

Supporting Information

Photocatalytic Reduction of CO₂ with H₂O over Graphene-Modified NiO_x-Ta₂O₅ Composites Photocatalyst: Coupling Yields of Methanol and Hydrogen

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Dedication ((optional))

Experimental Section

Materials

Graphite powder (99.95%, 325 mesh) was purchased from Alfa Aesar. Analytically pure Ta₂O₅ was obtained commercially from the Beijing Chemical Reagent Plant (Beijing, China) and used as received without further purification. Ultrapure water (resistivity $\geq 18 \text{ M}\Omega \text{ cm}$) was used during the experimental process. All solvents were purified according to standard methods.

Preparation of graphene oxide

Graphene oxide (GO) was obtained by chemical oxidation of exfoliated graphite oxide.¹ Graphite (3.0 g) was put into a mixture of concentrated H₂SO₄ (12 mL), K₂S₂O₈ (2.5 g) and P₂O₅ (2.5 g). The solution was heated to 80 °C and kept stirring for 5 h in an oil bath. The mixture was diluted with deionized water (500 mL), and the product was obtained by filtering through a 0.2 μm Nylon film and then dried under ambient condition. The product was then reoxidized to produce the graphite oxide. After the exfoliation by sonicating of a dispersion of graphite oxide (0.1 mg/mL) for 1 h, GO was recovered by filtration and the dried under vacuum.

Preparation of Ta₂O₅/graphene composite

Different weight content GO was dissolved in a solution of deionized water (20 mL) and ethanol (10 mL) by ultrasonic treatment for 1 h. Ta₂O₅ (200 mg) was added to the GO solution, which was then stirred for 2 h to obtain a homogeneous suspension. The suspension was placed in a 50 mL Teflon-sealed autoclave and maintained at 180 °C for 10 h to simultaneously reduce GO and deposit Ta₂O₅ on the carbon substrate. Finally, the resulting composite was recovered by filtration, rinsed three times with deionized water, and dried in a vacuum oven at 85 °C overnight.

Fabrication of Ni@NiO core-shell co-catalysts on composite

3 wt % Ni/NiO from an aqueous Ni(NO₃)₂ solution was loaded on Ta₂O₅/graphene composites by impregnation under sonication for 30 min,² followed by reduction with 2.5 mM NaBH₄ added dropwise under strong stirring for 30 min. The mixed solution was centrifuged and washed for several times with deionized water, and dried in a vacuum oven at 85 °C overnight. The samples were placed in crucibles and heated for 2 h in a furnace at 200 °C and then cooled slowly in the furnace.

In contrast, NiO loaded on Ta₂O₅/graphene composites was impregnation without reduction by 2.5 mM NaBH₄ under sonication for 30 min, then the mixed solution was placed in crucibles and sintered for 2 h in a furnace at 200 °C and then cooled slowly in the furnace.

Photocatalytic methanol and hydrogen generation

Methanol and hydrogen evolution experiments were performed in a 10 mL quartz cuvette containing photocatalyst (20 mg) in deionized water (8 mL). A 400W metal halide lamp was used as a light source. The quartz cuvette was sealed with a rubber septum and degassed by bubbling CO₂ through the suspension for 40 min under atmospheric pressure. All of the experiments were conducted at room temperature using distilled water. The gas products were measured by a gas chromatograph (GC-14C, Shimadzu Co.) that consists in a two channel GC. The first channel analyses H₂ using a column (3 m × 2 mm) containing 5 Å molecular sieves column with N₂ as carrier gas and TC detector. The analyses CO, CO₂, N₂, and O₂ with the same column and TC detector but using He as carrier gas. The two channel analyses hydrocarbons from C1 to C5 using a RT-Q plot column (2 m × 2 mm) and FID detector with N₂ as carrier gas and a FI detector. The amount of hydrogen evolution was calculated *versus* the amount of photocatalyst in the system. The cycle experiment of CO₂ reduction would open the sealed cuvette to release the hydrogen after each cyclability, and degassed again by bubbling CO₂ through the solution for 40 min, then the cuvette was sealed with a rubber septum to photocatalytic reaction again. The sample was taken by manually, and we took the volume of solution is 0.2 ul for methanol measurement, and the volume of aerometry is 400 ul for hydrogen measurement after every cycle irradiation for 6h.

