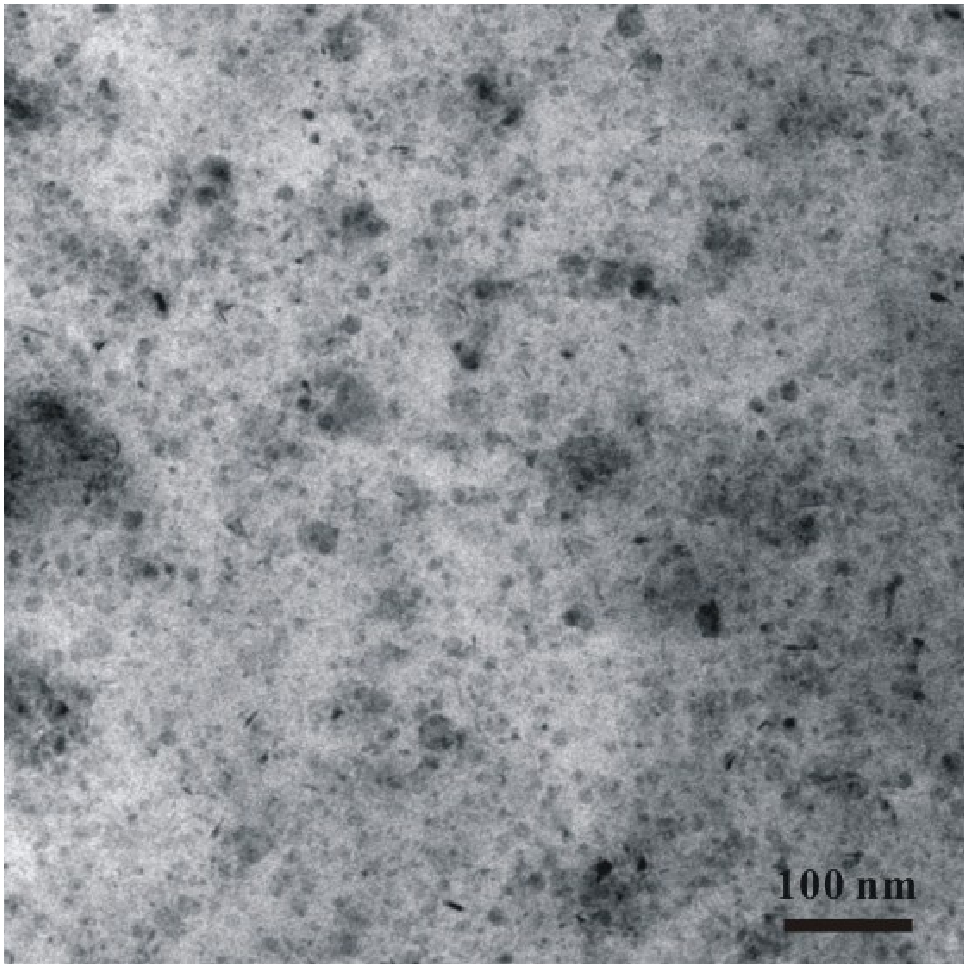


Figure S2. **Low-magnification TEM micrograph of NCs synthesized at reaction temperature of 170 °C. The NCs are heavily agglomerated and exhibit irregular size and shapes with poor size distributions.**

