

Electronic Supplementary Information

## **Dimension-matched plasmonic Au/TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposites as efficient wide-visible-light photocatalysts to convert CO<sub>2</sub> and mechanism insights**

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### **Experimental Section**

*Hydroxyl radical measurement.* Hydroxyl radicals ( $\bullet\text{OH}$ ) are important active species in photocatalytic reaction. Using coumarin as a labelled molecule to detect the content of hydroxyl radicals is an effective method with high sensitivity. The specific method for the hydroxyl radical test was as follows: 0.05 g of the catalyst was placed in 50 mL of coumarin solution at a concentration of  $2 \times 10^{-4}$  M. The mixture was stirred for 30 min before the experiment, to ensure that it reached the adsorption-desorption equilibrium. After irradiation for 1 hour, appropriate amount of the suspension was centrifuged in a 10 mL centrifuge tube and the supernatant was transferred into a Pyrex glass cell for the fluorescence measurement of 7-hydroxycoumarin by a spectrofluorometer (Perkin-Elmer LS55). To cut off UV-light, a light filter of 420 nm was placed between the light source and the reactor.

*CO<sub>2</sub> Temperature-programmed desorption measurement.* Temperature-programmed desorption (TPD) of carbon dioxide was carried out in a conventional apparatus by Chemisorption Analyzer equipped with a TCD detector. About 50 mg of catalysts were pretreated at 300 °C for 1 h under ultra-high-pure He gas flow with the rate of 30 mL min<sup>-1</sup>. The highly pure carbon dioxide was introduced at a constant temperature of 30 °C under

the flow rate of 30 mL min<sup>-1</sup> for 60 min. The physically adsorbed CO<sub>2</sub> was removed by being exposed with ultra-high-pure He at 30 °C for 60 min. Then the temperature was increased to 700 °C with the heating rate of 10 °C min<sup>-1</sup> under ultra-high-pure He. Finally, the desorbed CO<sub>2</sub> was monitored by Chemisorption Analyzer (Tp 5080 Chemisorb).