Characterization

Transmission electron microscopy (TEM) images were collected on a JEM-2100 (JEOL) microscope with an accelerating voltage of 120 kV. UV-vis diffuse reflectance spectra (DRS) were obtained on a Hitachi UV-3010 spectrophotometer over the 250–600 nm range using BaSO₄ as a reference. Powder XRD was performed on a Bruker D8-Advance X-ray diffractometer with monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FTIR) spectra were carried out using Perkin-Elmer spectrometer in the frequency range of 4000–450 cm⁻¹ with a resolution of 4 cm⁻¹. Raman spectra were recorded on an inVia-Reflex Raman microprobe with 514 nm laser excitation. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al K α radiation. The base pressure was about 3×10^{-9} m bar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. Fluorescence spectral measurements were carried out with a HITACHI F-4500 fluorescence spectrophotometer, all measurements were made using a 295 nm excitation wavelength. Raman spectra were recorded on an inVia-Reflex Raman microprobe with 514 nm laser excitation. Atomic force microscopy (AFM) images were obtained by a Bruker multimode 8, operating in tapping mode with a scan rate of 0.531 Hz and the sample/line of 512. An n-doped silicon tip with 1 - 10 Ω cm phosphorus (Veeco, MPP-11100-140) was used as the probe.

Electrochemical Impedance Spectra (EIS) and Photocurrent Response Measurements

The film electrodes of Ta₂O₅ with or without graphene composites were fabricated before measuring EIS and photocurrent generate response. The powders were mixed with ethanol (150 mg/mL), and then the resulting paste was spread onto a conducting fluorine-doped SnO₂ glass substrate (FTO, 15 Ω/square) with a glass rod using adhesive tape as spacers. The resulting films had a thickness of ~ 4 μm and active area of 1 cm². EIS measurements were performed in KCl solution (0.1 M) containing a 1:1 mixture of 0.5 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] on a CHI660A electrochemical workstation using a three-electrode cell at room temperature. A saturated calomel electrode and Pt foil were used as reference and counter electrodes, respectively. Impedance spectra were recorded using ZPlot/ZView software under an ac perturbation signal of 5 mV over a frequency range of 1 MHz to 100 mHz.

Photocurrent action spectra were measured using a two-electrode configuration, where the Ta₂O₅ with or without graphene photoanode served as the working electrode (active area of about 1 cm²) and a platinum wire was used as the counter electrode. A 500 W Xe lamp equipped with a monochromator was used as the light source, and the electrolyte was an aqueous solution of KNO₃ (0.1 M).

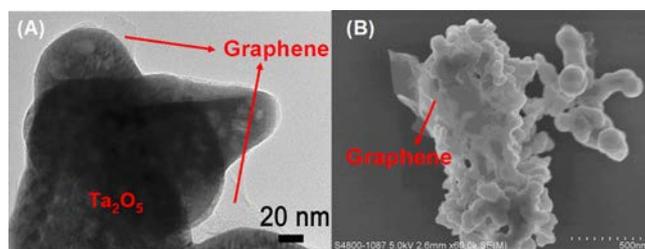


Fig. S1 (A) Typical TEM image of Ta₂O₅-rG, with Ta₂O₅ loading on the surface of reduction graphene. (B) The SEM image of Ta₂O₅-rG composites.

