Supporting information

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Experimental Section

1.1 Synthesis of $BiVO_4$ nanosheets (BVNS)

In a typical synthesis, 2.21 g of $BiCl_3$ and 1.05 g of cetyltrimethylammonium bromide (CTAB) were dissolved in 60 mL of ethylene glycol under vigorous magnetic stirring. Then, 2.80 g of $NaVO_3$ was added to the above system, and followed by continuous stirring for 30 min. Then, the mixture was transferred into a 50 mL Teflon-lined autoclave, sealed and heated at 120 °C for 12 h. After the system was cooled down to room temperature, the resulting products were washed with ethanol and deionized water for several times, and then dried at 60 °C in a vacuum oven. Finally, the obtained sample was fast calcined for 8 min at 400 °C. The sample was named as BVNS.

1.2 Synthesis of ZnPc/$BiVO_4$ nanocomposite (xZnPc/BVNS)

The nanocomposite was prepared by a hydroxyl-induced assembly method. In the typical synthesis, a proper amount of ZnPc was dispersed in 20 mL of ethanol under ultrasonication for 30 min, followed by continuous stirring for 1 h. Then, the above solution was added to the precursor of $BiVO_4$, and followed by continuous stirring for 30 min. Subsequently, the mixture was transferred into a 50 mL Teflon-lined autoclave, sealed and heated at 120 °C for 12 h. After the system was cooled down to room temperature, the resulting products were washed with ethanol and deionized water for several times, and then dried at 60 °C in a vacuum oven. Finally, the obtained sample was fast calcined for 8 min at 400°C. The sample was named as xZnPc/BVNS, where x is the mass ratio percentage of ZnPc to $BiVO_4$.

1.3 Synthesis of ZnPc/graphene/$BiVO_4$ nanocomposite (xZnPc/yG/BVNS)

There are two primary steps in this procedure. The first step is to prepare graphene functionalized $BiVO_4$ nanosheet. Graphene was prepared by a in situ self-generating template route, [1] and followed by acid-treatment. Acid-treated graphene (G) was prepared as follows: 0.5 g of graphene, HNO_3 (65%, 10 mL) and H_2SO_4 (98%, 30 mL) were added into a flask under vigorous stirring. The flask was immersed in an ultrasonic bath for 30 min, and then stirred for 30 min under refluxing conditions at 80 °C. This process was repeated 6 times. After cooling down to the room temperature, the reaction mixture was centrifuged and washed with deionized water until the pH of the mixture reached to about 7. Then, the solid was dried under vacuum at 60 °C for 24 h. Afterwards, a certain amount of G was dispersed in 60 mL of deionized water under ultrasonication for 60 min. Then, 0.5 g of $BiVO_4$ was added to the above solution, followed by continuous stirring for 60 min. Afterwards, the mixture was transferred into a 50 mL Teflon-lined autoclave, sealed and heated at 150 °C for 4 h. After the system was cooled down to room temperature, the resulting products were washed with deionized water for several times, and then dried at 60 °C in an oven. Finally, the obtained sample was calcined in N_2 for 4 h at 250 °C. The sample was named as yG/BVNS, where y is the mass ratio percentage of G to $BiVO_4$. The second step is to assembly ZnPc on G functionalized $BiVO_4$ nanosheet. 0.5 g of G/BVNS and a certain amount of ZnPc were dispersed in 50 mL of absolute ethyl alcohol under magnetic stirring for about 1 h. Then, the mixture was dried in a water bath at 60 °C. The sample was named as xZnPc/yG/BVNS.

