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Supporting Information

Bimetallic-graphene sandwiched core-satellite colloidal nanodendrites as an efficient visible-NIR-sun light active photo-system for carbon dioxide reduction

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This pdf file contains experimental procedures and seven figures (S1-S7).

1. General

All chemical reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received without further purification. C-flat^{TM} carbon grids (Electron Microscopy Sciences, Hatfield, PA, USA) and HR-TEM (JEOL-2010, Japan, 200 kV) were used for TEM analysis. Extinction spectra were obtained with a UV spectrometer (SCINCO, South Korea). Structural analyses were performed using X-ray diffraction (Rigaku D/MAX 2500Tokyo, Japan). The amount of CO_2 dissolved in the reaction samples was determined using an HI 3818 carbon dioxide test kit (Hanna Instruments, Romania). ^{1}H-NMR and ^{13}C-NMR analyses were carried out using a JEOL JNM AL-400 instrument. The GC-MS analysis was carried out on Agilent 7890A GC and Agilent 5975C mass selective detector (Agilent Technologies, Santa Clara, CA, USA). Fourier transform infrared (FT-IR) spectra were recorded on a Jasco FTIR-4200 spectrophotometer (Maryland, USA). Renishaw, Raman micro system 2000 (Derbyshire, England) was used for the Raman analysis. A Xe lamp (300 W, Ceramaxs, Waltham, USA; power density = 6.11 W/cm^2) was used as a visible light (390–770 nm) source (Fig. S3). In addition, a near-infrared (NIR) laser (OCLA Laser, Passive Cooled InGaAs diode laser, LaserLab® South Korea, 808 nm, output power = 1 – 15 W/cm^2) was used. A solar simulator (Newport) with a power density of 0.23 W/cm^2 was used.

2. Methods

2.1 Preparation of nanosized graphene oxide (GO). Graphene oxide (GO) was prepared by the modified Hummer's method.[1] A 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (180:20 mL) was added to a mixture of graphite flakes (1.5 g). With stirring and cooling in an ice bath, $KMnO_4$ (9.0 g) was slowly added to the reaction mixture, producing a slight exotherm of 35–40 °C. The reaction was then heated to between 50 and 55 °C and stirred for 12 h. The reaction mixture was cooled to room temperature and then poured into iced-water (200 mL) containing 30% H_2O_2 (2.0 mL). The solution was then filtered through a metal US Standard testing sieve (300 μm). The filtrate was centrifuged (8,000 rpm for 30 min) and the supernatant was decanted. The remaining gel-like product was then washed in succession with water (200 mL), HCl (30%, 200 mL), ethanol (200 mL), and then again with water until the solution pH was 5.0–6.0. The resulting suspension was filtered through a PTFE membrane with a pore size of 0.45 µm and then lyophilized to produce a fluffy GO powder. GO powder (10.0 mg) was dissolved in triple-distilled water (>18 MΩ, 20 mL) and exfoliated by prolonged sonication (40% amplitude, 500 W, 4.0 h). The solution was centrifuged several times until no precipitate was settled down (15,000 rpm, 20 min).

2.2 Preparation of Pt@Au@rGO. Graphene oxide (GO) coating on AuNPs have been performed through simple electrostatic interaction by dropping positively charged AuNP (particle size = 30 nm, optical density (O.D.) = 1.0) into the negatively charged nano-sized GO solution. The GO layer on AuNPs was converted to rGO using Chemical method[2], 10 ml of GO-AuNPs solution was reacted with 250 µL of ammonia solution (28%) and 50 µL of hydrazine monohydrate (NH_2NH_2-H_2O) at 95 °C for 1 h. After the completion of reaction, the particles solution was cooled down to room temperature and centrifuged two times at 12,000 rpm for 15 min to remove the reagents (hydrozine and ammonia) and then re-dispersed in distilled water. Ultra-small Pt nanoparticles (3-4 nm) were decorated uniformly on Au@rGO by adding ascorbic acid (0.6 mL) to the Au@rGO solution (10 mL, O.D. = 1.0), along with 90 µL of 0.01 M $H_2PtCl_6 \cdot 6H_2O$ and 90 µL of 0.01 M HCl.[3] After addition, the reaction mixture was placed undisturbed for 12 h at 28 °C, and then centrifuged (10 000 rpm/15 min) and resulted nanoparticles (Pt@Au@rGO) re-dispersed in distilled water (10 mL).