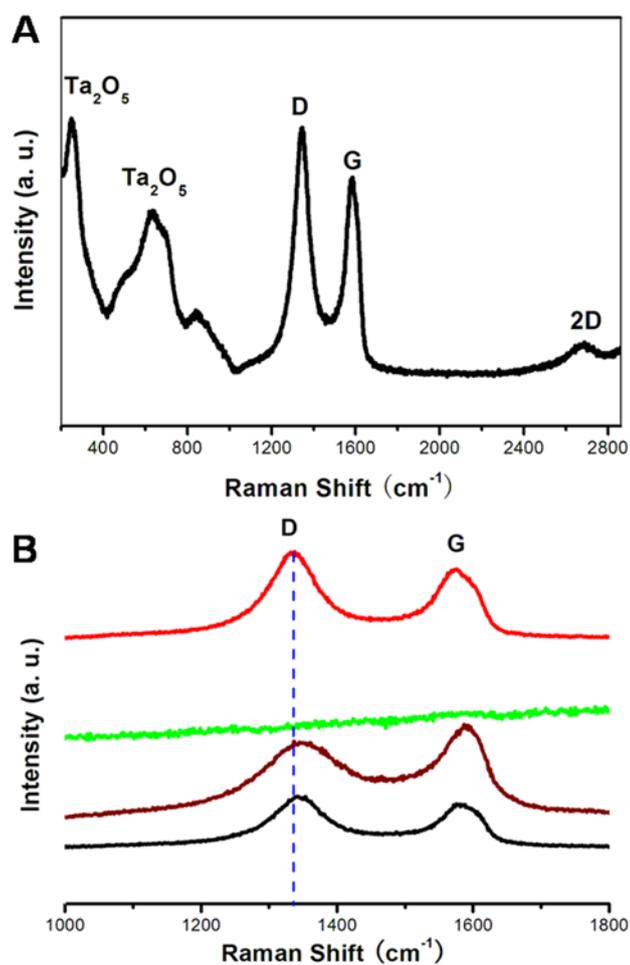


Fig. S2 (A) Raman spectra of Ta₂O₅-rG composites. (B) Raman spectra of reduction graphene (black line), graphene oxide (wine line), pure Ta₂O₅ (green line) and Ta₂O₅-rG composites (red line)

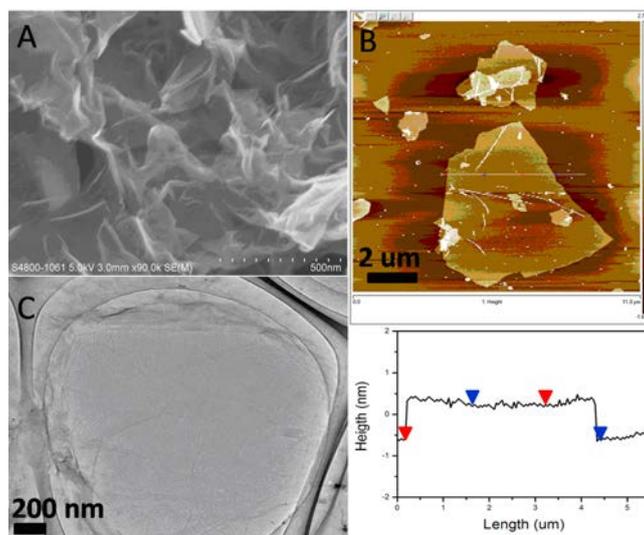


Fig. S3. (A) SEM, (B) AFM and (C) TEM of images of GO sheets, with the inset of (B) showing that the thickness of the GO fragment is ca. 0.829 nm.

