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Cobalt Selenide: A Versatile Cocatalysts for Photocatalytic Water Oxidation with Visible Light

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Experimental Section

All the chemicals were purchased without further purification. The purity of $Co(AC)_2 \cdot 3H_2O$, Na_2SeO_3, urea, ammonium tungstate, ammonium vanadium, and bismuth nitrate are 99 %.

Synthesis of $CoSe_2$: $CoSe_2$ was synthesized according to the literature with a few modifications. In a typical procedure, 1mmol (0.249 g) of $Co(AC)_2 \cdot 3H_2O$ was added into 25 mL of DI water or 5 mL H_2O/20 mL ethanol solution under magnetic stirring. About 10 min later, 5 mL of DETA (diethylenetriamine) and 1 mmol (0.173 g) of Na_2SeO_3 were added. After further stirring for 0.5 h in a beaker to dissolve completely, the homogeneous solution was transferred into a 50mL Teflon-lined autoclave, which was sealed and maintained at 180□ °C for 12 or 4 h and then naturally cooled to room temperature. The resulting solid product was collected and washed with DI water. Then, the nanocomposite powder was obtained by freeze-drying for next characterizations.

Synthesis of g-C_3N_4: g-C_3N_4 was obtained with a traditional polymerization fashion. Typically, 10 g urea was placed into a crucible with a cover. Then it was heated at 550 °C for 2 h with a heating rate of 5 °C/ min. The final pink yellow powder was obtained after cooled to room temperature.

Synthesis of WO_3 and $BiVO_4$: WO_3 was synthesized by direct anneal ammonium tungstate at 550 °C for 4 h. $BiVO_4$ was prepared by a homogenous precipitation according to a similar procedure reported previously.[19] Typically, urea (5 g) was dissolved in the mixed solution of ammonium vanadium and bismuth nitrate, then the solution was heated to 363 K with stirring. The urea hydrolysis led to an increase in the pH of the solution, resulting in the crystallization of $BiVO_4$. After the crystalline $BiVO_4$ powder was formed, the slurry was continuously stirred at 363 K for 24 h. The product was filtered, washed, and dried.

Synthesis of $CoSe_2$ Modified g-C_3N_4, WO_3 and $BiVO_4$: In a typical process, a certain amounts of $CoSe_2$ (1, 2, 3, and 5 wt%) was added into a solution containing 0.1 g g-C_3N_4, WO_3 or $BiVO_4$. The mixture was kept in ultrasonic bath for 10 min. The final products were obtained after drying with a vapour and dried in an oven at 80 °C for 10 hours.

Synthesis of CoO_x and CoS_x Modified g-C_3N_4: CoO_x and CoS_x modified g-C_3N_4 was prepared via a immersion strategy. In a typical process, a certain amounts of $Co(AC)_2 \cdot 3H_2O$ and carbon nitride powders were mixed together in 5 mL of DI water. Then, after stirred for 5 min, the mixture was evaporated with a water vapour. The solids were then calcined in the air or H_2S flow at 300 °C for 1 h. The final samples were collected after naturally cooled to room temperature.

Characterization: XRD measurements were performed on a Bruker D8 Advance diffractometer with Cu Ka1 radiation. The UV/Vis spectra were recorded on a Varian Cary 500 Scan UV/Vis system. Electron paramagnetic resonance (EPR) measurements were carried out on a Bruker model A300 spectrometer. Themorphology of the sample was investigated by field emission scanning electron microscopy (SEM) (JSM-6700F). TEM was performed on a FEI Tencai 20 microscope. X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo ESCALAB250 instrument with a monochromatized Al Kα line source (200 W). Photoluminescence spectra were recorded on an Edinburgh FI / FSTCSPC 920 spectrophotometer. 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.

Photocatalytic test for water oxidation: Photocatalytic O_2 production was carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. For each reaction, 50 mg catalyst powder was well dispersed in an aqueous solution (100 mL) containing $AgNO_3$ (0.01M) as an electron acceptor and La_2O_3 (0.2g) as a pH buffer agent. The reaction solution was evacuated several times to remove air completely prior to irradiation with a 300 W Xeon lamp with a working current of 15 A (Shenzhen ShengKang Technology Co., Ltd, China, LX300F). The wavelength of the incident light was controlled by applying some appropriate long-pass cut-off filters. The temperature of the reaction solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed *in-situ* by gas chromatography equipped with a thermal conductive detector (TCD) and a 5Å molecular sieve column, using Argon as the carrier gas.