2.3 Preparation of core-shell Au@TiO_2. First, 10 mL of AuNPs (cysteamine modified, O.D. = 1.0) were mixed with 1400 µL of ammonia (4%, in ethanol) and 50 µL of titanium isopropoxide solution (3 μL of titanium isopropoxide mixed with 500 μL ethanol) and stirred for 12 h in dark at room temperature. After that, the resultant mixture was washed twice with distilled water and re-dispersed in 10 mL of distilled water. 4-5 nm layer of TiO_2 has been formed on AuNPs (Fig. S1b). There is a red shift in the UV spectrum from 525 nm (black line) to 540 nm (red line) as AuNPs were coated with TiO_2 layer (Fig. S1f).

2.4 Preparation of core-satellite Pt@AuNPs

The spherical AuNPs (λ_{max} = 520 nm) were synthesized by using citrate-modified.[4] In a 100 mL boiling solution of $HAuCl_4$ (0.5mM) 2.2 mL of sodium citrate (38.8 mM) was added with continuous stirring. The resulting mixture was refluxed for 20 min to reduce completely as the color turned to wine red. After that, the final reaction mixture was centrifuged at 1000 rpm for 2 times and re-dispersed in distilled water for further use. Bimetallic Pt-Au nanoparticles were prepared by adding ascorbic acid (60 μL) to the AuNPs solution (1 mL, O.D. = 1.0), along with 9 μL of 0.01 M $H_2PtCl_6 \cdot 6H_2O$ and 9 μL of 0.01 M HCl. After addition, the reaction mixture was placed undisturbed for 12 h at 28 °C, and then centrifuged (8000 rpm) and re-dispersed in distilled water. 3-4 nm of PtNPs were uniformly coated on AuNPs (Fig. S1b, supporting information).

2.5 Preparation of core-satellite Ag@AuNPs

Bimetallic core-satellite Ag-Au nanoparticles have been prepared by electrostatic attraction between positive surface charged AuNPs and negative surface charged AgNPs. In 5 mL of AgNPs (3-5 nm, O.D. = 0.30) 1 mL of AuNPs (30 nm, O.D. = 1.0) have been added dropwise with continuous shaking. After the complete addition of AuNPs, the reaction mixture was allowed to shake slowly for 1 h and then re-dispersed in distilled water by centrifuging down at 2000 rpm. In order to avoid aggregation 100 uL of SDS (1%) was added to the mixture. Ag nanoparticles (3-5 nm) were uniformly coated on AuNPs (Fig. S1c, supporting information).

2.6 Photo-conversion reaction of CO_2 in aqueous medium. In a typical photo-conversion reaction of CO_2, the nanoparticles solution (10 mL, OD at 520 nm = 1.0) was placed in a Pyrex glass reactor (window diameter = 10 mm) equipped with a water circulation jacket (Fig. S2b-c). Then, the CO_2 was purged in to nanoparticles solution for 30 min to saturation (0.24 mg/mL). A Xe lamp was used for visible light irradiation whereas NIR (808 nm) laser (Fig. S2d) has been used as a source of NIR light irradiation.

2.7 Temperature dependent CO_2 reduction

In order to study the effect of temperature on the progress of reaction, CO_2 photoconversion reaction was carried out for 30 minutes of reaction time. Reaction samples were taken out after every 10 minutes and analyzed with GC and NMR for product quantification.

