# Supplementary Information

# Synergistic effect of spatially isolated $Ni_2P$ and NiO redox cocatalysts on g-$C_3N_4$ for sustainably efficient $CO_2$ photocatalytic reduction

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## 1. Experiments

(1) Batch experiments of $CO_2$ photocatalytic reduction

0.05 g photocatalysts were coated on a 2.5 × 2.5 $cm^2$ glass film, and 10 mL deionized water were added in the middle of the reactor. The reactor was then vacuumed and filled with pure $CO_2$ at ambient pressure, and such operation was repeated three times. The reactor was

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irradiated by a 300 W Xe lamp with a 420-nm cutoff filter for 4 h, then the gas products were evaluated with an Agilent 7890B gas chromatography (USA) equipped with a TCD detector connected to a Molecular Sieve 5A column, with He used as the carrier gas.

(2) Photodeposition experiments

0.1 g $Ni_2P/NiO/CN(0.25)$ were dispersed in 40 mL deionized water in a semi-closed glass container, after fully mixed for 10 min, 2 mL $AgNO_3$ (10 mM) and 2 mL $Mn(NO_3)_2$ solution (10 mM) were added. After $N_2$ purged for 15 min, the suspension was irradiated by a 300 W Xe lamp with a 420 nm cutoff filter for 3 h, during which $N_2$ was always purged to maintain an inert atmosphere. The filtrates were then adequately washed with deionized water, dried in a vacuum oven at 60°C.

**2. Figures and charts**

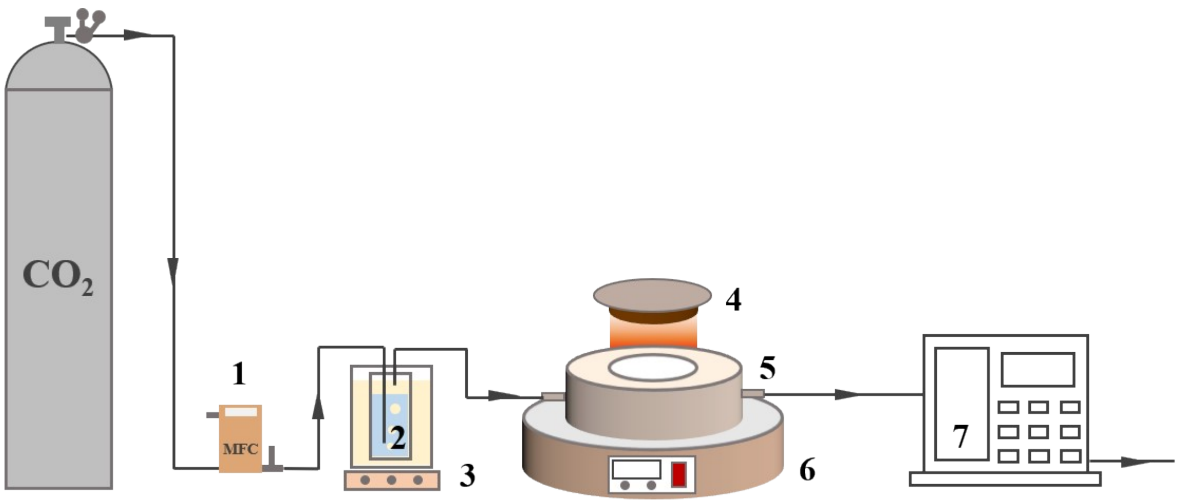


Figure S1. Schematic diagram of $CO_2$ photocatalytic reduction system (1-mass controller, 2-water bubbler, 3-temperature controller for the water bubbler, 4-Xeon light, 5-photocatalytic reactor, 6-remperature controller for the photocatalytic reactor, 7-gas chromatography).