Table S1. OER of $CoSe_2$ modified g-C_3N_4 samples.

Solvent[a]	**T / h**[b]	**λ / nm**	**Amount of cocatalyst / wt %**	**OER / µmol h^{-1}**
H_2O	12	>300	3	19.2
H_2O/ethanol	12	>300	3	27
H_2O/ethanol	4	>300	3	34
H_2O/ethanol	4	>420	3	9

a: the solvent used for the synthesis of $CoSe_2$; b: hydrothermal treatment time.

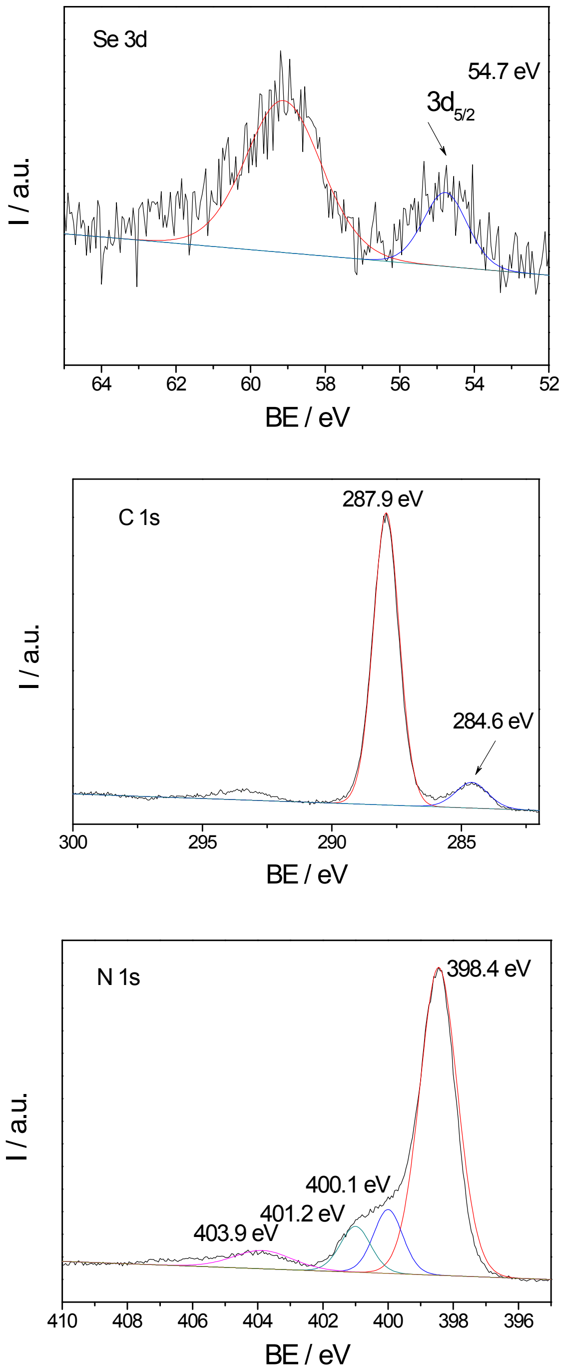

Figure S1. High resolution XPS for Se 3d, C 1s, and N 2p of $CoSe_2$ modified g-C_3N_4 samples.