2.8 Two-step mechanism of CO_2 photocpnversion

To support the two-step mechanism, in the first step, the aqueous solution of the Pt@Au@rGO (without CO_2) was irradiated with visible light (Xe lamp) and connected to an H_2 indicator (blue colored aqueous copper sulfate solution). There was a color change and precipitation in the indicator solution was observed due to the reduction of Cu^{2+} to Cu^{+} and Cu by H_2 gas. In the second experiment, the formation of HCOOH was observed while H_2 gas was reacted with CO_2 for 4 h at room temperature. The chemical yield for HCOOH formation was found to be 0.72% (Fig. 4f), which is lesser as compared to Pt@Au@rGO mediated reaction, due to the absence of plasmonic photoconversion pathways and addition formic acid formation routes.[5]

2.9 HCOOH formation under H_2 gas reaction with CO_2

Formic acid formation through CO_2 reduction without light irradiation was carried out in the presence of a continuous flow of H_2 for 5 h. H_2 gas was produced by the addition of an aluminum foil to NaOH solution (200 mL, 2.0 M).[6] The as-generated H_2 gas was flowed into CO_2 saturated distilled water constantly for 5 h. Then, after the completion of reaction the pH was adjusted to 12.0 with dilute NaOH and the resulting solution was rotary evaporated to dryness. The final product was analyzed by ^{1}H-NMR and ^{13}C-NMR.

2.10 CO_2 photo-reduction reaction product analysis

After the completion of reaction (3 h) the resulted reaction mixture was centrifuged at 15,000 rpm/15 min to remove nanoparticles and to obtain the supernatant containing product. Then the solution was analyzed with gas chromatography−mass spectrometry (GC-MS). For GC analysis, the oven temperature was varied from 35 °C to 100 °C using helium gas as the carrier gas with an injector temperature of 200 °C and a sampling time of 20 min for GC-MS analysis. The equation obtained from the standard deviation curve was used to calculate the number of moles of formic acid formed.

Also, the pH of resulted reaction mixture was adjusted to 12 by the addition of dilute NaOH solution to convert HCOOH to sodium formate ($HCOO^-Na^+$). After rotary evaporation, the final product was analyzed with ^{1}H-NMR, ^{13}C-NMR (600 MHz, $CDCl_3$), FTIR and Raman spectroscopic studies. The quantum yield (QY) and chemical yield (CY) were calculated using GC and ^{1}H-NMR analysis techniques.

The small aliquots (10 μL) of CO_2 reduction reaction mixtures were placed on a quartz substrate and allowed to dry and then analyzed for Raman spectroscopy (the samples were analyzed with

532 nm laser excitation (50 mW)). Spectral data was collected over the range 400–1800 cm^{-1} with 10 sec of integration time.

2.11 Chemical yield calculation

(1) The amount of CO_2 in 10 mL solution was found to be 2.4 mg, as calculated by using a carbon dioxide kit (HI 3818, Hanna Instruments, Romania) and the procedure given along with it. The titration flask was rinsed with a CO_2 purged aqueous sample (5 mL) and 1 drop of phenolphthalein indicator was added. There was no change in the color of the indicator solution was observed. After that, the mixture was titrated with the HI 3818-0 solution provided by the carbon dioxide kit until the emergence of pink color. The total amount consumed for the titration was multiplied by 100 to obtain the quantity (ppm) of CO_2. The experiment was repeated for three times.

(2) The quantification of formic acid was carried out using a standard deviation curve plotted using ^{1}H-NMR (five standard samples of formic acid in $CDCl_3$ with increasing concentrations ranging from 0.015 mM to 0.15 mM) and GC-MS analysis.

(3) The chemical yield was calculated by dividing the molar concentration of formic acid formed by the molar concentration of carbon dioxide dissolved in the reaction sample. For example:

The equation obtained from standard deviation curve (NMR):-

Moles of HCOOH ÷ 10 mL = 0.0001809 M (from standard deviation curve)

Moles of CO_2 ÷ 10 mL = 0.005455 M (calculated using the carbon dioxide kit)

Chemical yield = moles of HCOOH ÷ Moles of CO_2 × 100

$$= 0.0001809 \div 0.005455 \times 100 = 3.31\% \qquad (1)$$

2.12 Quantum yield calculation

The quantum yield of produced formic acid was calculated by using following equation:

QY (%) = number of reacted electrons ÷ number of incident photons × 100%

= 2 × number of formic acid molecules/ number of incident photons × 100% (2)