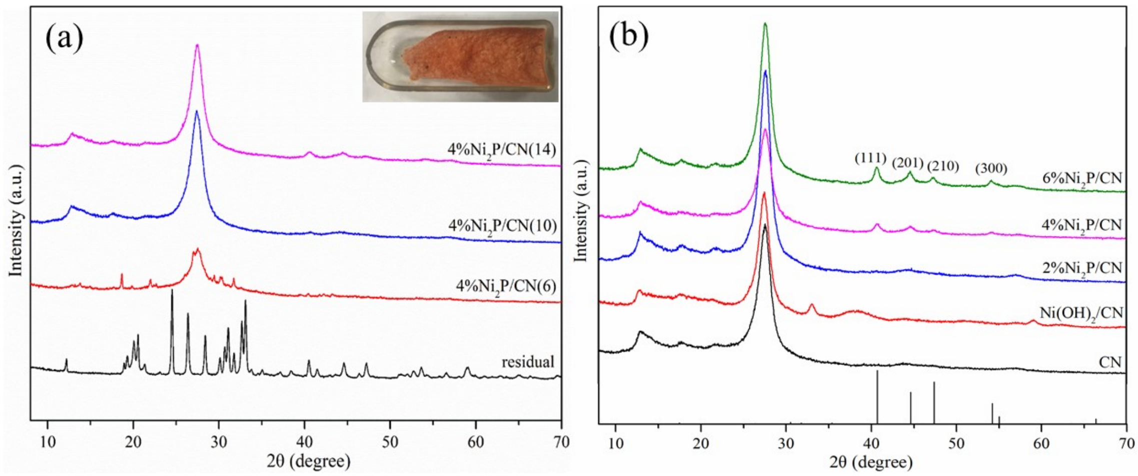


Figure S2. XRD patterns of 4%$Ni_2P$/CN($x$) (the insert was the image of the residuals of $Na_2HPO_2{\cdot}H_2O$ after calcination) (a) and $x$$Ni_2P$/CN samples (b).

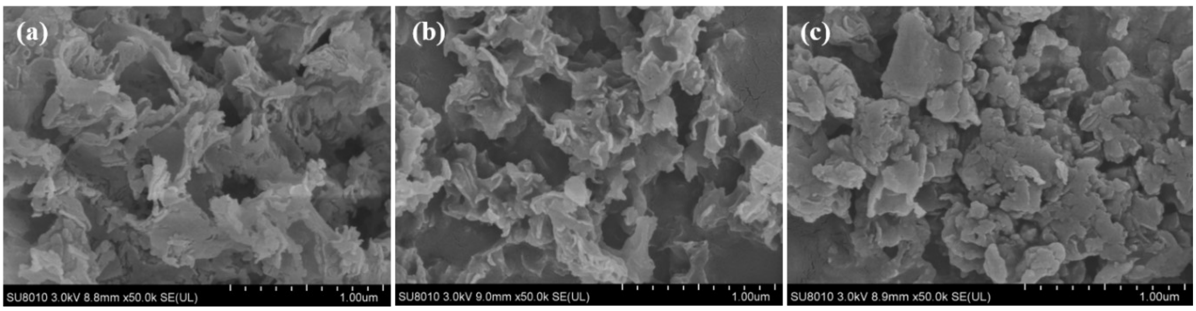


Figure S3 SEM images of CN (a), $Ni(OH)_2$/CN (b), $Ni_2P$/NiO/CN(1).

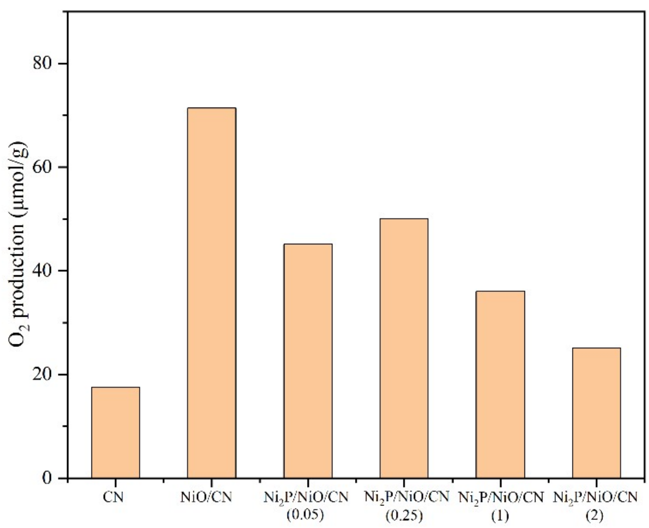


Figure S4. $O_2$ evolution over CN, NiO/CN, and $Ni_2P$/NiO/CN(MR) under visible-light irradiation for 4 h in batch experiments.