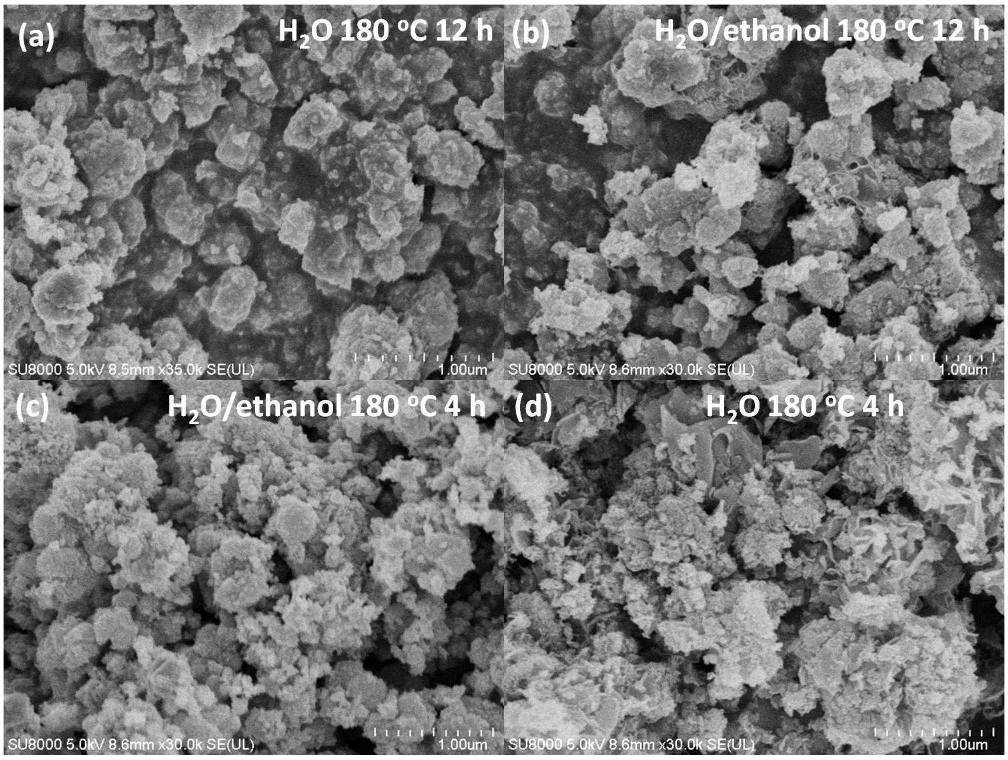

Figure S2. SEM imagines of CoSe2 synthesized at different conditions.

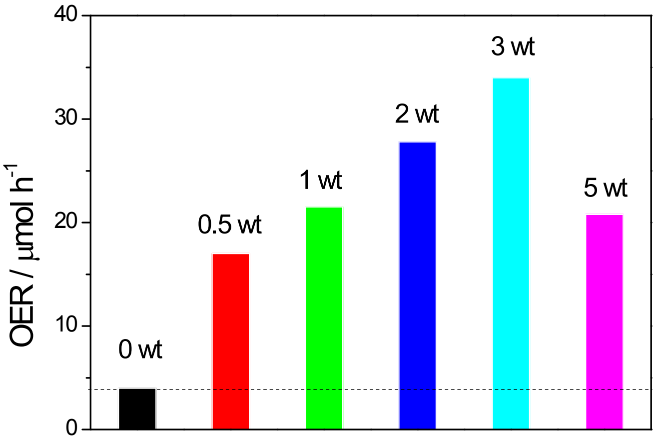

Figure S3. OER of different amounts of CoSe2 modified g-C_3N_4 samples.

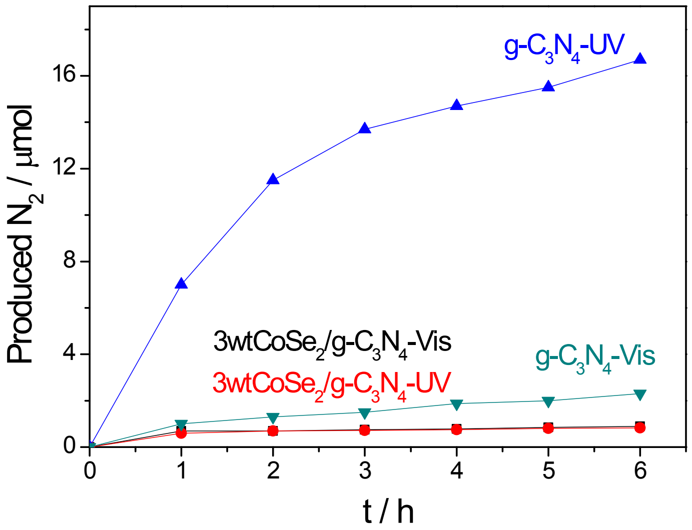

Figure S4. Time course of produced N_2 for pure g-C_3N_4 and 3 wt $CoSe_2$/g-C_3N_4 under visible and UV irradiation.