Number of incident photons = moles of Fe^{2+} ÷ $\phi_\lambda \times t \times F$ (3)

(Moles of Fe^{2+} (calculated) = 0.03588, ϕ_λ = quantum yield of Fe^{2+} ion concentration = 0.65, t = time = 20 s,

F = mean fraction of light absorbed by ferrioxalate solution = 0.1488

Number of incident photons = 0.03588 ÷ 0.65 × 20 × 0.1488

= 0.01855 photons s^{-1} (4)

QY (%) = 2 × number of formic acid molecules/number of incident photons × 100%

= 2 × 0.0001809/0.01855 × 100 = 1.95% (5)

The number of incident photons was measured by the ferrioxalate actinometer method (equations (3) and (4)).[7] The actinometer solution was prepared as follows. In a 100-mL flask, an aqueous solution of $Fe_2(SO_4)_3$ (5 mL, 0.2 M) and an aqueous solution of $K_2C_2O_4$ (5 mL 1.2 M) were added. Then, this mixture was diluted to 100 mL volume by using distilled water. Then, the above actinometer solution (40 mL) was irradiated under visible light for 20 s.

Consequently, the ferrous ion concentration was determined by the formation of the iron-phenanthroline complex, detected by UV-visible spectrophotometry at 510 nm. The analytical procedure was as follows. In a 100-mL flask, the actinometer solution (1 mL) after irradiation, an aqueous solution of 1,10-phenanthroline (2 mL, 0.2 wt %), and a buffer solution (0.5 mL) of pH

= 4–5 were mixed and diluted to 100 mL with distilled water, and kept in the dark for 30 min. After 30 min, absorbance of the solution at 510 nm was measured using a UV-visible spectrophotometer. A comparative test was conducted by following the above mentioned procedure for the blank solution (actinometer solution without irradiation), and the ferrous ion concentration was calculated by UV-visible spectrophotometric observation at 510 nm.