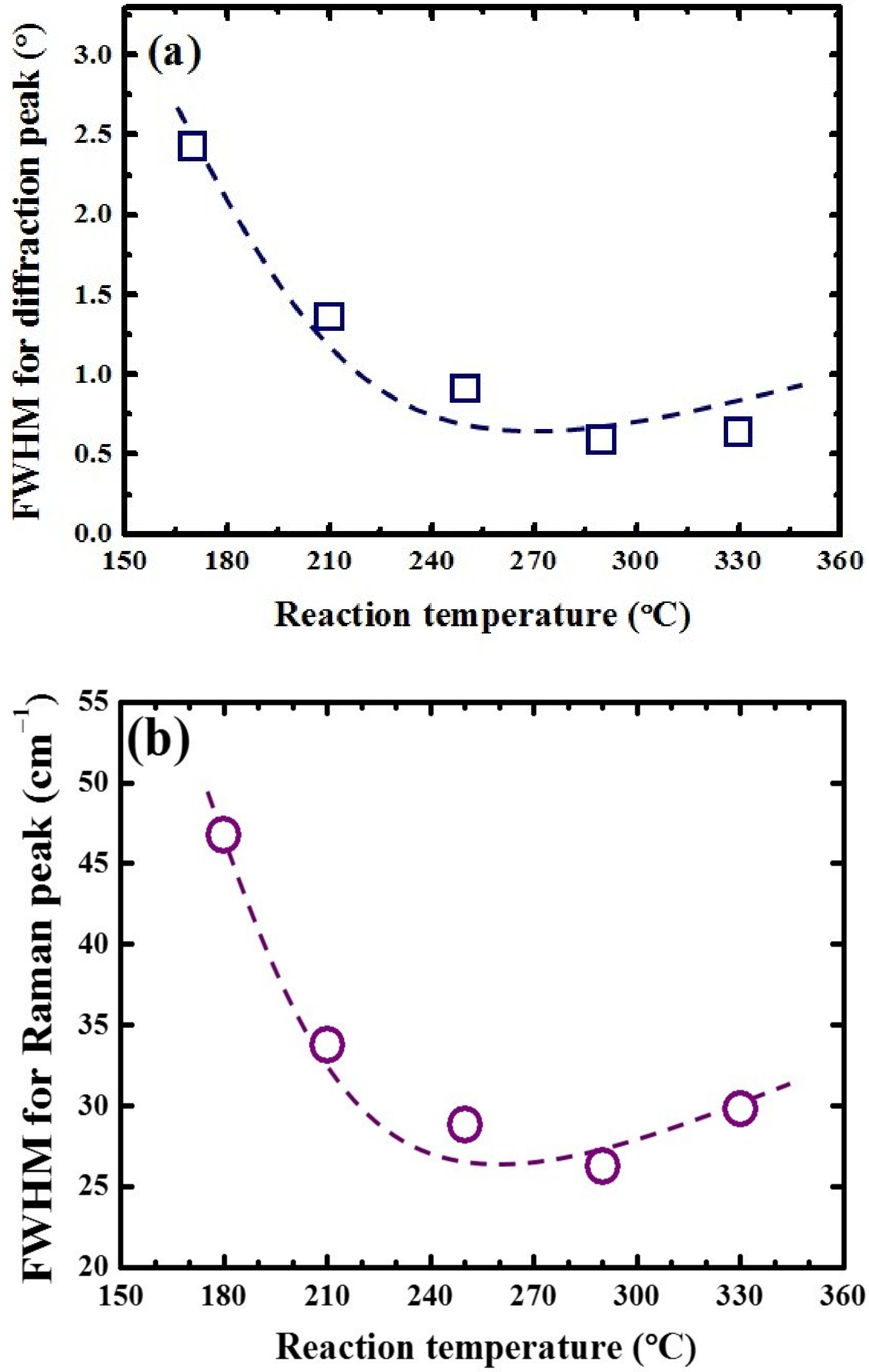


Figure S3. FWHM values for (a) X-ray diffraction (XRD) and (b) Raman peaks in the CZTS NCs synthesized at different reaction temperatures. FWHM values were obtained using Gaussian-fitting equation.

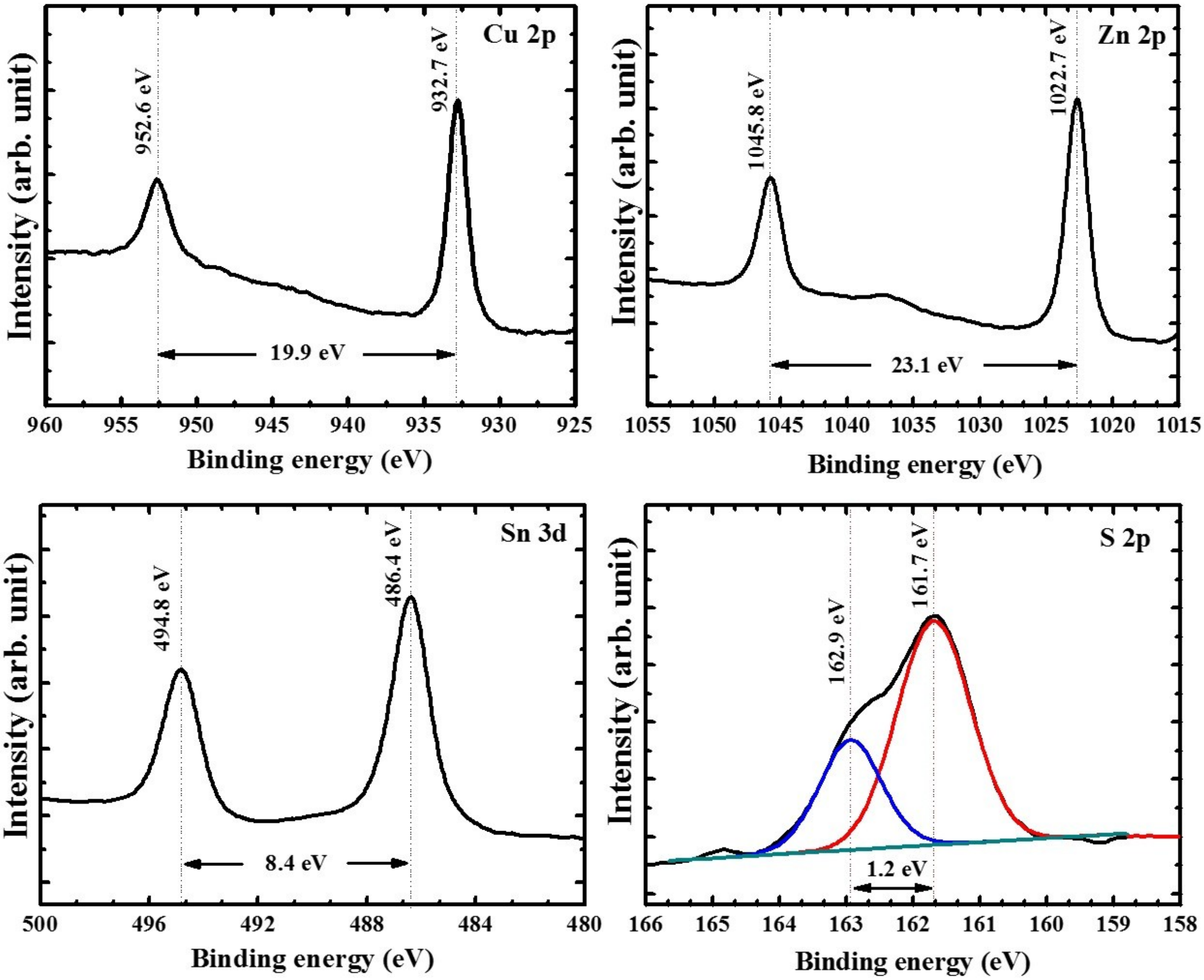


Figure S4. High-resolution X-ray photoelectron spectrometry (XPS) analysis of the four constituent elements; Cu 2p, Zn 2p, Sn 3d, and S 2p core levels at reaction temperature of 250 °C. The carbon 1s line corresponding to 285.0 eV was used to calibrate the binding energies in the spectrometer.