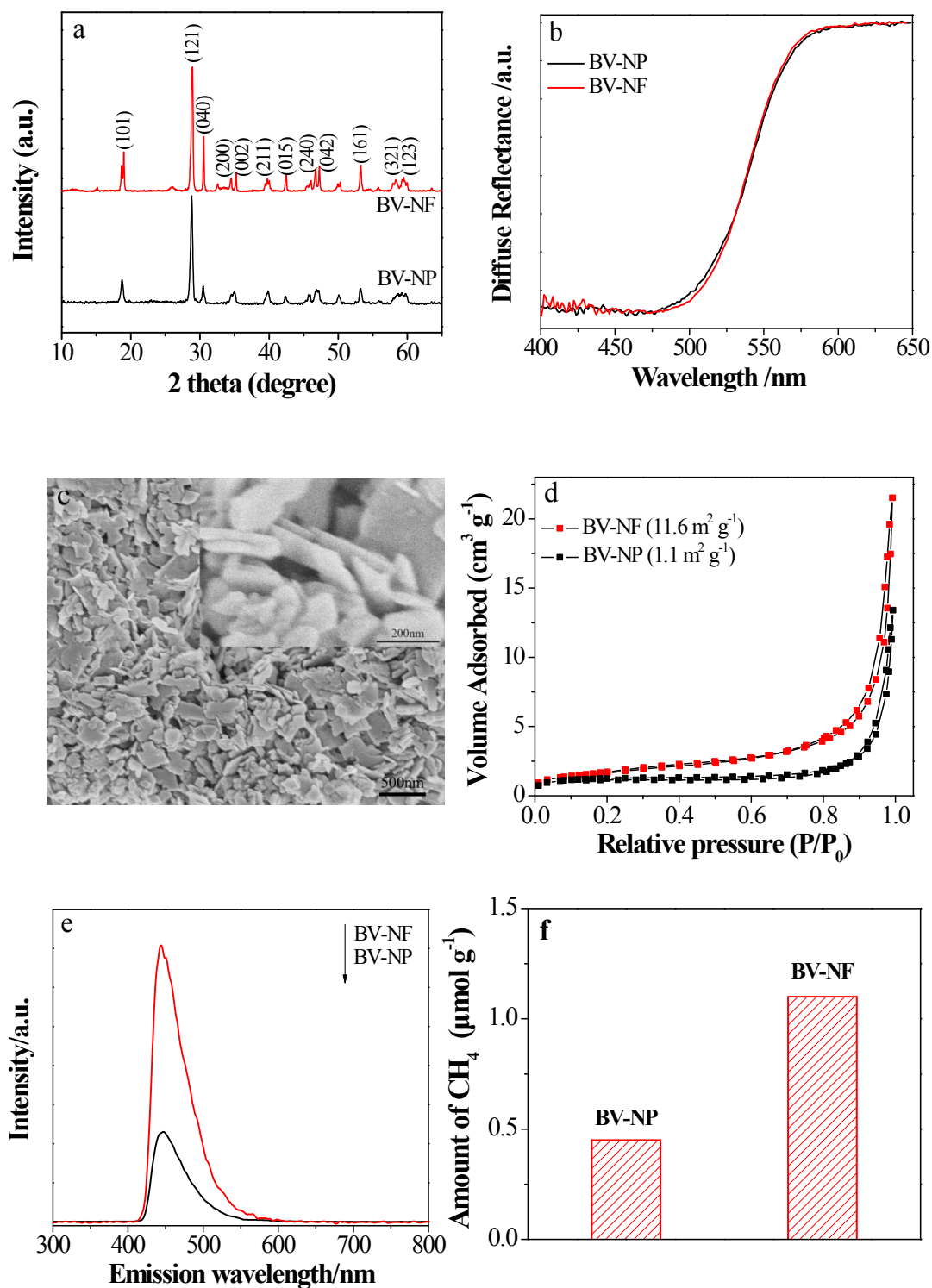
*In situ DRIFTS Measurement.* The in situ DRIFTS analysis were carried out in an in situ diffuse reflectance pool with a Bruker Vector FTIR spectrometer (6700) and high-sensitivity MCT detector which was cooled by liquid N<sub>2</sub>. Firstly, a certain amount of KBr was filled into the reaction cell, then covered with 0.2 g of the catalyst on its surface. When the test was officially started, the filled catalyst was placed in the test chamber and heated to 175°C under N<sub>2</sub> flow (15mL min<sup>-1</sup>) for 30 min to remove adsorbed impurities and then cooled to room temperature. In order to simulate the photocatalytic CO<sub>2</sub> reduction process, the methanol aqueous solution was firstly placed in a scrubbing cylinder, then N<sub>2</sub> (15mL min<sup>-1</sup>) was bubbled to pass into the sample cell. In this condition, a certain amount of methanol could be adsorb on the surface of sample and then purged with N<sub>2</sub>. Subsequently, the sample was irradiated under visible light. A 300 W Xenon arc lamp with a 420 CUT filter was used as the light source.

*Electrochemical Reduction Measurement.* Electrochemical reduction measurement were carried out in a traditional three-electrode system. The working electrode was a 0.3 cm diameter glassy carbon (GC) electrode, as the reference electrode, and a Pt sheet was used as the counter electrode. Five milligrams of different samples mixed with 20 μL of 5 wt % Nafion ionomer was dissolved in 0.18 mL of ethanol aqueous solution. The catalyst ink was ultrasound for 30 min, and a suitable mass of the ink was uniformly dropped onto the clean GC electrode surface and dried in air. A BAS 100B electrochemical workstation was employed to test electrochemical activity and stability of a series of catalysts. At the beginning, electrode potentials were cycled between two potential limits until perfectly overlapping, afterward the I-V curves were obtained. The electrolytes for test were 1 M Na<sub>2</sub>SO<sub>4</sub>. All the experiments were performed at room temperature (about 25 °C).