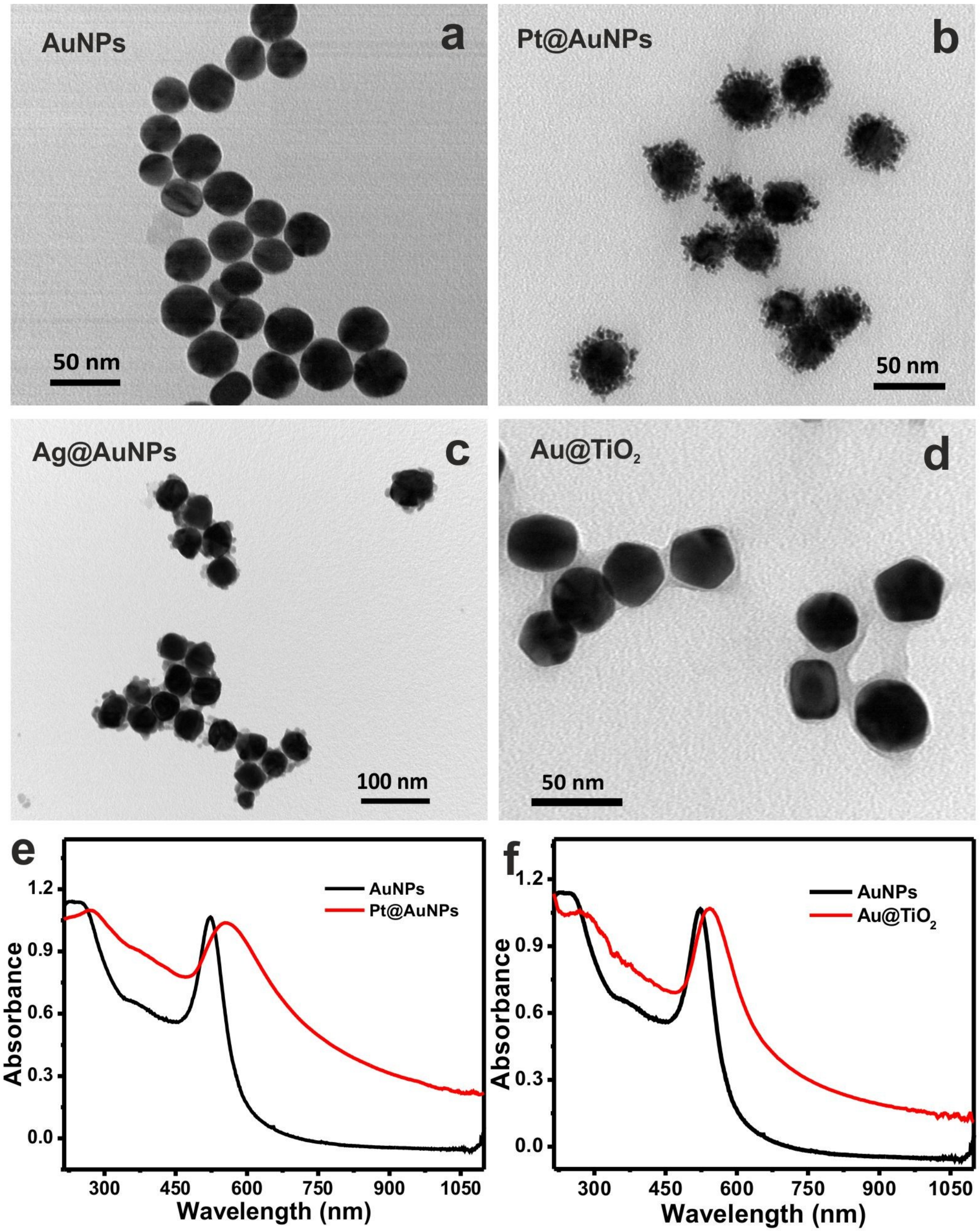

Fig. S1. TEM images of (**a**) AuNPs, (**b**) Pt@AuNPs, (**c**) Ag@AuNPs, and (**d**) Au@TiO$_2$. Comparative UV spetra of (e) AuNPs and Pt@AuNPs, and (f) AuNPs and Au@TiO$_2$.

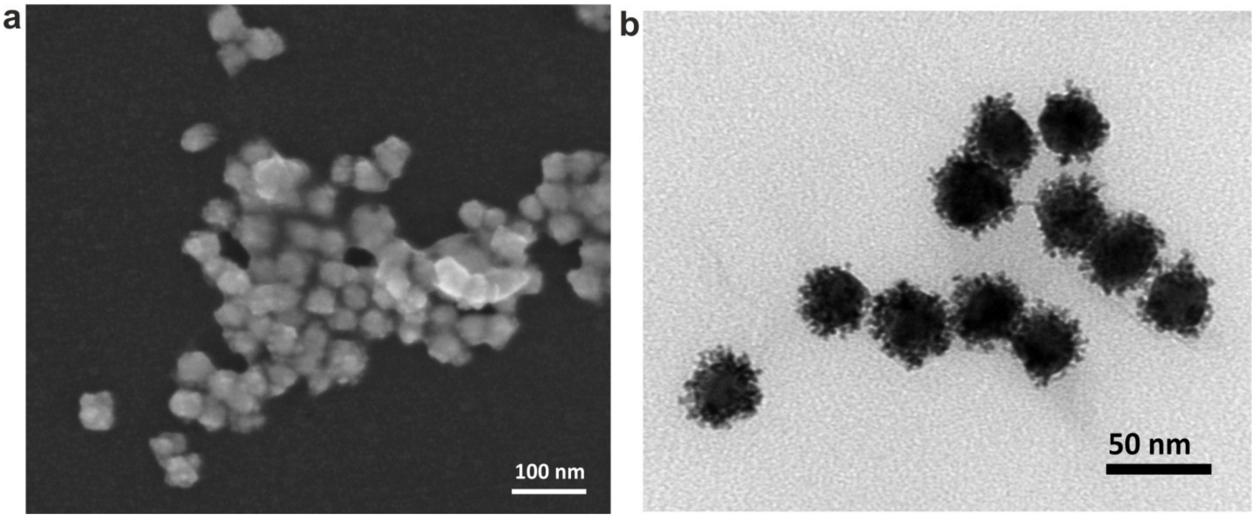

Fig. S2. (a) FESEM, and **(b)** TEM images of Pt@Au@rGO.

