

Supplementary Information

Integration of Au nanoparticles with a g-C₃N₄ based heterostructure: switching charge transfer from type-II to Z-scheme for enhanced visible light photocatalysis

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Experimental Section

Photocatalyst Preparation: BCN was prepared by heating melamine in a covered crucible at 550 °C for 4h. CNNS was prepared by heating BCN at 520 °C for 2h in the air. Au nanoparticle-decorated CNNS (Au/CNNS) was prepared by deposition of 0.5 wt%, 1 wt% and 1.5 wt% Au on 0.1 g CNNS using a solar light simulator (AM 1.5) as a light source in water/methanol solution (50 ml solution containing 20 vol.% methanol). The Au/CNNS/W₁₈O₄₉ composite was prepared via a hydrothermal method. Typically, 0.3 g WCl₆ was dissolved in 60 mL of absolute ethanol, then a certain amount of Au/CNNS were added in, and subject to stirring for 1h to slow down the hydrolysis of WCl₆. The obtained solution was transferred to a Teflon-lined autoclave and heated at 180 °C for 24h. The resultant products were collected, washed with deionized water and ethanol for several times, and finally dried overnight. Bare W₁₈O₄₉ was prepared similarly to Au/CNNS/W₁₈O₄₉ composite except that only 0.3 g WCl₆ was added in 60 mL of absolute ethanol.

Characterization: The crystal structure of the prepared photocatalysts were characterized by using a powder X-ray diffraction (XRD) system (Rigaku D/Max Ultima II, Cu K α radiation). The optical absorption properties of the photocatalysts were measured on a Cary Win UV-visible spectrophotometer using BaSO₄ as the reflectance standard reference. The morphology of the photocatalysts was characterized with a scanning electron microscope (SEM, FE-SEM, ZEISS ultra 55). TEM and HRTEM images were taken on a transmission electron microscope (TEM, FEI Tecnai F30). BET surface area were recorded using a BEL SORP-mini II (BEL Japan INC., Japan). The PL spectrums were recorded by using NanoLog Spec fluorescence spectrometer with an excitation wavelength of 370 nm. The detection of hydroxyl radicals (\bullet OH) was performed by ESR method, briefly, 10 mg catalyst was put into 1 ml DMPO solution (0.9ml H₂O contains 0.1

ml DMPO). Then the solution was exposed to visible light irradiation with stirring. After 10 min irradiation, 0.1 ml solution was collected for ESR measurement. The ESR measurements were carried out with JEOL JES-FA-200 at room temperature.

Photoelectrochemical Measurement: The transient photocurrent measurements were carried out using a CHI 760E electrochemical workstation. The as-prepared $W_{18}O_{49}$, CNNS, CNNS/ $W_{18}O_{49}$ and Au/CNNS/ $W_{18}O_{49}$ photoanodes were used as the working electrode, Pt foil as the counter electrode, Ag/AgCl electrode as the reference electrode, and 0.5 M Na_2SO_4 solution was used as the electrolyte. A solar light simulator (AM 1.5) with a UV-cutoff filter ($\lambda > 420$ nm) was used as the visible light source. The photocurrent was measured at 0.7 V bias voltage versus Ag/AgCl. The Mott-Schottky plots were obtained in the dark at 1000 and 500 Hz.

Photocatalytic Experiments: The photocatalytic activities of samples were evaluated by photocatalytic reduction of Cr(VI) under visible-light irradiation of a solar light simulator (AM 1.5) with a UV-cutoff filter ($\lambda > 420$ nm). Potassium dichromate ($K_2Cr_2O_7$) was selected as a Cr(VI) compound. The photocatalytic reduction of Cr(VI) was performed in a quartz reactor containing 80 mg photocatalyst, 80 ml of Cr(VI) solution (20 mg L^{-1} based on Cr in a dilute $K_2Cr_2O_7$ solution) and 50 mg oxalic acid as sacrificial agent. The solution was stirred for 60 min in the dark to reach adsorption equilibrium and then was exposed to visible light irradiation. The Cr content in the reaction solution was determined using the diphenylcarbazide (DPC) method. In brief, 1 mL of reaction solution after photocatalytic reduction of Cr(VI) was mixed with 9 mL of 0.2 M H_2SO_4 . Subsequently, 0.2 mL of freshly prepared 0.25% (w/v) DPC in acetone was added. After stirring the mixture for about 15-30 s, it was allowed to stand for 10-15 min so as to ensure full color development, and then measured at 540 nm by UV-vis spectra. The

photocatalytic efficiency was determined by dividing C/C_0 , where C is the remained Cr(VI) concentration and C_0 is the starting Cr(VI) concentration.