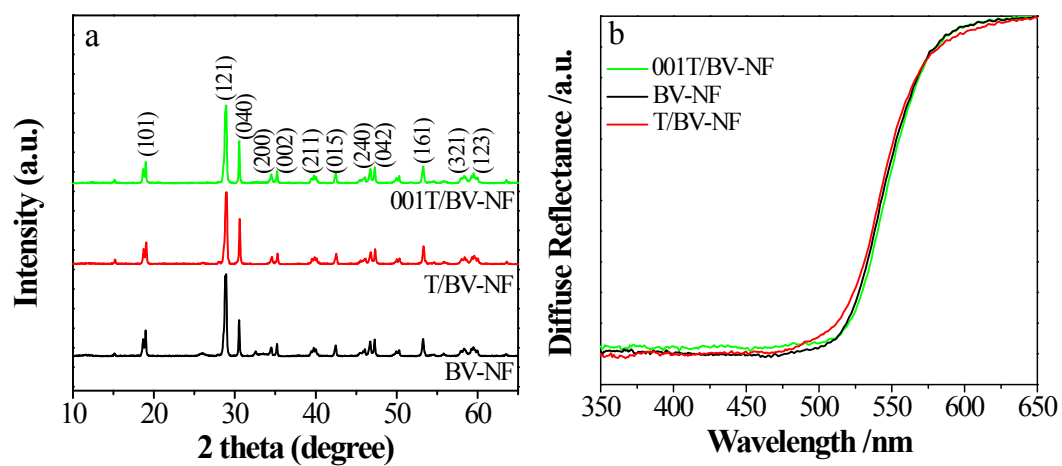
*PEC measurement.* PEC experiments were performed in a quartz cell using 500 W xenon lamp with a cut-off filter ( $\lambda > 420$  nm) as the illumination source, and 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution as the electrolyte. The nanocomposite film was used as working electrode, a

platinum plate (99.9%) was used as the counter electrode, and a saturated KCl Ag/AgCl electrode was used as the reference electrode. High purity nitrogen gas (99.999%) was bubbled through the electrolyte before and during the experiments. The applied potential was controlled using a commercial computer-controlled potentiostat (Princeton Applied Research Versa STAT 3). The photocurrent density at different excitation wavelengths was measured, for which monochromatic light was obtained by passing light from a 500 W xenon lamp through a monochromator (CM110, Spectral Products). Electrochemical impedance spectroscopy (EIS) measurements were performed using a three-electrode configuration, over the frequency range  $10^{-2}$  to  $10^5$  Hz with amplitude of 10 mV (RMS) and a bias of 0.4 V.

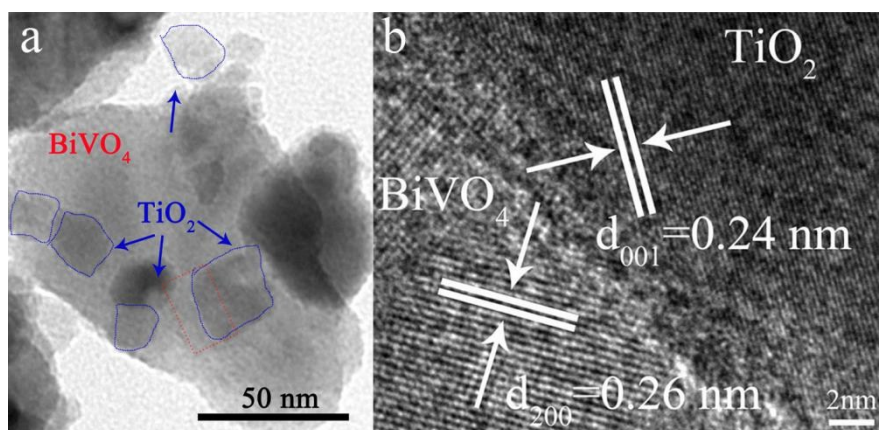
*Photocatalytic activities for CO<sub>2</sub> conversion.* 0.2 g of powder sample was suspended in a mixed solution containing 5 mL of water with magnetic stirring in a cylindrical steel reactor with 100 mL volume and 3.5 cm<sup>2</sup> area. A 300 W Xenon arc lamp was used as the light source. High pure CO<sub>2</sub> gas was passed through water and then entered into the reaction setup for reaching ambient pressure. The photocatalyst was allowed to equilibrate in the CO<sub>2</sub>/H<sub>2</sub>O system for 1 hour, and followed by irradiation for 4 hours. During irradiation, about 0.5 mL of gas produced was taken from the reaction cell at given time intervals for CO and O<sub>2</sub> concentration analysis using a gas chromatograph (GC-7920 with TCD, Au Light, Beijing), and for CH<sub>4</sub> concentration analysis using a gas chromatograph (GC-2014 with FID, Shimadzu Co., Japan).