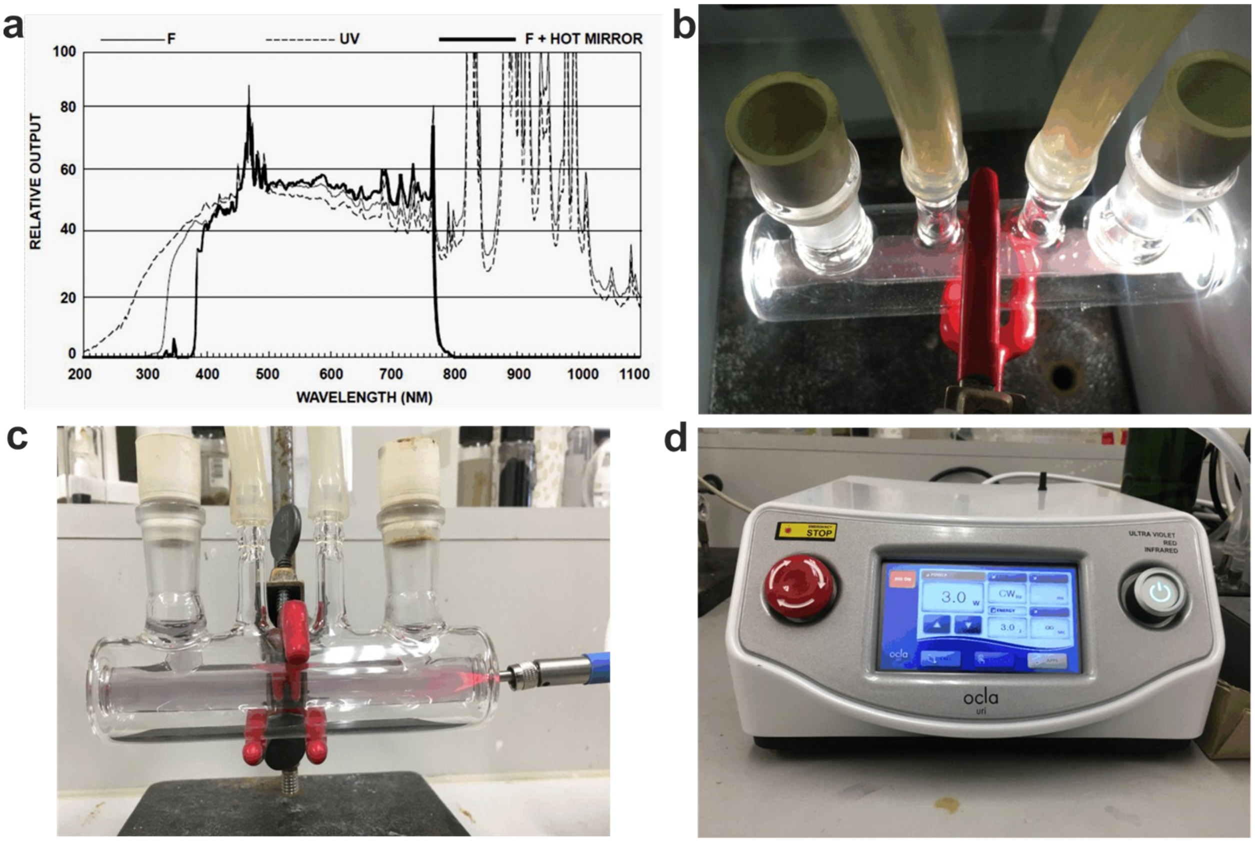

Fig. S3. (a) Output spectra of Xe lamp (Cermax, PE300BFA, 300 Watts). Instrumental setup for CO_2 photoconversion. (**b**) The Xe lamp (390 – 770 nm) irradiated glass reactor (Pyrex, 10 ml) with water circulation jacket. (**c**) The NIR laser (808 nm) irradiated the reaction vessel. (d) 808 nm NIR laser.