Supplementary Figures and Tables

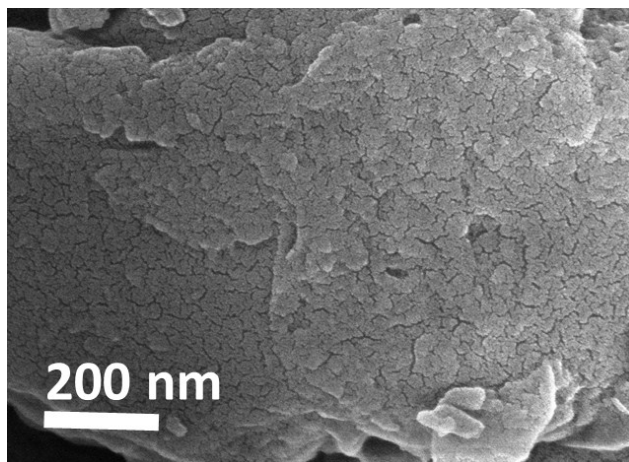


Figure S1. SEM image of BCN.

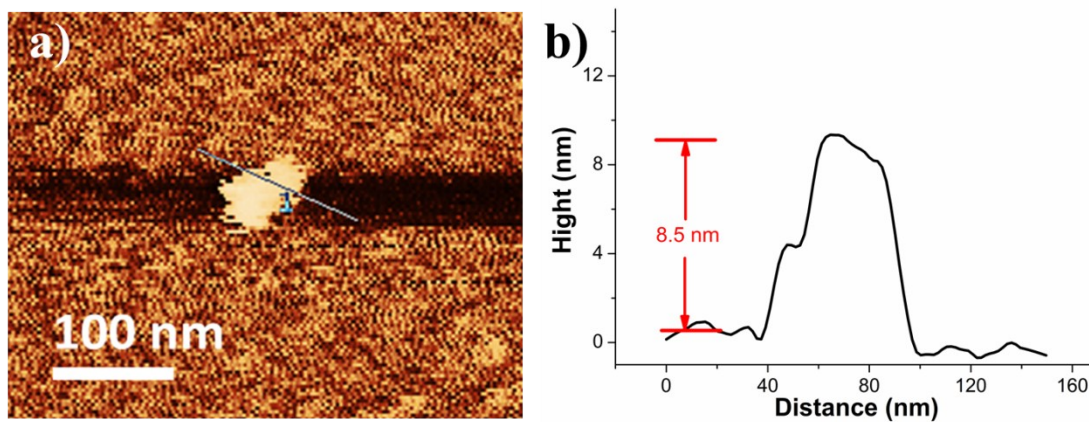


Figure S2. AFM image and the corresponding height distribution of CNNS.

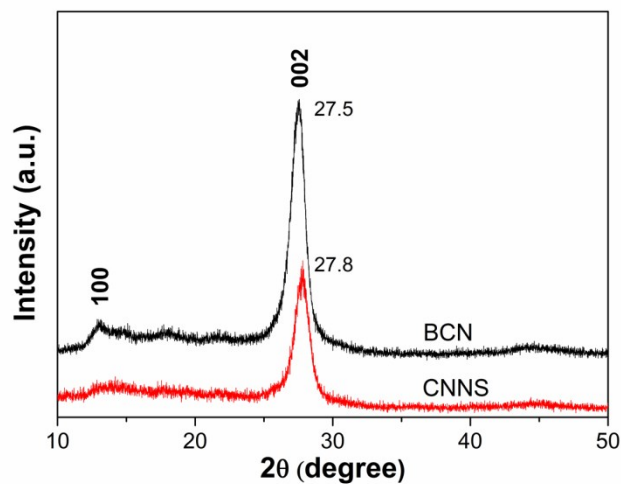


Figure S3. XRD pattern of BCN and CNNS.

Table S1. Summary of BET surface areas of samples.

Samples	BET surface area (m ² g ⁻¹)
BCN	8.6
CNNS	48.9
W ₁₈ O ₄₉	20.5
Au/CNNS/W ₁₈ O ₄₉	33.2

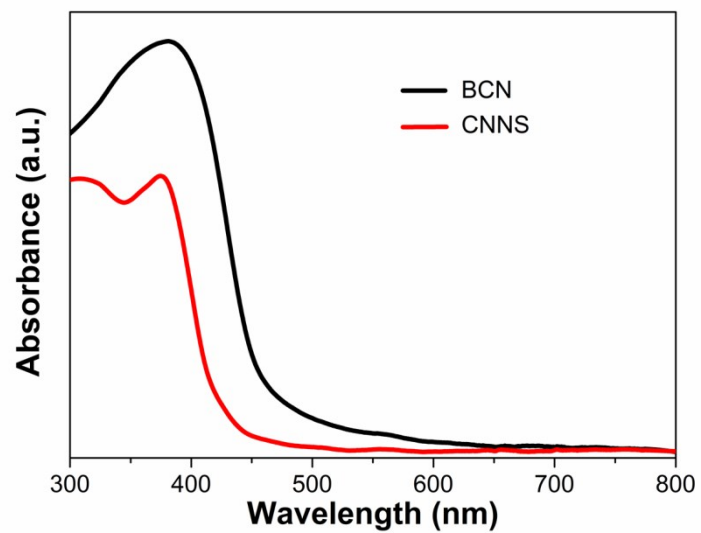


Figure S4. UV-vis spectra of BCN and CNNS.