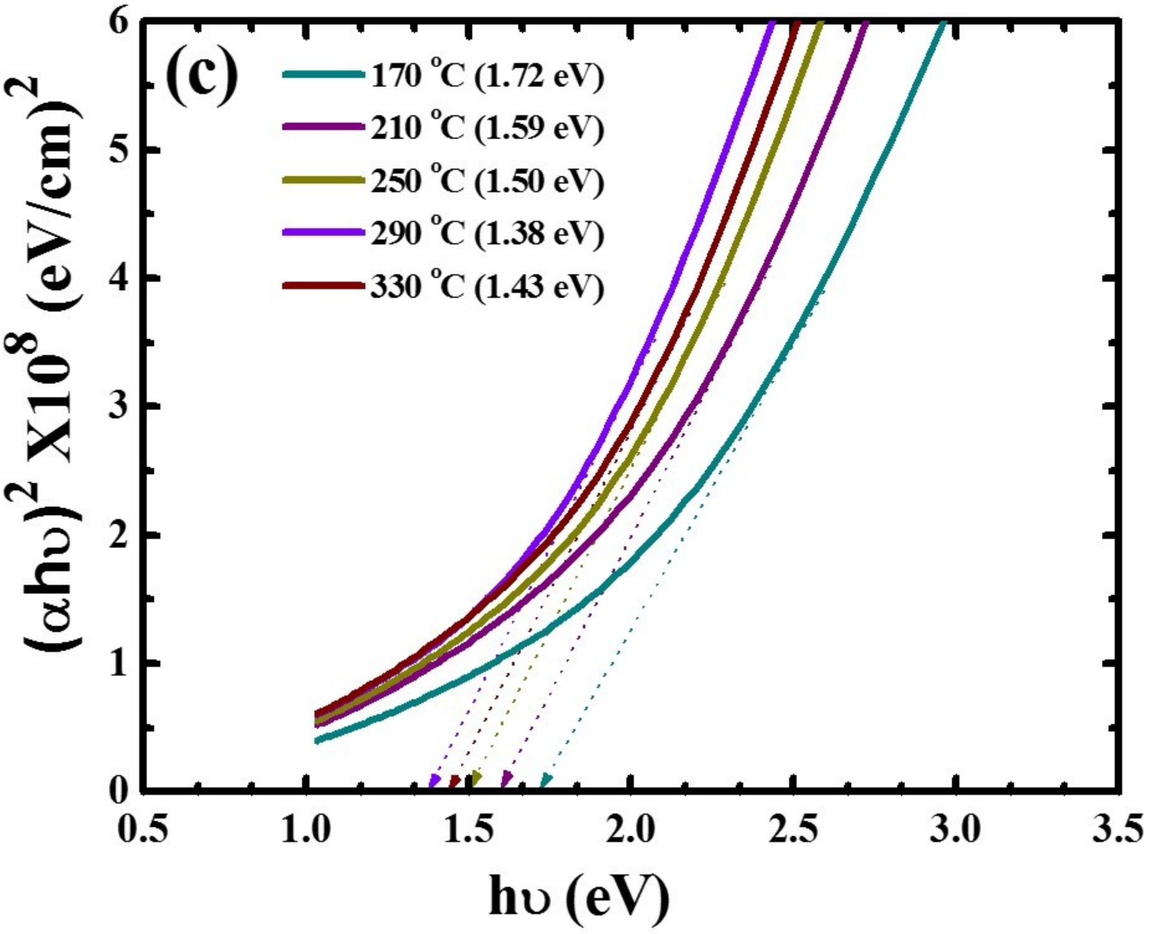


Figure S5. Plots of $(ah\upsilon)^2$ vs photon energy (hυ) of the CZTS NCs synthesized at different reaction temperatures.

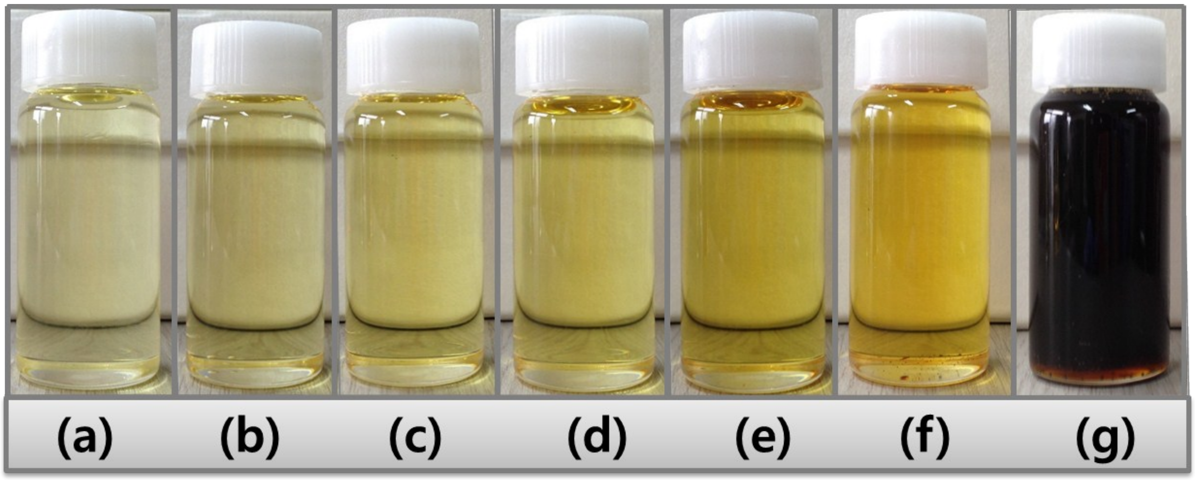


Figure S6. Photographs of vegetable oil (a) before and after heat treatment at (b) 150 ^{o}C, (c) 170 ^{o}C, (d) 210 ^{o}C, (e) 250 ^{o}C, (f) 290 ^{o}C, and (g) 310 ^{o}C