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (1)$$

$$H_2O \longrightarrow 1/2O_2 + 2H^+ + 2e^- \qquad (2)$$

$$CO_2 + e^- \longrightarrow CO_2^- \qquad (3)$$

$$CO_2 + H^+ + 2e^- \longrightarrow HCO_2^- \qquad (4)$$

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O \qquad (5)$$

$$CO_2 + 4H^+ + 4e^- \longrightarrow HCHO + H_2O \qquad (6)$$

$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O \qquad (7)$$

$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O \qquad (8)$$

Scheme S1. Reaction paths for photocatalytic CO_2 reduction.

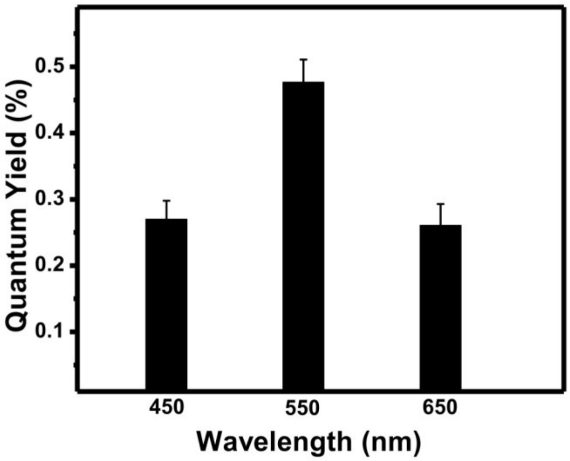

Fig. S4. Quantum yield estimated for the photocatalytic CO_2 reduction to HCOOH using Pt@rGO-AuNPs at different incident monochromatic wavelengths.

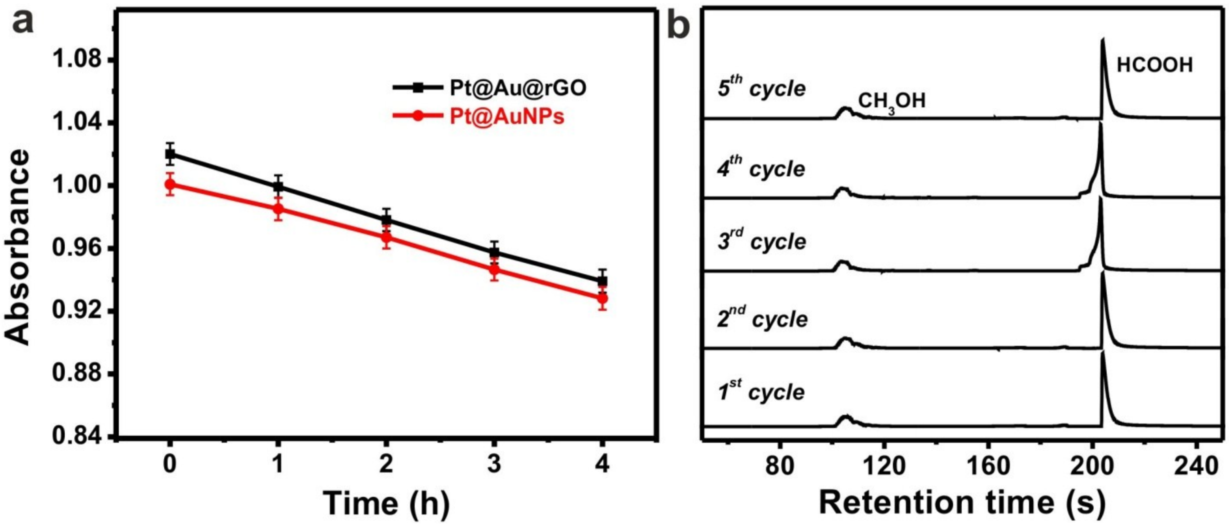

Fig. S5. (a) Stability of Pt@AuNPs, Pt@Au@rGO-N, and Pt@Au@rGO in visible light illumination for four hours. **(b)** Comparative Gas chromatogram for Pt@Au@rGO mediated reaction product after 4.0 h of visible light irradiation for five recycles.

