Electronic Supplementary Information (ESI)

for

A Sulfur-Mediated Synthesis of Carbon Nitride: Band-Gap Engineering and Improved Functions for Photocatalysis

Jinshui Zhang, Jianhua Sun, Kazuhiko Maeda, Kazunari Domen, Ping Liu, Markus Antonietti, Xianzhi Fu and Xinchen Wang*

Experimental Section

Synthesis. CNS samples were synthesized by heating trithiocyanuric acid (2g) at certain temperature for 2 h under flowing nitrogen gas (10 mL/min). The sample was denoted as CNSx, where *x* refers to the condensation temperature.

Characterization. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer with CuKα1 radiation. The UV/vis spectra were performed on a Varian Cary 500 Scan UV-visible system. FTIR spectra were recorded on a BioRad FTS 6000 spectrometer. Transmission electron microscopy (TEM) was recorded on a FEI Tencai 20 microscope.

Electrochemical analysis. The working electrode was prepared on fluoride-tin oxide (FTO) conductor glass, which was cleaned by sonication in chloroform, acetone and ethanol for 30 min, respectively. The glass was then rinsed with millipore water and kept in isopropanol for 24 h. 50 mg powder was mixed with 8 mL dimethylformamide under sonication for 30 min to get slurry. The slurry was spreading onto FTO glass whose side part was previously protected using Scotch tape. After air drying, the electrode was fired at 350 ^{o}C for 30 min in air to improve adhesion. A copper wire was connected to the side part of the FTO glass using a conductive tape. Uncoated parts of the electrode were isolated with epoxy resin, and the exposed area of the electrode was 0.25 cm^{2}. Electrochemical measurements were performed in a conventional three electrode cell, using a Pt plate and a Ag/AgCl electrode (3 M KCl) as counter electrode and reference electrode, respectively. The electrolyte was a 0.2 M Na_2SO_4 aqueous solution without additive and was purged with nitrogen gas for 2 h prior to the measurements. The working electrodes were immersed in the electrolyte for 60 s before any measurement was taken. The photocurrent measurements were conducted with a BAS Epsilon workstation, with the working electrodes irradiated from the back side in order to minimize the influence of thickness of the semiconductor layer. The visible light was generated by a 300 w xenon lamp (PLS-SXE300) with 420 nm and IR cut-off filters, and was chopped manually. The electrochemical impedance spectroscopy experiments were taken on a Precision PARC workstation with 10 mV perturbation signal.

Photocatalytic Test. Reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. H_2-production half reaction was performed by dispersing 50 mg of catalyst powder in an aqueous solution (100 mL) containing triethanolamine (10 vol.%) as sacrificial electron donor. Pt was photodeposited on the catalysts using H_2PtCl_6 dissolved in the reactant solution. For the O_2-production reaction, 50 mg catalyst powder 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 reactant solution was evacuated several times to remove air completely prior to irradiation under a 300 W Xe lamp and a water-cooling filter. Visible light irradiation was realized by attaching a 420 nm cut-off filter at the light source. The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector.

Bandgap determination. The bandgap energy of the sample was determined using the following equation: $\eta(\lambda)h\nu = A (h\nu - E_g)^n$ Where *A* is a constant, and *n* equals 0.5. According to Figure S1, the plots of $(\eta h\nu)^{1/2}$ versus $h\nu$. Straight lines were observed and the intercepts were obtained at 2.70 eV, 2.72 eV,

and 2.67 eV for g-C$_3$N$_4$, CNS$_{600}$ and CNS$_{650}$, respectively, which corresponds to their bandgap energies.