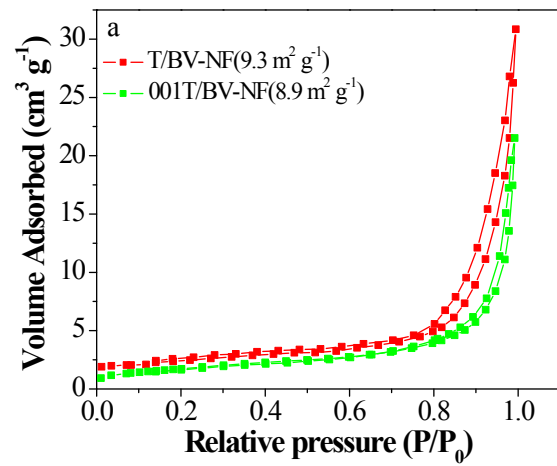
**Figure S1.** XRD patterns (a), DRS spectra (b), SEM images (c),  $\text{N}_2$  adsorption/desorption isotherm curves (d), Fluorescence spectra related to the formed hydroxyl radicals (e) and Photocatalytic activities for  $\text{CO}_2$  conversion (f) of BV-NP and BV-NF.



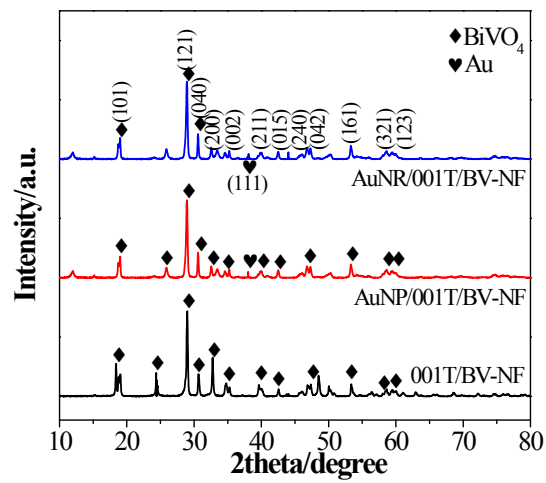
**Figure S2.** XRD patterns (a) and DRS spectra (b) of BV-NF, T/BV-NF and 001T/BV-NF.



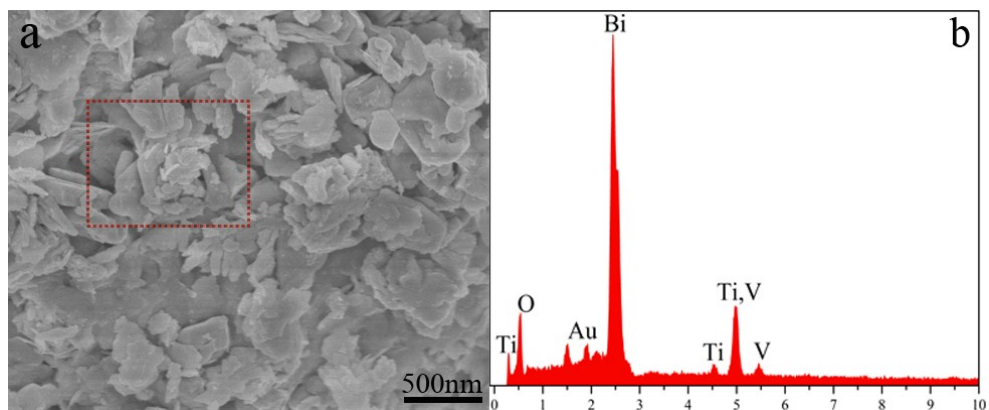
**Figure S3.** TEM (a) and HRTEM images (b) of 001T/BV-NF.