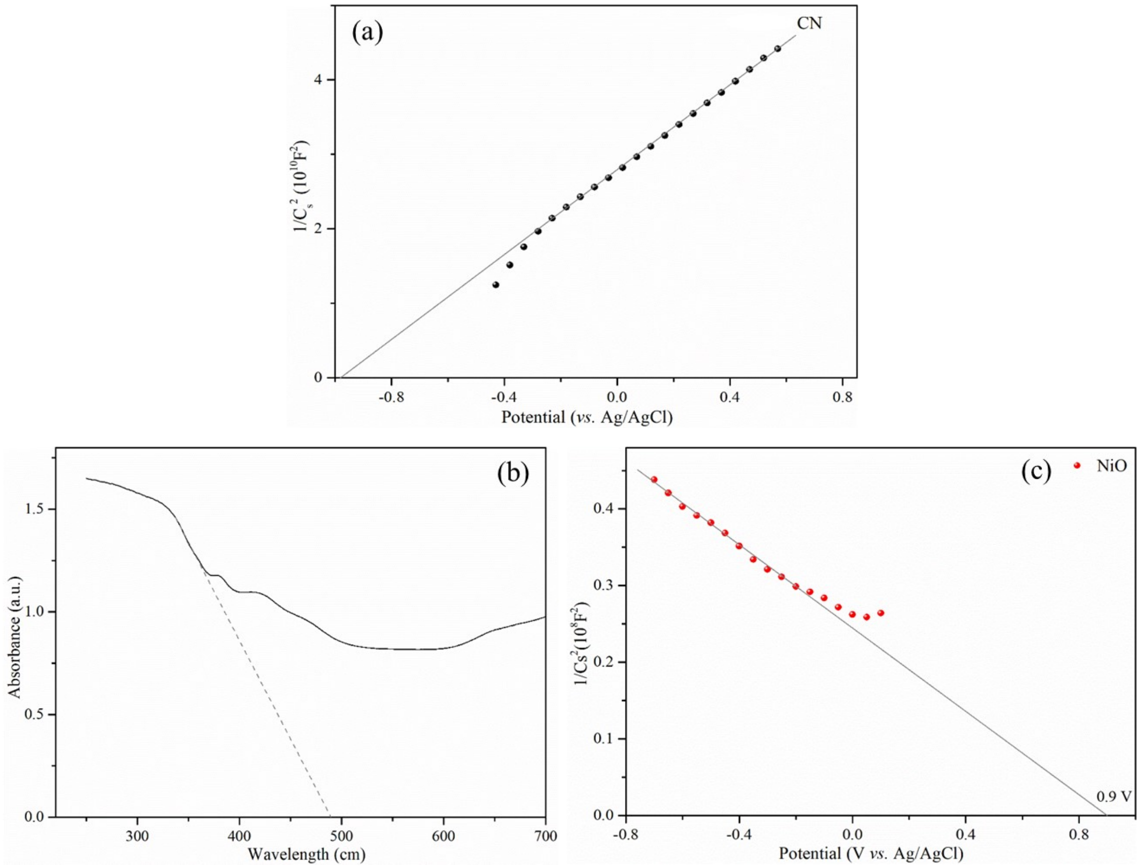


Figure S5. MS curves of CN (a), UV-vis spectra (b) and MS curve (c) of NiO.

Table S1. BET surface area ($S_{BET}$), average pore volume and pore size of CN, NiO and $Ni_2P$/NiO/CN(MR) samples.

| Sample | $S_{BET}$ ($m^2$/g) | Average Pore Size (nm) | Pore Volume ($cm^3$/g) |
|---|---|---|---|
| CN | 59.70 | 7.30 | 0.186 |
| NiO/CN | 66.45 | 6.90 | 0.234 |
| $Ni_2P$/NiO/CN(0.05) | 61.21 | 8.05 | 0.249 |
| $Ni_2P$/NiO/CN(0.125) | 54.76 | 8.04 | 0.243 |
| $Ni_2P$/NiO/CN(0.25) | 46.73 | 7.99 | 0.238 |
| $Ni_2P$/NiO/CN(1) | 46.68 | 7.86 | 0.223 |