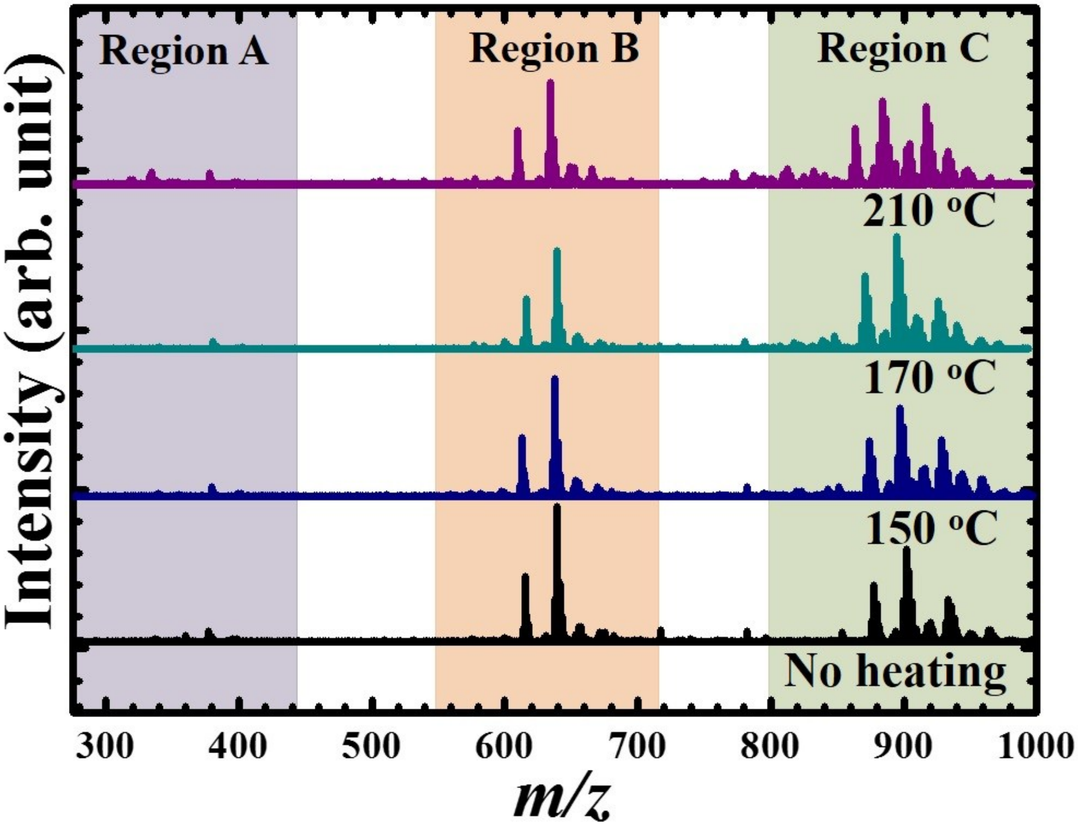
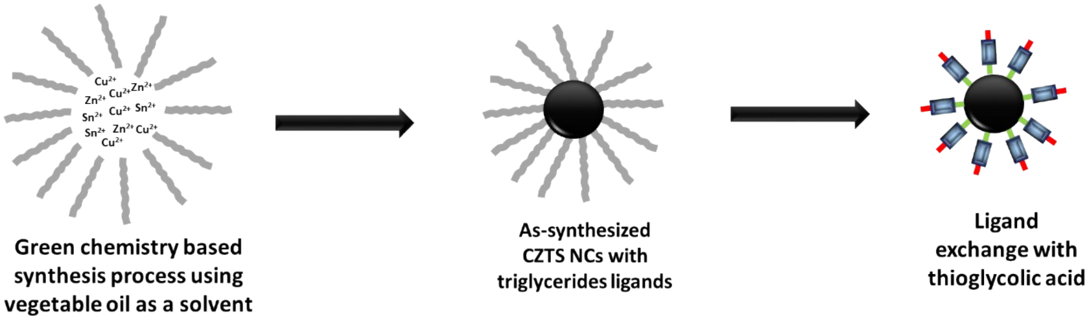
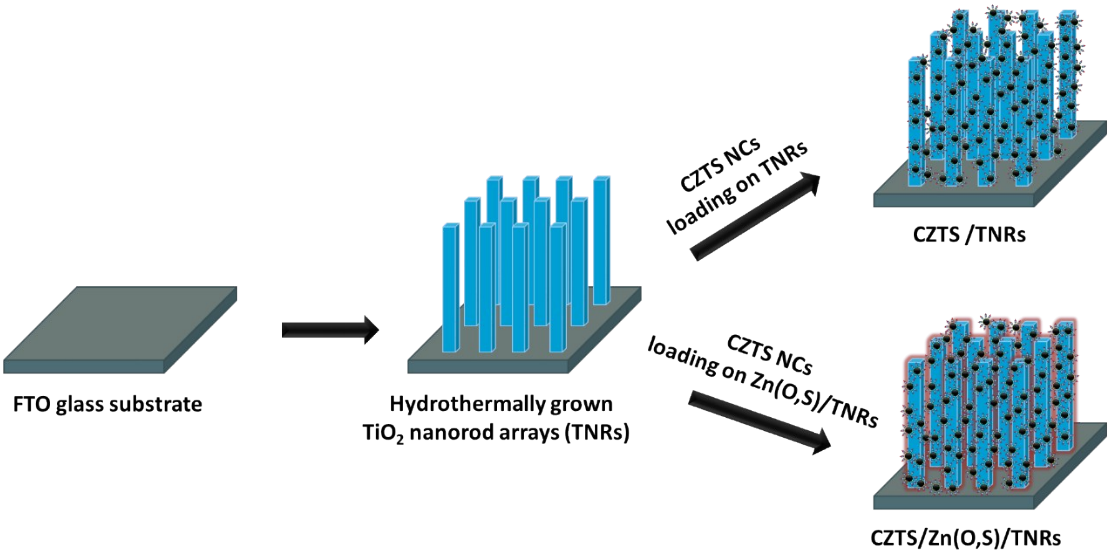


Figure S7. ESI-MS spectra of vegetable oil without and after a heat treatment at different temperatures for 10 min.

(a) Green chemistry based synthesis of CZTS NCs



(b) Application of CZTS NCs as an earth abundant sensitizer to 1D nano-structured PEC device



Scheme S1. Schematic representations of the (a) green chemistry based synthesis of CZTS NCs, their ligand exchange process, and (b) application of CZTS NCs as an earth-abundant sensitizer to 1-D nanostructured PEC device.