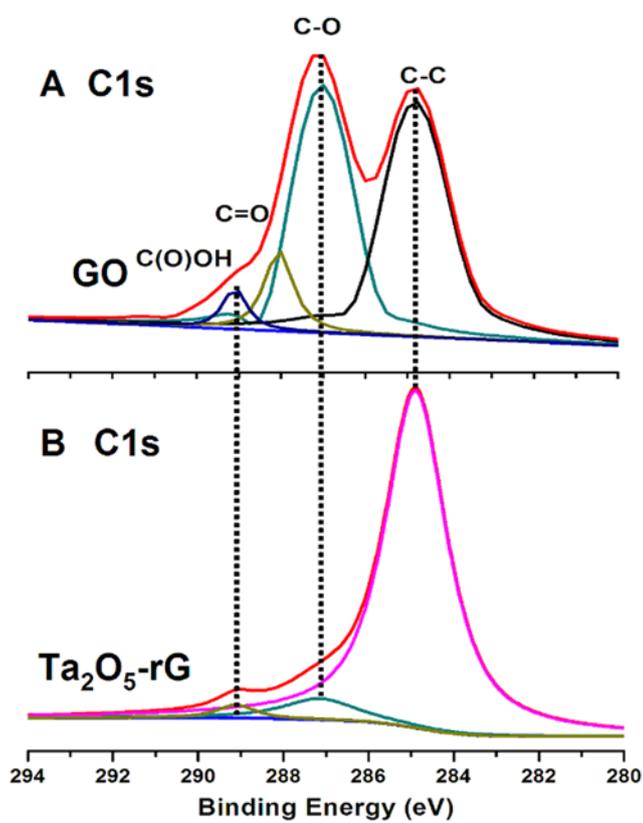


Fig. S4 XPS spectra of (A) C1s of the Graphene oxide, (B) C 1s of Ta₂O₅-rG composites.

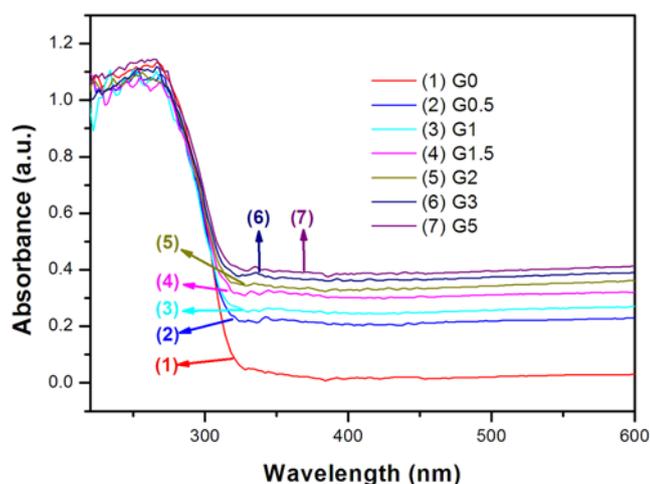


Fig. S5 UV-vis diffuse reflectance spectra (DRS) for Ta₂O₅-rG comprised with different graphene content.

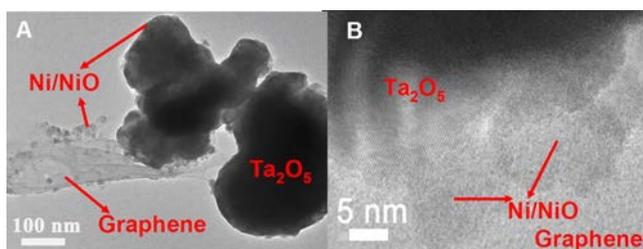


Fig. S6 Morphology of Ni/NiO loaded Ta₂O₅-rG. (A) TEM image showing NiO_x particles loaded on Ta₂O₅-rG. (B) High-resolution TEM image displaying Ni/NiO core-shell structure nanoparticles.

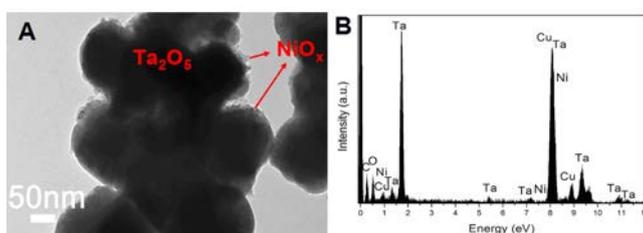


Fig. S7 Morphology and composition analysis of Ni/NiO loaded on pure Ta₂O₅ nanoparticle. (A) TEM image of Ni/NiO loaded on pure Ta₂O₅. (B) Energy dispersive spectroscopy (EDS) of Ni/NiO loaded on pure Ta₂O₅.