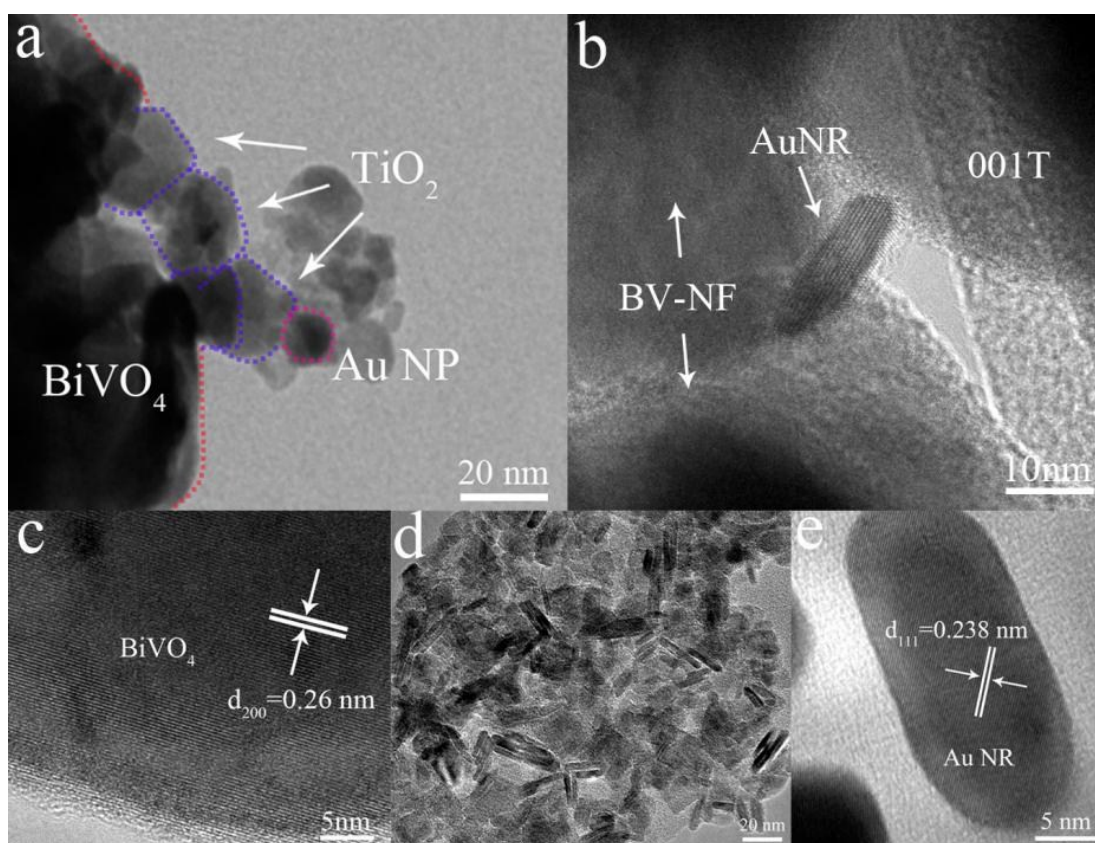
**Figure S4.** N<sub>2</sub> adsorption/desorption isotherm curves of T/BV-NF and 001T/BV-NF.



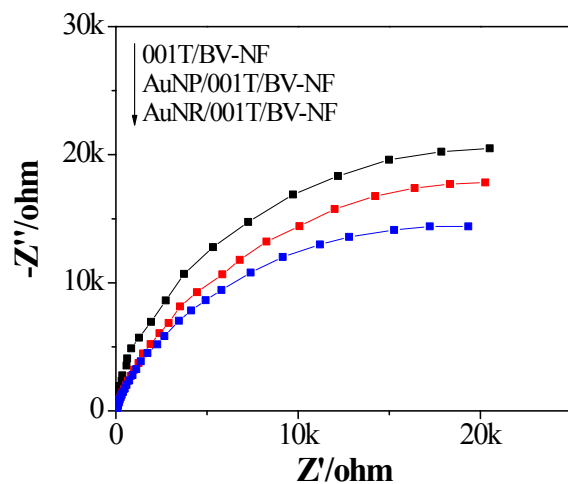
**Figure S5.** XRD patterns of 001T/BV-NF, AuNP/001T/BV-NF and AuNR/001T/BV-NF.