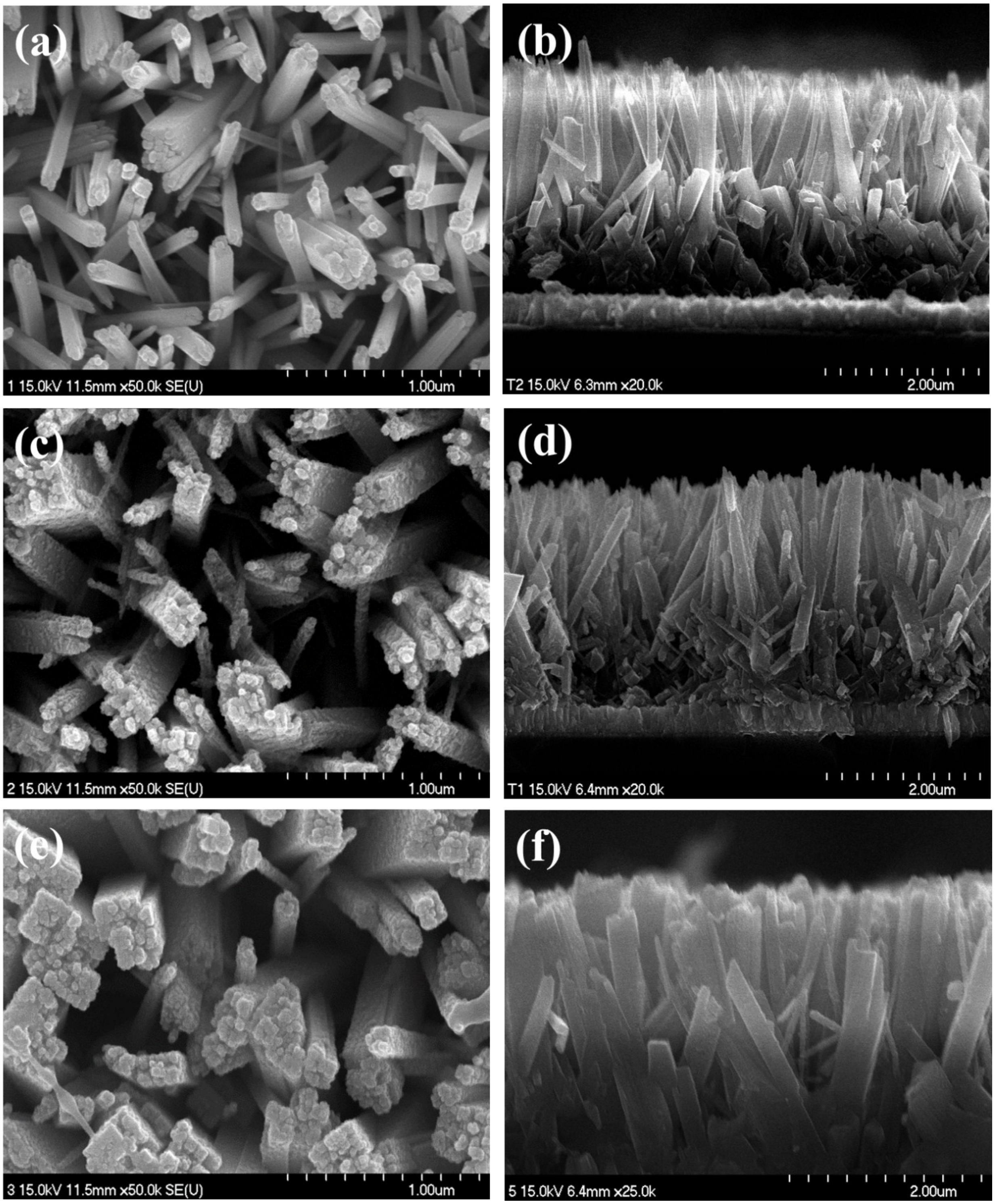


Figure S8. Surface and cross sectional FE-SEM images for ((a) and (b)) TNRs, ((c) and (d)) LE CZTS/ TNRs, ((e) and (f)) LE CZTS/Zn(O,S)/ TNRs, respectively. CZTS NCs are uniformly coated on the surface of TNRs and as well as on the surface of Zn(O,S)/ TNRs.