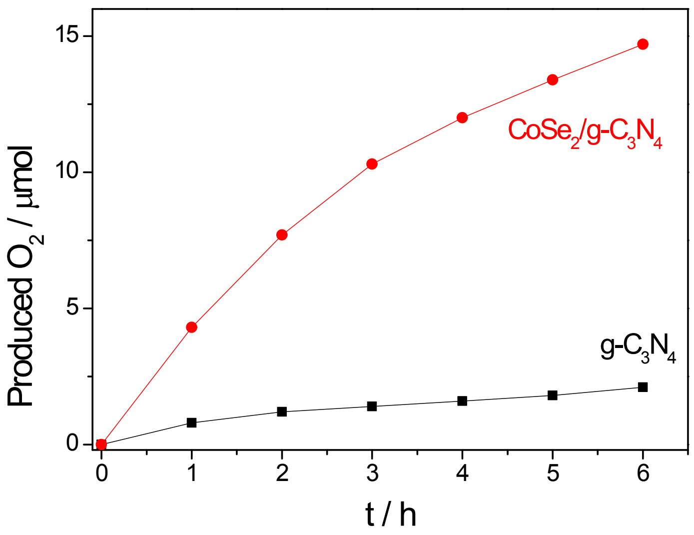

Figure S5. Time course of produced O_2 for pure g-C_3N_4 and 3 wt $CoSe_2$/g-C_3N_4 under visible irradiation (λ> 420 nm).

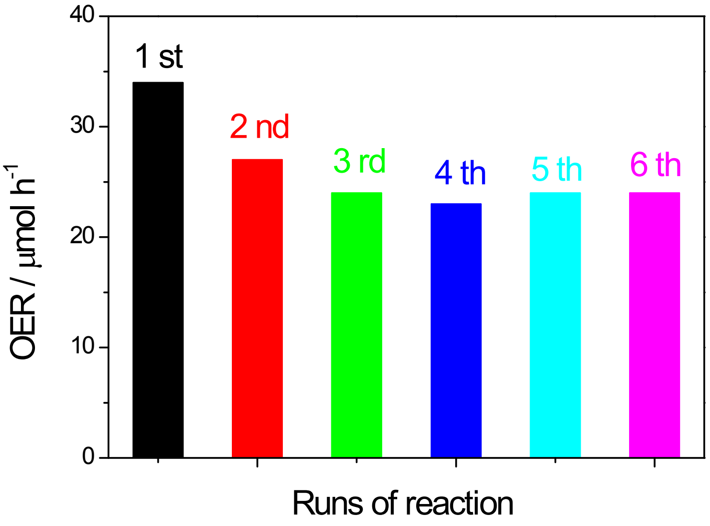

Figure S6. OER of recycled 3 wt $CoSe_2$/g-C_3N_4 under UV-Vis (λ> 300 nm).