1.4 Characterization

The X-ray powder diffraction (XRD) patterns of the samples were recorded by using a Bruker D8 advance diffractometer with CuKα radiation. The UV-Vis diffuse reflectance spectra (UV-Vis DRS) of the samples were acquired on a Model Shimadzu UV 2550 spectrophotometer with $BaSO_4$ as a reference. The Fourier-transform infrared (FT-IR) spectra of the samples were collected with a Bruker Equiox 55 spectrometer, KBr as the diluents. The morphology of the samples was analyzed by transmission electron microscopy (TEM) on a FEI-Titan ST instrument with an acceleration voltage of 300 kV. The FEI-Titan ST equipped with Energy-dispersive X-ray (EDX) detector was used to acquire element analyses of the samples. The surface photovoltage spectroscopy (SPS) measurements for samples were implemented on home-built apparatus, equipped with a lock-in amplifier (SR830, USA) synchronized with a light chopper (SR540, USA). The X-ray photoelectron spectroscopy (XPS) was tested by Kratos-AXIS ULTRA DLD. Al (Mono) was used as the X-ray source.

1.5 Hydroxyl radical measurement

Hydroxyl radicals (•OH) are important active species in photocatalytic reaction. Using coumarin as a labeled 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: 0.02 g of the catalyst was placed in 50 mL of coumarin solution at a concentration of 2×10^{-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.

1.6 CO_2 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^{-1}. The highly pure carbon dioxide was introduced at a constant temperature of 30 °C under the flow rate of 30 mL min^{-1} for 60 min. The physically adsorbed CO_2 was removed by being exposed with ultra-high-pure He at 30 °C for 60 min. Then the temperature was increased to 400 °C with the heating rate of 10 °C min^{-1} under ultra-high-pure He. Finally, the desorbed CO_2 was monitored by Chemisorption Analyzer (Tp 5080 Chemisorb).

1.7 Photoelectrochemical and electrochemical measurements

Photoelectrochemical (PEC) and electrochemical reduction measurements were carried out in a traditional three-electrode system. The prepared sample was used as working electrode, a platinum plate (99.9%) was used as the counter electrode, a saturated KCl Ag/AgCl electrode was used as the reference electrode, and 0.5 M Na_2SO_4 solution as the electrolyte. High purity nitrogen gas (99.999%) was bubbled through the electrolyte before and during the experiments. PEC experiments were performed in a quartz cell using a 500 W xenon lamp with a cut-off filter ($\lambda > 420$ nm) as the illumination source. An IVIUM V13806 electrochemical workstation was employed to test photoelectrochemical and electrochemical performance of a series of catalysts. All the experiments were performed at room temperature (about 25 °C).

1.8 Photocatalytic activities for CO_2 conversion

0.1 g of powder sample was suspended in 5 mL of water with magnetic stirring in a cylindrical steel reactor with 100 mL volume and 3.5 cm^2 area. A 300 W Xenon arc lamp was used as the light source with a 420 nm cut-off filter. High pure CO_2 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_2/H_2O system for 20 min, and followed by irradiation for 4 hours. During irradiation, about 0.25 mL of gas produced was taken from the reaction cell at given time intervals for CO and CH_4 concentration analysis using a gas chromatograph (GC-7920 with both TCD and FID detectors, Au Light, Beijing), and for O_2 concentration analysis using a gas chromatograph (GC-7900 with TCD, Perfect Light, Beijing).

Supporting Figures

Fig. S1 XRD patterns of BVNS, 1.5G/BVNS, 4ZnPc/BVNS and 4ZnPc/1.5G/BVNS.

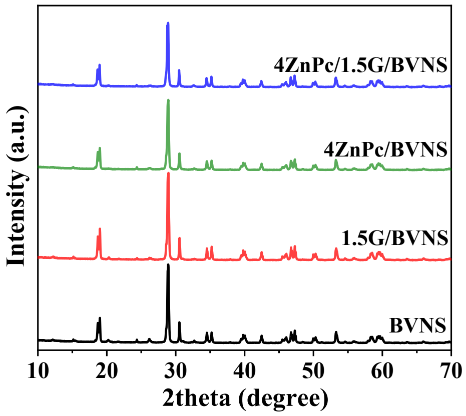


Fig. S2 TEM (a) and HRTEM (b) images of BVNS.