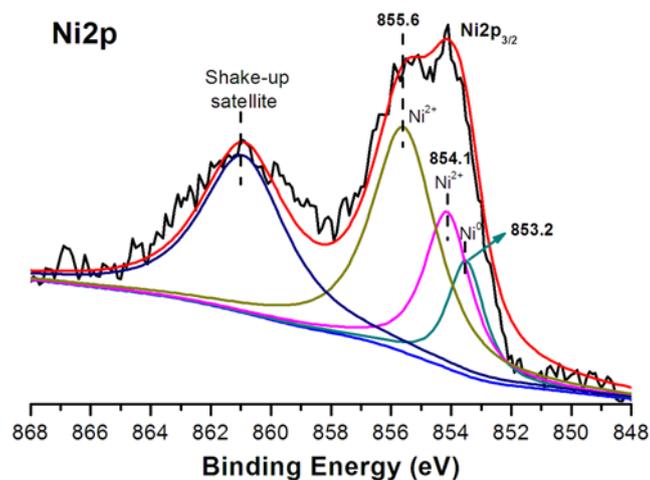


Fig. S8 XPS spectra of Ni2p of Ni/NiO loaded Ta₂O₅-rG composites.

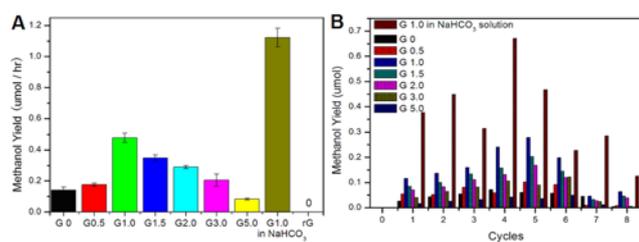


Fig. S9 Methanol yield of different photocatalysts in aerated aqueous CO₂ or NaHCO₃ solution under a 400 W metal halogen lamp used as a light source (A) average methanol yield per hour, (B) every cycle methanol yield.

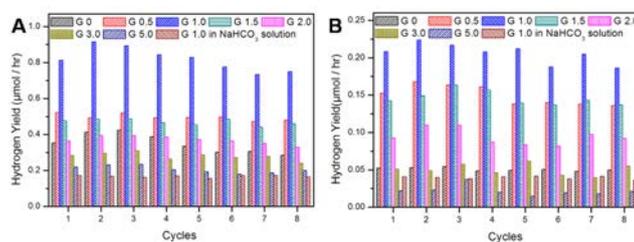


Fig. S10 Hydrogen yield capability based on different photocatalysts per hour under metal halide lamp irradiation (A) in saturated CO₂ aqueous or NaHCO₃ solution, (B) in saturated N₂ aqueous.

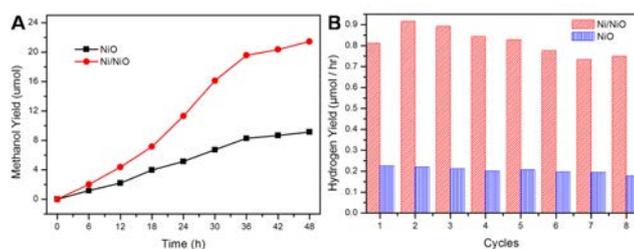


Fig. S11 Methanol and hydrogen yields based on different pretreatment method of photocatalyst G1.0 under a 400 W metal halogen lamp used as a light source. (A) Relationship between methanol yield as a functional of irradiation time in aerated CO₂ aqueous solution. (B) Hydrogen evolution in aerated aqueous solutions of CO₂. The sample was irradiated for 6 h in each cycle.