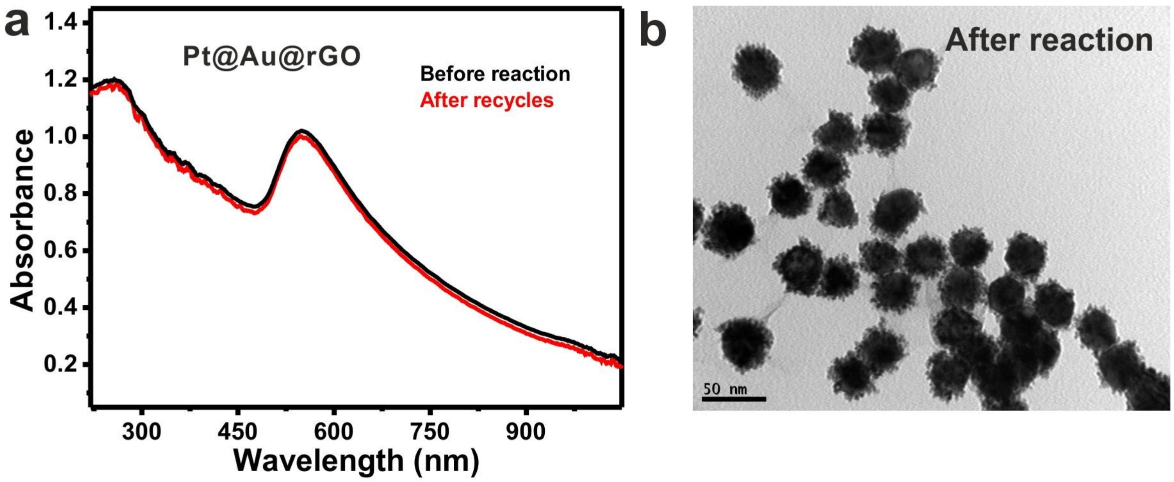

Fig. S6. (a) UV-Visible spectrum of Pt@Au@rGO nanoparticles before and after five reaction cycles. TEM images of Pt@Au@rGO **(b)** before and **(c)** after five recycles.

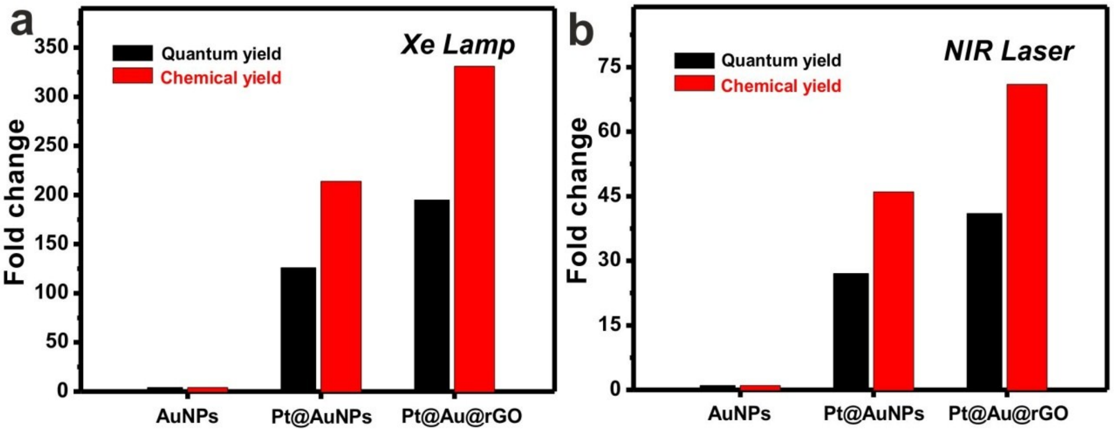

Fig. S7. Comparative fold change for the quantum and chemical yield of AuNPs, Pt@AuNPs, and Pt@Au@rGO mediated CO_2 reduction in **(a)** visible light and **(b)** NIR light irradiation.

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