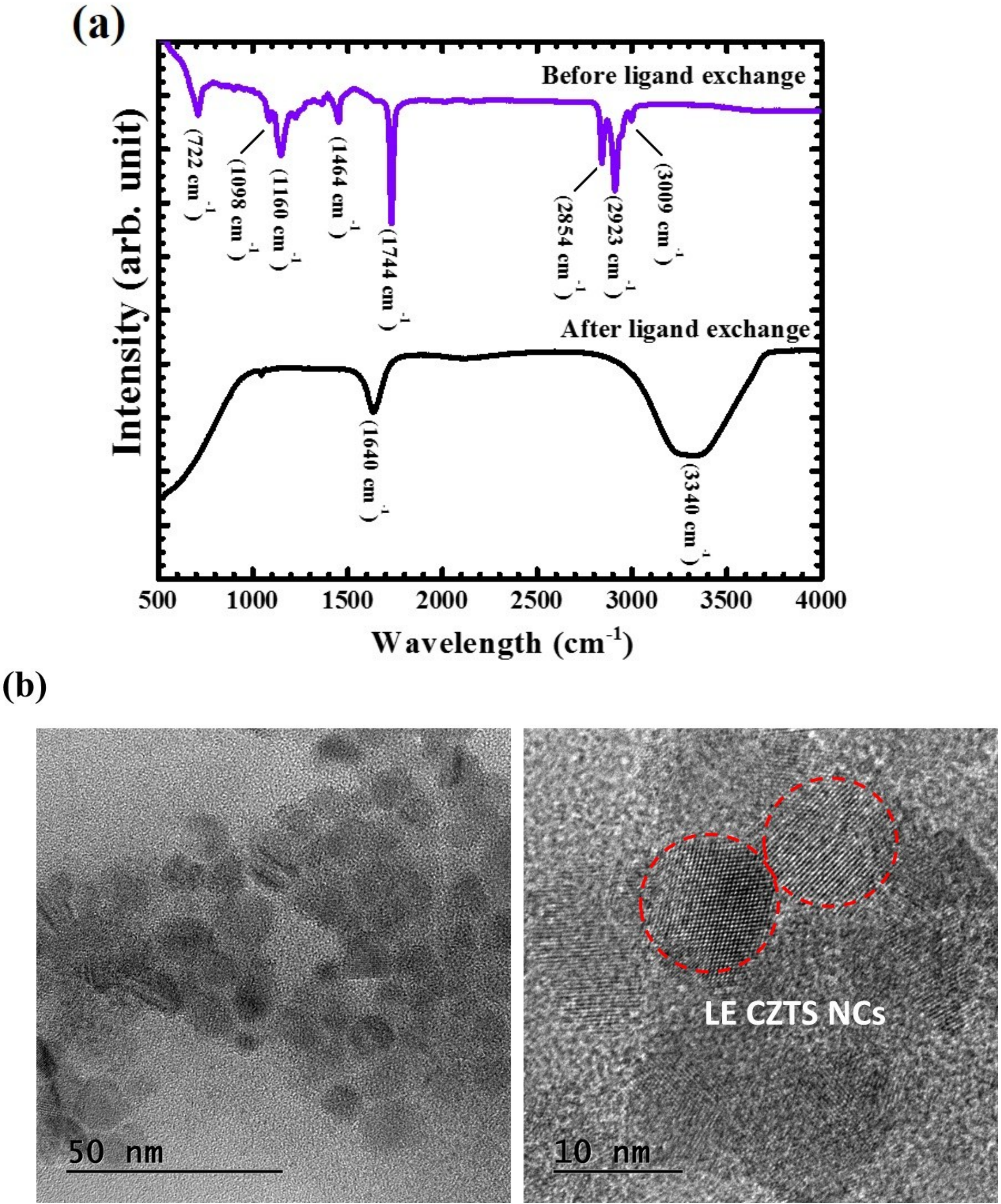


Figure S9. (a) ATR-FTIR spectra of CZTS NCs without (W/O) and with ligand exchange (LE) process and (b) Low and high magnification TEM images of CZTS NCs after LE process, which shows the size of around 10 nm.

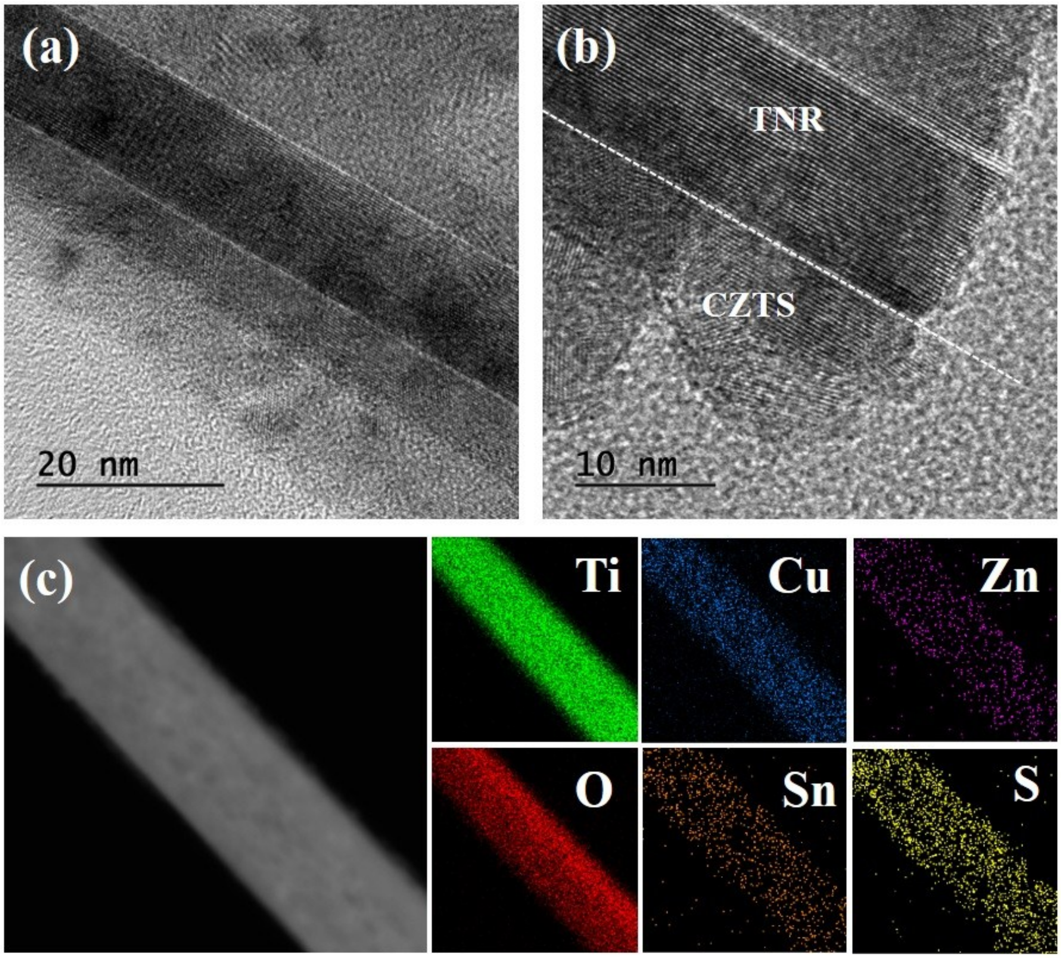


Figure S10. (a) High-magnification and (b) HR-TEM images of LE CZTS/ TNRs structure, and (c) STEM high angle annular dark field (HAADF) mode image and STEM-EDS mapping of Ti, O, Cu, Zn, Sn, and S elements.