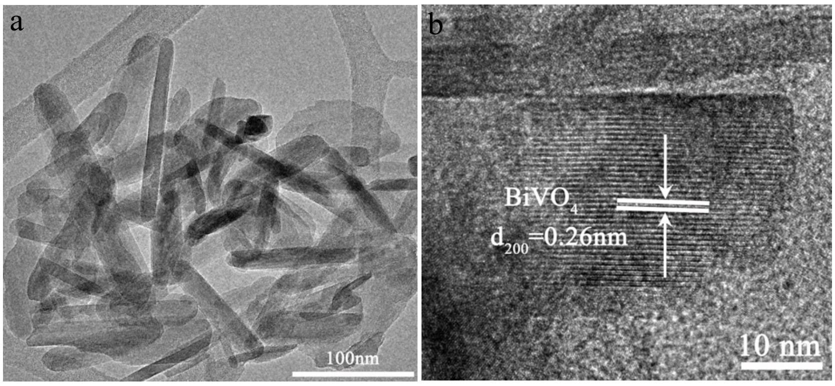


Fig. S3 HAADF-STEM image of 4ZnPc/1.5G/BVNS and the corresponding EDX mapping images of elemental Bi, V, O, C, N and Zn.

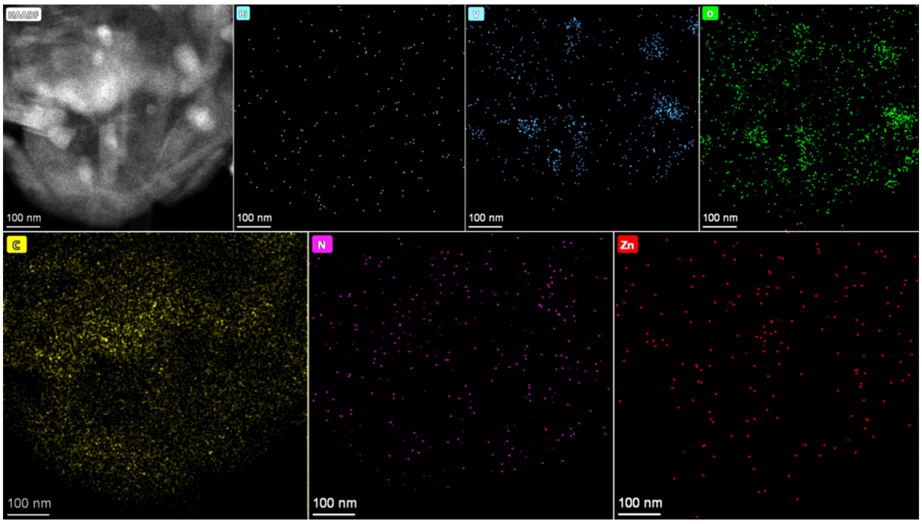


Fig. S4 XPS spectra of Bi 4f, O 1s, and V 2p for BVNS and 1.5G/BVNS.