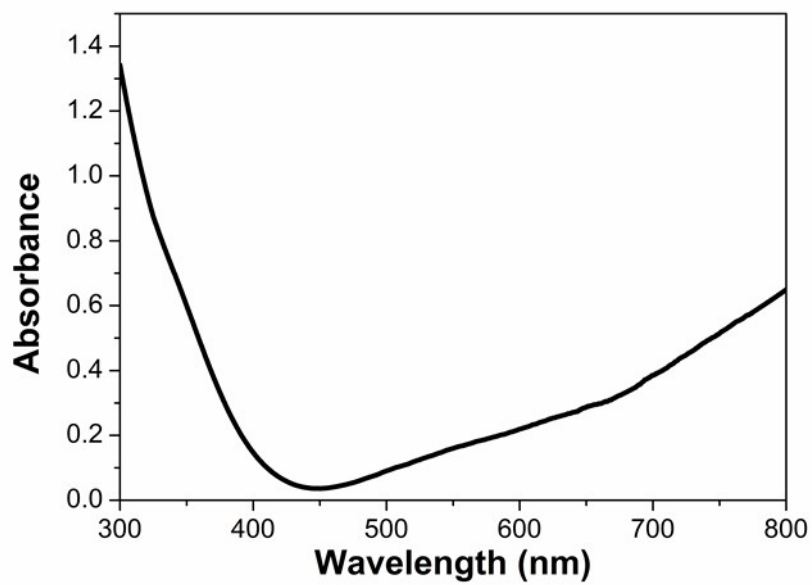


Figure S5. UV-vis absorption spectrum of $W_{18}O_{49}$.

Table S2. Comparison of photocatalytic performances for Cr(VI) reduction over Au/CNNS/W₁₈O₄₉ samples with different weight ratios.

Au/CNNS/W ₁₈ O ₄₉ samples with different weight ratios	Reduction efficiency in 30 minutes
Au: CNNS: W ₁₈ O ₄₉ = 0.005: 1: 1.2	62%
Au: CNNS: W ₁₈ O ₄₉ = 0.015: 1: 1.2	79%
Au: CNNS: W ₁₈ O ₄₉ = 0.01: 1: 1.2	87%
Au: CNNS: W ₁₈ O ₄₉ = 0.01: 1: 0.8	82%
Au: CNNS: W ₁₈ O ₄₉ = 0.01: 1: 1.6	74%

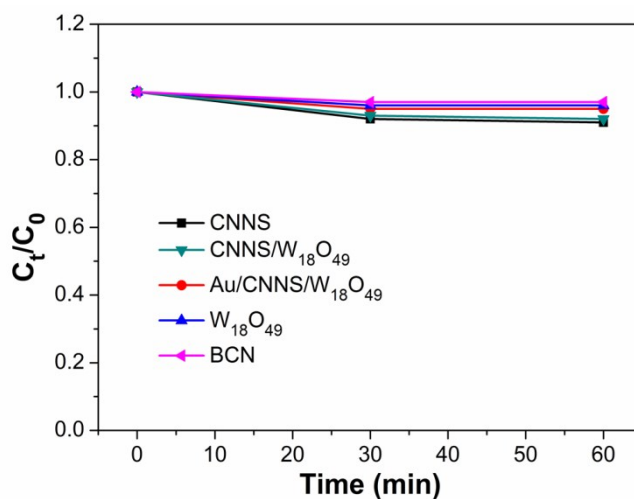


Figure S6. Cr(VI) absorption performances of samples in the dark.

Table S3. Activity comparison of various photocatalysts for Cr(VI) reduction.

Photocatalysts	Light source	Initial Cr(VI) amount	Reaction time (min)	Sacrificial agent	Reference
Au/CNNS/W ₁₈ O ₄₉	AM 1.5, visible-light ($\lambda > 420$ nm)	80 ml, 20 ppm	45	oxalic acid	This work
MIL-101(Cr)@NH ₂ -MIL-125(Ti)	300 W Xe lamp, visible-light ($\lambda > 420$ nm)	50 ml, 10 ppm	120	H ₂ O	1
Iron doped g-C ₃ N ₄ /MoS ₂	500 W Xe lamp, visible-light ($\lambda > 420$ nm)	50 ml, 20 ppm	150	RhB	2
N, S co-doped CeO ₂	150 W Xe lamp, visible-light ($\lambda > 400$ nm)	50 ml, 50 ppm	120	H ₂ O	3
Sn ⁴⁺ self-doped hollow SnS	300 W Xe lamp, visible-light ($\lambda > 420$ nm)	40 ml, 8 ppm	60	H ₂ O	4
MIL-53(Fe)-RGO	300 W Xe lamp, visible-light (λ : 420-760 nm)	40 ml, 20 ppm	80	ammonium oxalate	5
Pd@UiO-66(NH ₂)	300 W Xe lamp, visible-light ($\lambda > 420$ nm)	40 ml, 10 ppm	90	H ₂ O	6