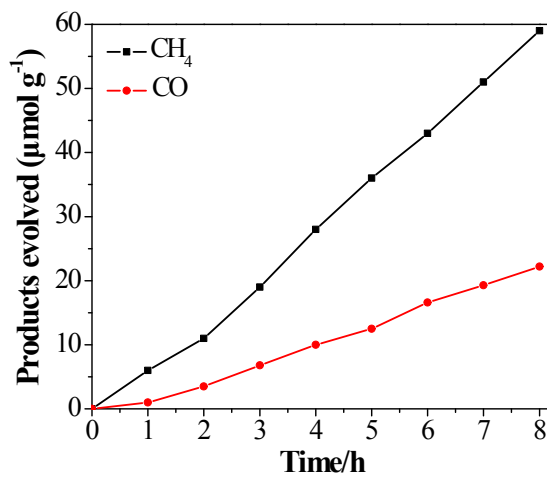
**Figure S6.** SEM image (a) and energy dispersive spectrometry (b) of AuNR/001T/BV-NF nanocomposite.



**Figure S7.** TEM images of AuNP/001T/BV-NF (a), AuNR/001T/BV-NF (b), BV-NF (c), 001T (d) and AuNR (e).

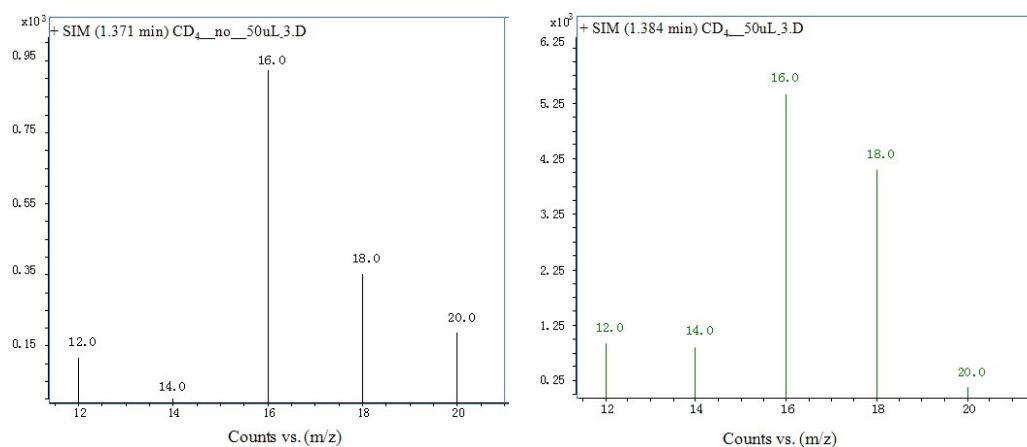


**Figure S8.** Electrochemical impedance spectra of 001T/BV-NF, AuNP/001T/BV-NF and AuNR/001T/BV-NF.

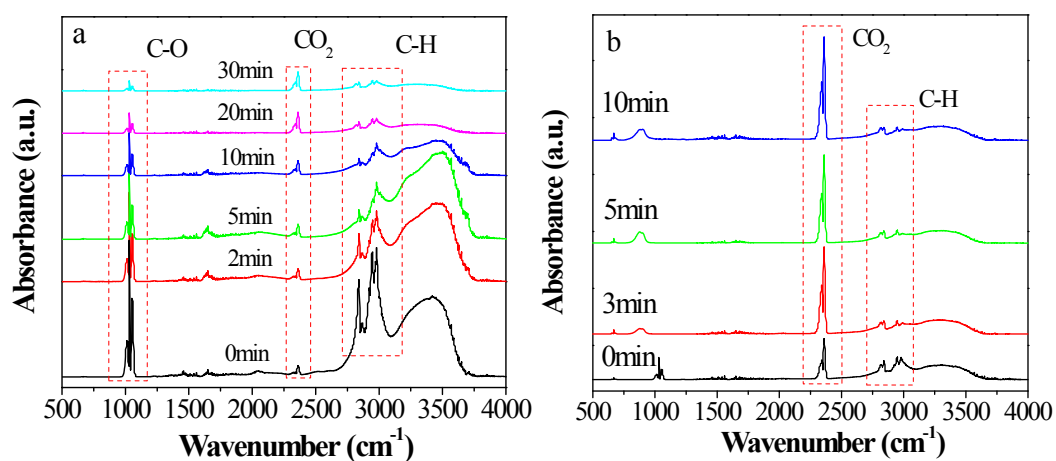


**Figure S9.** The Amounts of evolved CH<sub>4</sub> and CO under visible light irradiation for 8 hours of AuNR/001T/BV-NF nanocomposite in water.

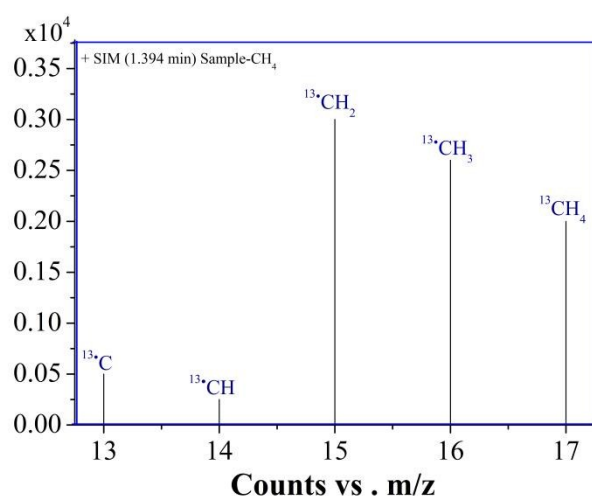




**Figure S10.** The GC-Mass analysis of photocatalytic reduction products of CO<sub>2</sub> on AuNR/001T/BV-NF after irradiation for 6h without methanol (a) and with methanol (b).



**Figure S11.** In-situ DRIFTS spectra of AuNR loaded 001T/BV-NF nanocomposite after methanol adsorption for 30 min (a) and under visible light irradiation for 10 min (b).



**Figure S12.