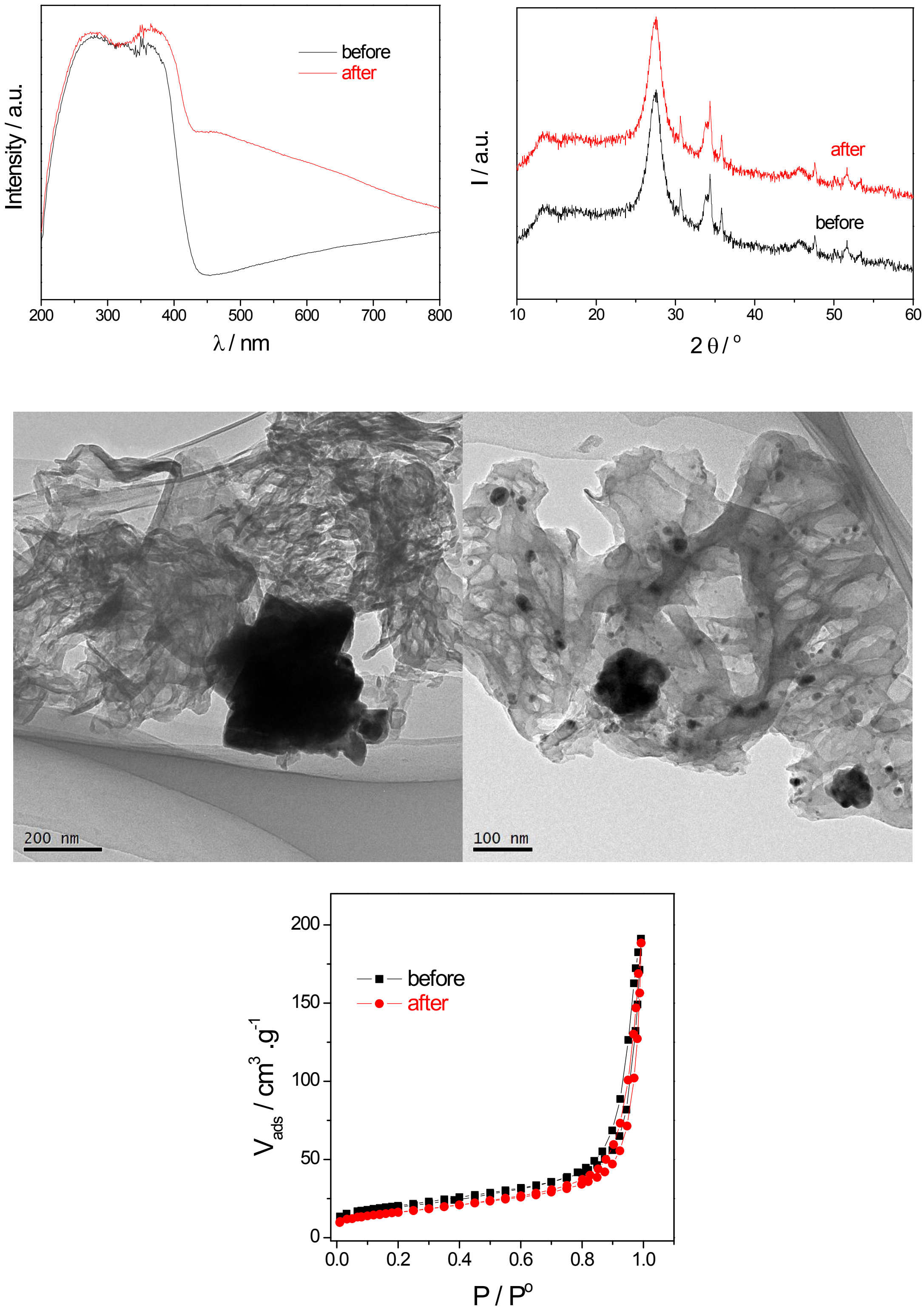

Figure S7. DRS, XRD, BET, and TEM of 3 wt $CoSe_2$/g-C_3N_4 before and after photocatalytic water oxidation.