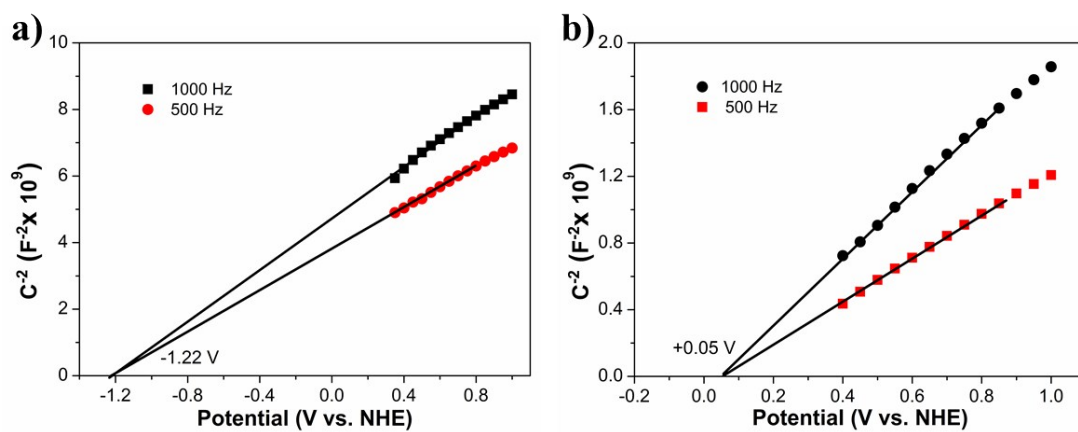


Figure S7. MS plots of (a) CNNS and (b) W₁₈O₄₉.

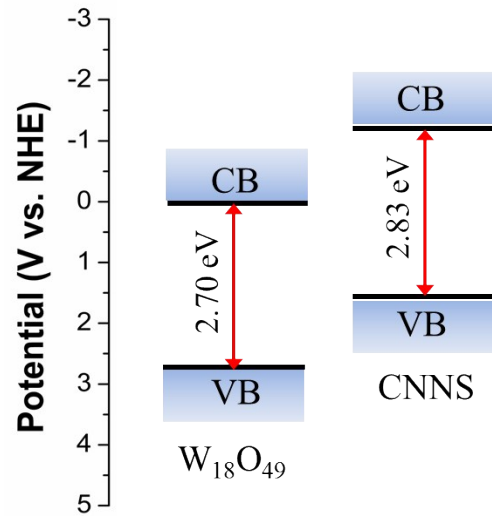


Figure S8. Band alignments of CNNS and $W_{18}O_{49}$.

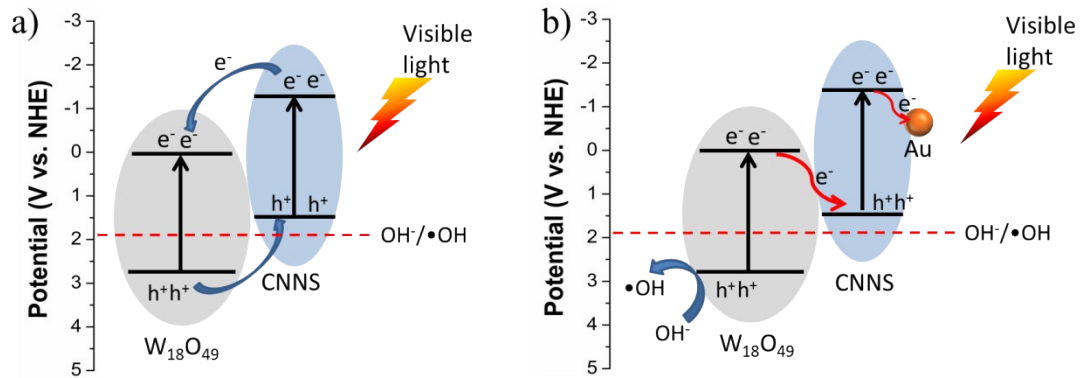


Figure S9. (a) Type II charge-transfer mechanism of CNNS/ $W_{18}O_{49}$ composite. (b) Z-scheme charge transfer mechanism of Au/CNNS/ $W_{18}O_{49}$.

Reference

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