Figure S1. Bandgap determination of g-C$_3$N$_4$, CNS$_{600}$ and CNS$_{650}$ from the $(\eta h\nu)^{1/2}$ versus hν plots.
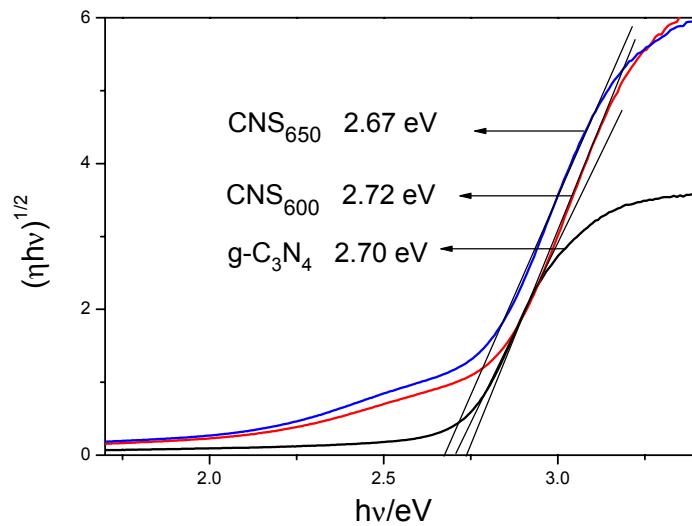
Figure S2. FTIR spectrum of g-C$_3$N$_4$ and CNS$_{600}$.
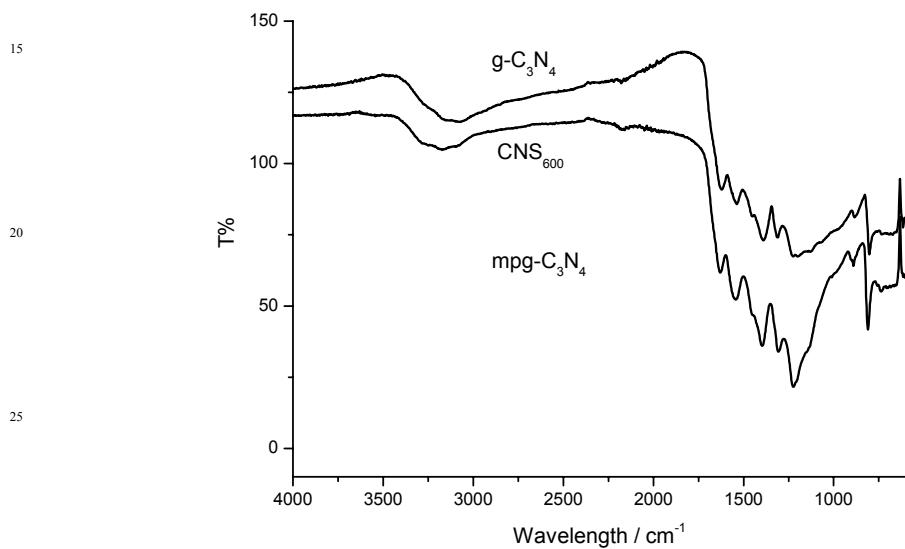
**Figure S3**. Electrochemical Mott-Schottky plots of g-C$_3$N$_4$ and CNS samples.