** m/z values for tested gas fuel after photocatalytic reduction of isotopic  $^{13}\text{C}\text{O}_2$  by GC-7890B/MS5977A (America Aligent) under light irradiation for 6 h.

Category	Co-catalyst	Light resource	Major product	Rmax $\mu\text{mol/h}^{-1}\text{g}^{-1}$	Ref.
Anatase $\text{TiO}_2$ by Coexposed {001} and {101} Facets	Free	300 W Xe-lamp	$\text{CH}_4$	1.35	J. Am. Chem. Soc. 2014, 136, 8839-8842
Hexahedron Prism-Anchored Octahedral $\text{CeO}_2$	Free	300 W Xe-lamp	$\text{CH}_4$	1.12	J. Am. Chem. Soc. 2015, 137, 9547-9550
Co-ZIF-9/ $\text{TiO}_2$	Free	300 W Xe-lamp	$\text{CH}_4$ CO	0.99 8.79	J. Mater. Chem. A 2016,4, 15126-15133
$\text{CsPbBr}_3$ QD/GO	Free	100 W Xe-lamp	$\text{CH}_4$ CO	2.47 4.89	J. Am. Chem. Soc. 2017, 139, 5660–5663
<b>AuNR/001T/BV-NF</b>	<b>Au</b>	<b>300 W Xe-lamp</b>	<b><math>\text{CH}_4</math></b> <b>CO</b>	<b>7.5</b> <b>2.5</b>	<b>Our work</b>

**Table S1.** Comparison of our photocatalytic activities for  $\text{CO}_2$  conversion with the previous works.