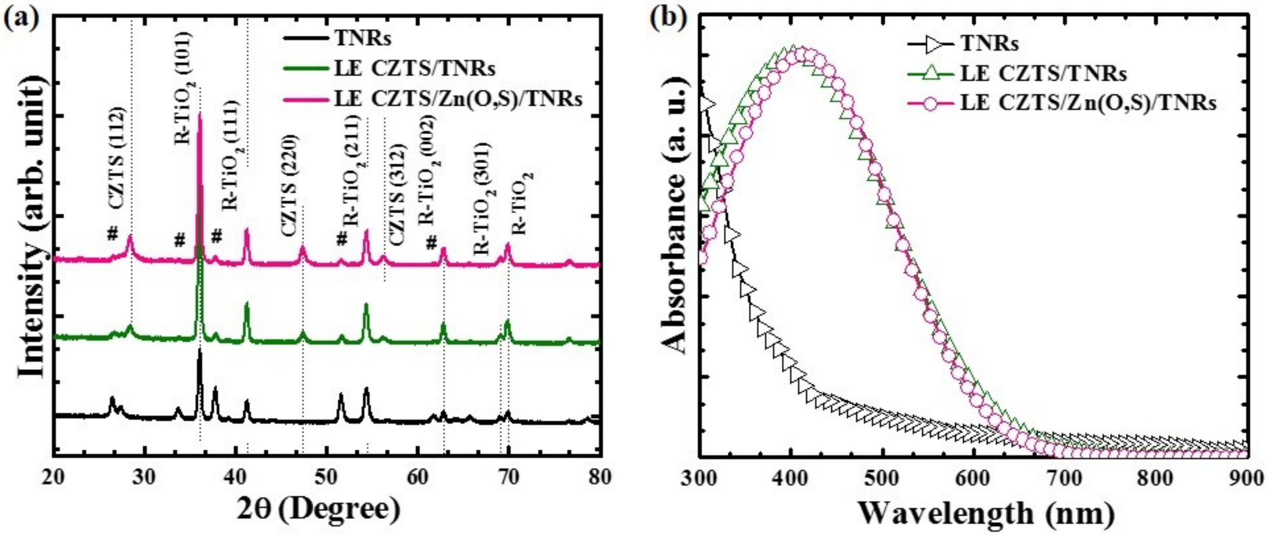


Figure S11. (a) X-ray diffraction (XRD) patterns and (b) absorbance for TNRs, LE CZTS/ TNRs, and LE CZTS/Zn(O,S)/TNRs structures.

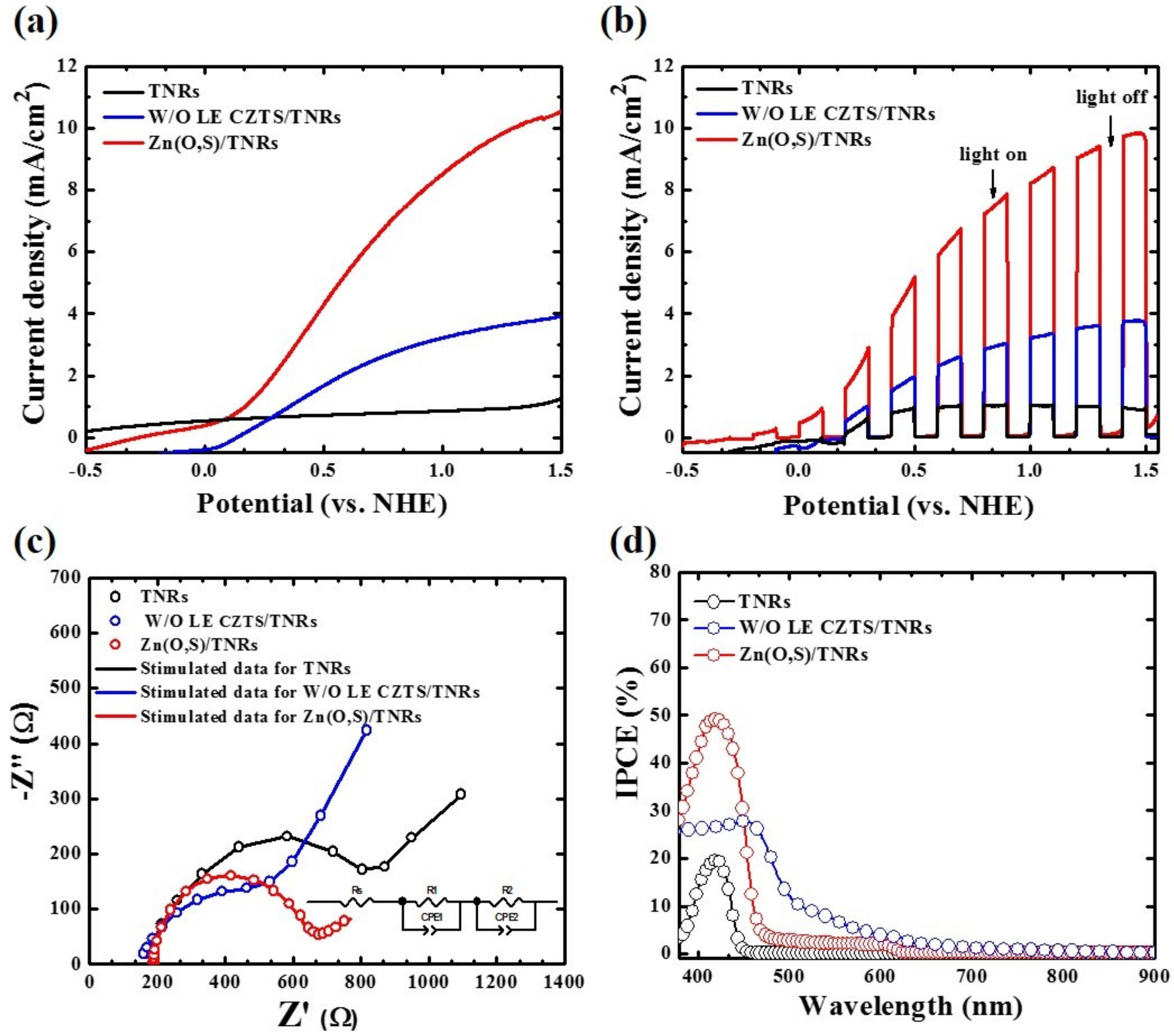


Figure S12. (a) Photocurrent densities-voltage (J-V) curve under illumination with one sun condtions(100 mW/cm^2 with AM 1.5), (b) chopped on/off cycles, (c) the incident photo-to-current conversion efficiency (IPCE), and (d) electrochemical impedance spectra (EIS) of TNRs, W/O LE CZTS/ TNRs, and Zn(O,S)/ TNRs. Electrolyte solution is Na_2SO_4 (pH 6.8).