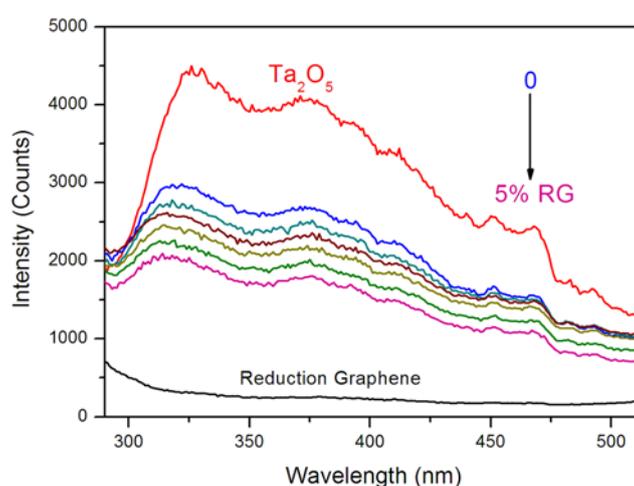


Fig. S12 Photoluminescence spectra of Ta₂O₅, Ta₂O₅-rG composites with different graphene content and pure reduction graphene, showing the clearly emission quenching of Ta₂O₅ for graphene collecting and transfer electron from conductor band of Ta₂O₅.

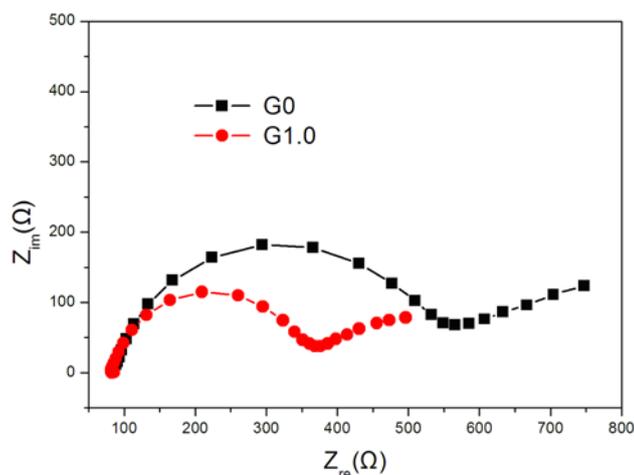


Fig. S13 Nyquist plots of electrochemical impedance spectra (EIS) for G0 and G1.0 electrodes. The EIS measurements were performed in the presence of 1 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) mixture as a redox probe in 0.1 M KCl aqueous solution.

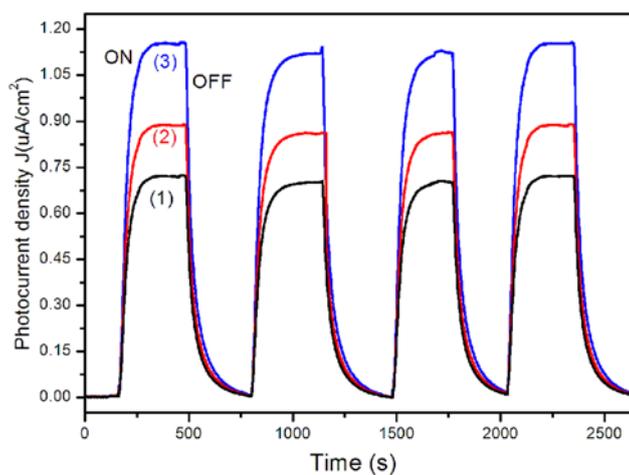


Fig. S14 The on-off photocurrent under Xe lamp illumination (I-t) without bias in a two-electrode configuration for the (1) Ta₂O₅, (2) Ni/NiO loaded on pure Ta₂O₅ and (3) Ni/NiO loaded Ta₂O₅-rG composites as photoanodes in 0.1 M KNO₃ solution.

References

- 1 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339–1339.
- 2 C. W. Tsai, H. M. Chen, R. S. Liu, K. Asakura and T. S. Chan, *J. Phys. Chem. C*, 2011, **115**, 10180–10186.