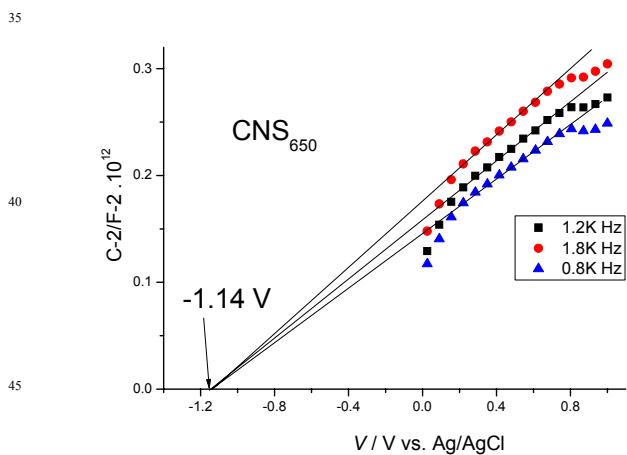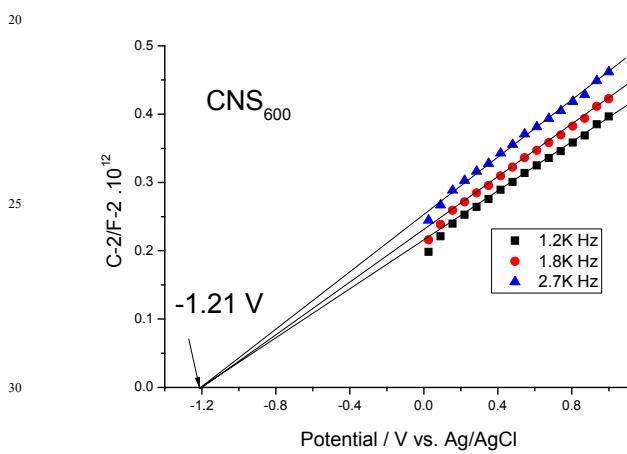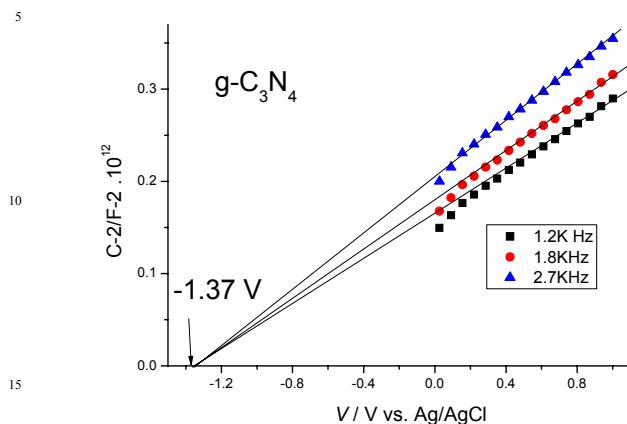
**Figure S4**. Electrochemical Mott-Schottky plots of g-C₃N₄ and CNS samples.
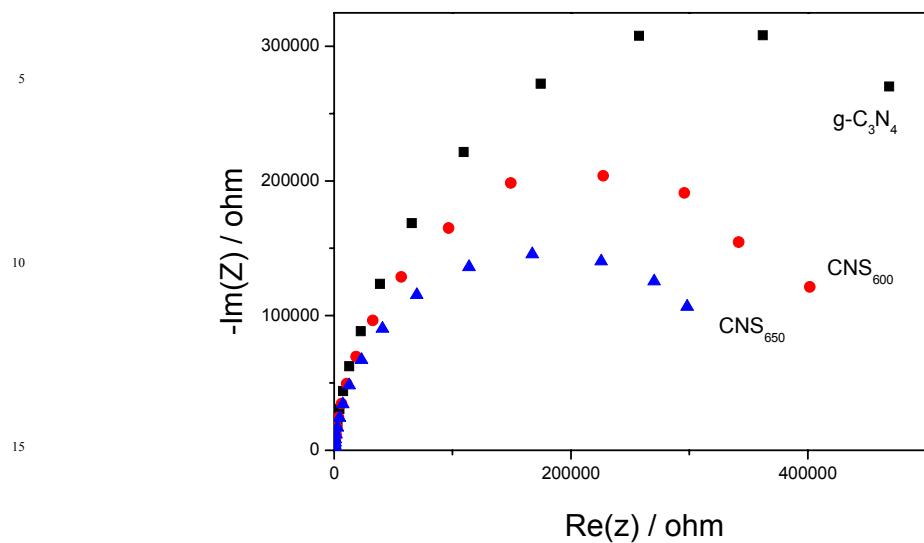
Figure S5. p-type and n-type photocurrents as a function of incident light using different cut-off filters. And the value of the photocurrent was matched with the optical absorption of the CNS samples.