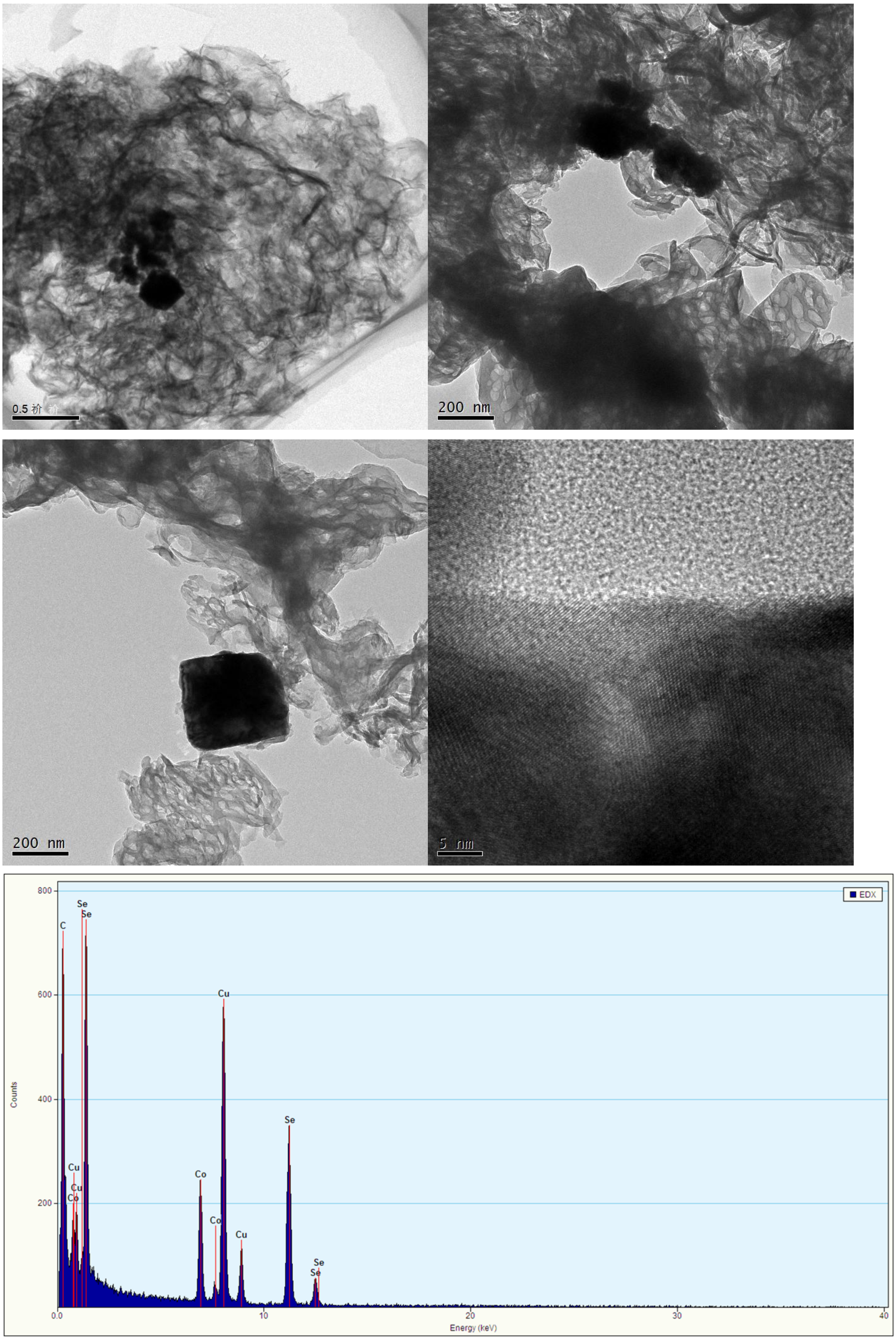

Figure S8. TEM and EDS analysis of $CoSe_2/g\text{-}C_3N_4$ before photocatalytic reaction.