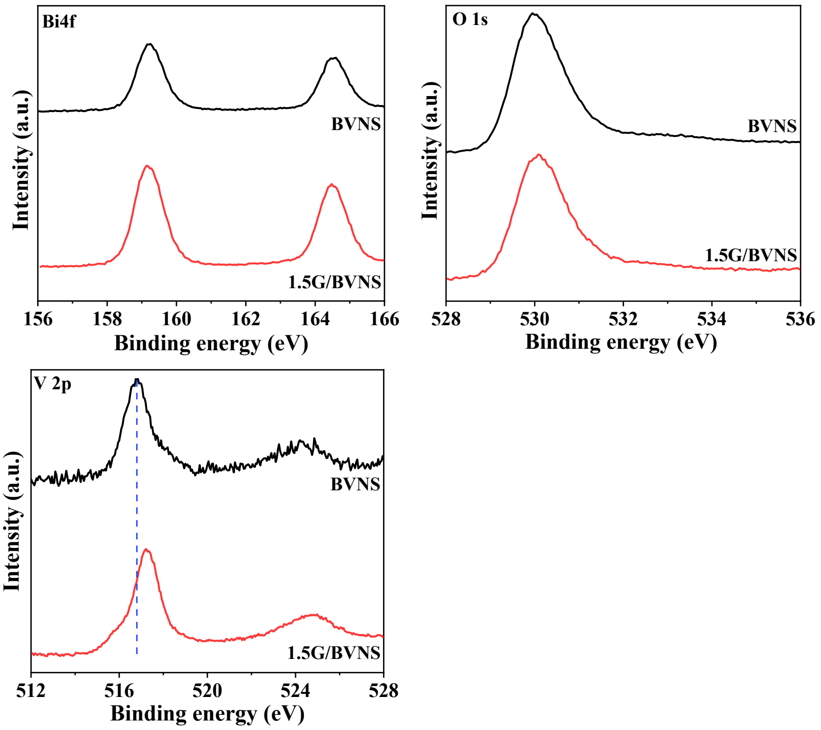


Fig. S5 XPS spectra of Zn 2p for 4ZnPc/1.5G/BVNS, 4ZnPc/BVNS and ZnPc.

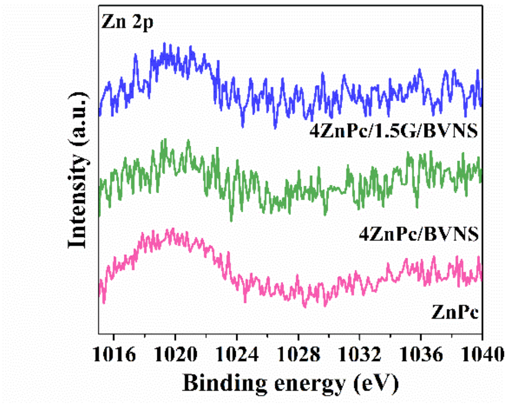


Fig. S6 Fluorescence spectra related to the formed hydroxyl radicals of BVNS, xZnPc/BVNS and xZnPc/G/BVNS under visible-light irradiation.

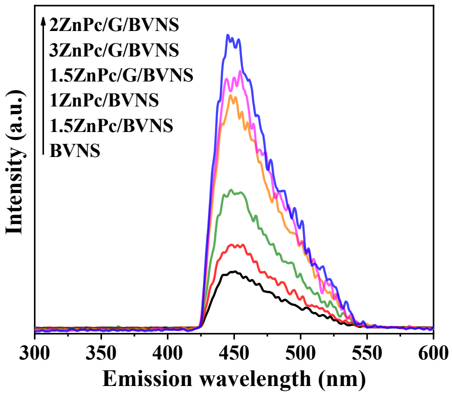


Fig. S7 Fluorescence spectra related to the formed hydroxyl radicals of 3ZnPc/G/BVNS and xZnPc/1.5G/BVNS under visible-light irradiation.

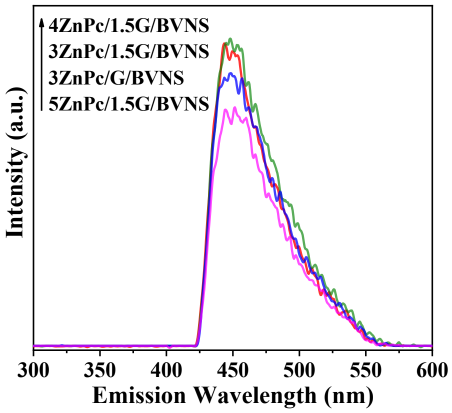


Fig. S8 Linear sweep voltammetric (LSV) scans of 4ZnPc/1.5G/BVNS, 4ZnPc/BVNS, 1.5G/BVNS and BVNS under visible-light irradiation.