Table S1. Elemental compositions and compositional ratios of CZTS NCs synthesized at different reaction temperatures. The elemental compositions were obtained using EDS spectrum taken in TEM equipment. TEM samples were made using carbon meshed Ni grid. The CZTS NCs are measured before ligand exchange process.

Sample	Cu (at. %)	Zn (at. %)	Sn (at. %)	S (at. %)	Cu/(Zn+Sn)	Cu/Sn	Zn/Sn	S/(Cu+Zn+Sn)
Precursor	25	12.5	12.5	4	1	2	1	1
210 ^{o}C	33.1	9.8	16.9	44.7	1.24	3.37	0.57	0.74
250 ^{o}C	24.4	10.9	13.1	51.7	1.02	2.4	0.83	1.07
290 ^{o}C	25.1	8.3	13.4	53.2	1.16	1.87	0.62	1.20
330 ^{o}C	25.3	11.2	13.3	50.2	1.03	2.26	0.84	1.01

Table S2. Parameters determined from EIS fitting of TNRs, LE CZTS/ TNRs and LE CZTS/Zn(O,S)/ TNRs photoelectrodes

Photoelectrodes	R_s (Ω)	R_{CE} (Ω)	R_{CT} (Ω)
TNRs	73	698	1626
LE CZTS/ TNRs	71	113	438
LE CZTS/Zn(O,S)/ TNRs	68	52	212

Cost-effective calculation

The aim of our research is dedicated to the synthesis of highly monodisperse CZTS NCs using low-cost and environmental benign “vegetable oil” as a solvent, which presents the reduction of the manufacturing costs of NCs in eco-friendly ways, thereby paving the road for the alternative low-cost and eco-friendly synthesis of variety of NCs.

We calculated the full price of 1 g of CZTS NCs synthesized using oleylamine and vegetable oil as solvents based on real laboratory-scale prices (Table S3, S4) of the materials and presented a comparative cost required scenario for 1 gram synthesis of NCs at the laboratory scale. It is observed that the almost about 2 times cost reduction can be possible by using vegetable oil as a solvent for synthesis of CZTS NCs exhibiting similar properties as that of using oleylamine as a solvent, which proves the effectiveness of the green synthetic approach employed for the synthesis of NCs in this study.

Table S3. Prices of the raw materials for CZTS NCs synthesis. Note that the prices are considered as per the prices from Sigma Aldrich except for the price of vegetable oil*, which is purchased from local commercial shop.

Name of Chemicals	Sigma Aldrich lab scale price (in South Korean Won (KRW) and US Dollar ($))
Copper acetate	602,000 KRW per 25 g, 501.4 $ per 25 g Purity: 99.99 %
Zinc acetate dihydrate	419,000 KRW per 25 g, 349 $ per 25 g Purity: 99.99 %
Tin chloride anhydrous	397,000 KRW per 5 g, 330.6 $ per 5 g Purity: 99.99 %
Sulfur	173,000 KRW per 1 Kg, 144.1 $ per 1 Kg Purity: 99.5 %
Oleylamine	430, 000 KRW per 1.5 Kg, 358.11 per 1.5 Kg Purity: 98 %
***Vegetable oil**	3362 KRW per 1.8 L, 2.8 $ per 1.8 L Purity: 100 %
Chloroform	127,000 KRW per 1 Kg, 105.8 $ per 0.8 Kg Purity: 99 %
Ethanol	165, 000 KRW per 1 Kg, 137.4 $ per 0.5 Kg Purity: 99 %

Table S4. Cost calculation for 1 g synthesis of CZTS NCs based on the prices of raw materials. We choose amount of the precursors that we used for 1.86 g CZTS NCs synthesis as weight template (up-scaled by factor 10).

Name of Chemicals	**Weight**	**Price ($)**
Copper acetate	0.908 g = 0.000908 Kg	0.01821
Zinc acetate dihydrate	0.548 g = 0.000548 Kg	0.00765
Tin chloride anhydrous	0.474 g = 0.000474 Kg	0.03134
Sulfur	0.3206 g = 0.0003206 Kg	0.04629
***Vegetable oil**	50 ml = 0.05 L	0.07778
Oleylamine	15.78 g = 0.01578 Kg	3.7673
Chloroform	9.5 g = 0.0095 Kg	1.2563
Ethanol	12.5 g = 0.0125 Kg	3.435
Total (using oleylamine as a solvent)		8.5621
Total (using vegetable oil as a solvent)		**4.8725**
For one Gram (using oleylamine as a solvent)		6.1746/1.86 = 4.6032 $
For one Gram (using vegetable oil as a solvent)		**4.8725/1.86 = 2.6196 $**

Reference

1. S. W. Shin, M. P. Suryawanshi, H. K. Hong, G. Yun, D. H. Lim, J. Y. Heo, S. H. Kang, and J. H. Kim, *Electrochimica Acta*, 2016, **219**, 470-481.
2. X. Yu, J. Liu, A. Genc, M. Ibanez, Z. Luo, A. Shavel, J. Arbiol, G. Zhang, Y. Zhang and A. Cabot, *Langmuir,* 2015, **31**, 10555-10561.
3. K. Kim, A. Razzaq, S. Sorcar, Y. Park, C. A. Grimes and S.I. In, *RSC Adv.*, 2016, **6**, 38964-38971.
4. S. D. Kim, Y. K. Park, C. H. Bu and D. W. Jung, *Bull. Korean Chem. Soc.*, 2016, **37**, 1071-1075.
5. T. Tang, Z. Xie, S. Zhou, Y. Zhang, Z. Yuan, L. Zhang and L. Yin, *ACS Appl. Mater. Interfaces*, 2016, **8**, 22201-22212.