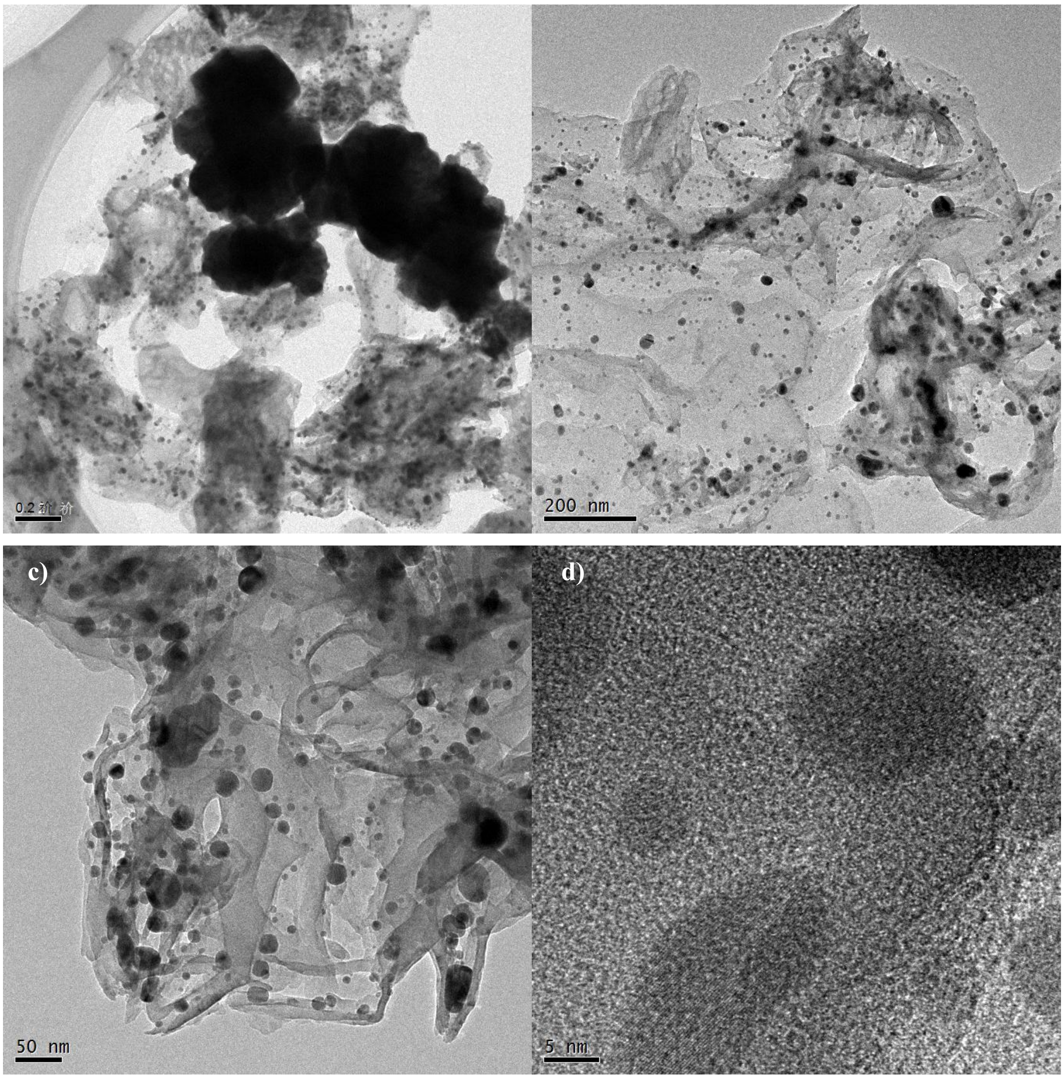

Figure S9. TEM pictures of $CoSe_2$/g-C_3N_4 after photocatalytic reaction.

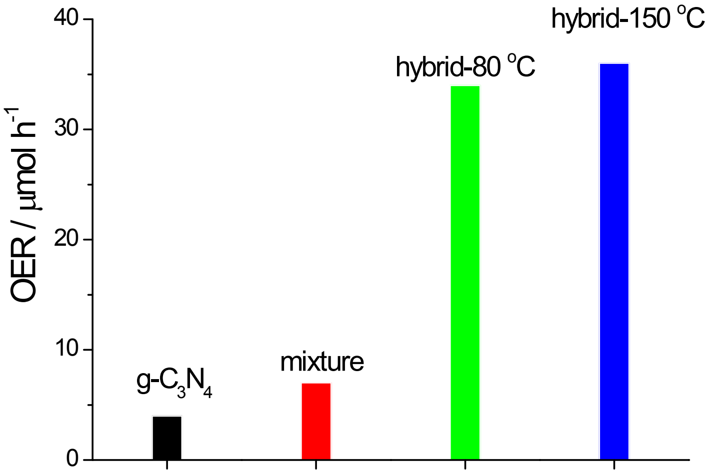

Figure S10. OER of pure g-C_3N_4, g-C_3N_4 and $CoSe_2$ mixture, $CoSe_2$/g-C_3N_4 hybrid thermal treated at 80 and 150 °C.