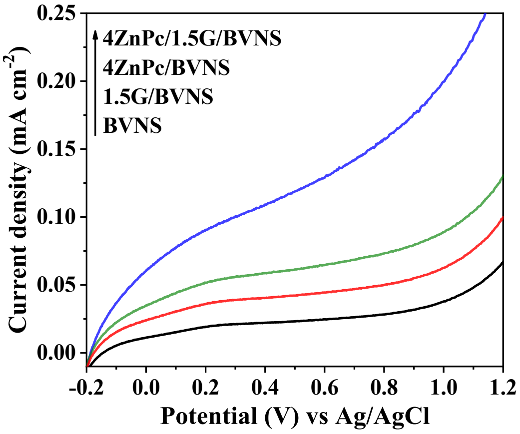


Fig. S9 Photocurrent-time curves of 4ZnPc/1.5G/BVNS, 4ZnPc/BVNS, 1.5G/BVNS and BVNS under chopped visible-light irradiation.

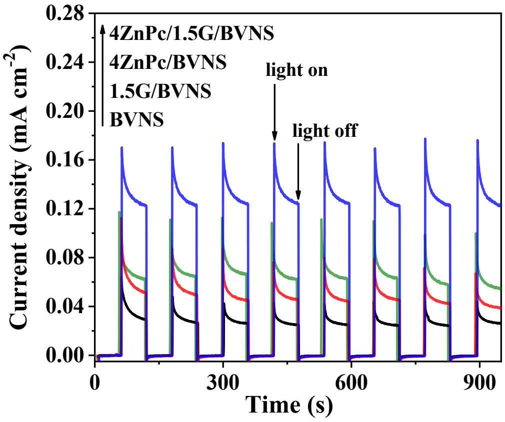


Fig. S10 Photocatalytic activities for CO_2 conversion of BVNS, xZnPc/BVNS and xZnPc/G/BVNS under visible-light irradiation.

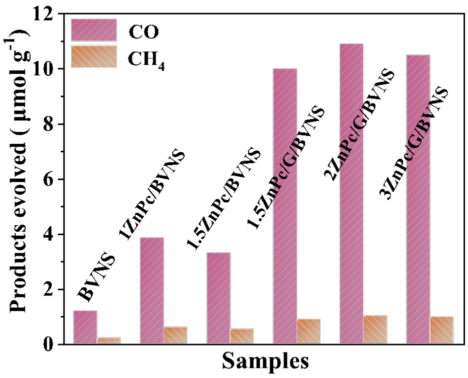


Fig. S11 Photocatalytic activities for CO_2 conversion of 3ZnPc/G/BVNS and xZnPc/1.5G/BVNS under visible-light irradiation.

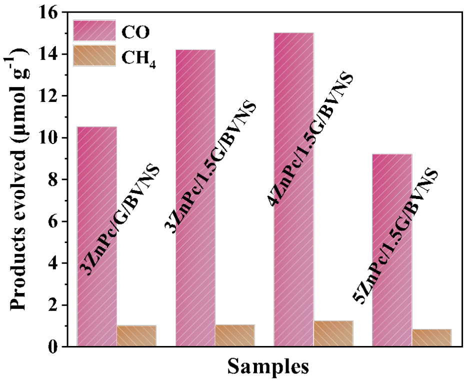


Fig. S12 DRS spectra of 4ZnPc/1.5G/BVNS nanocomposite before and after reactions.

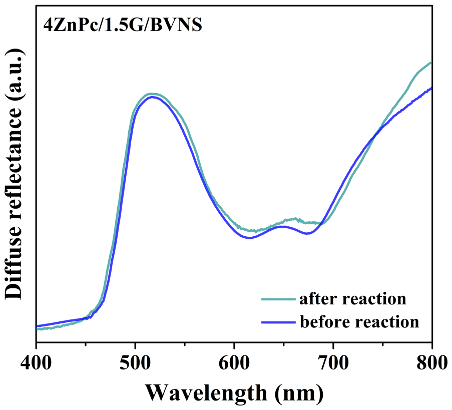


Fig. S13 SPS responses of 4ZnPc/1.5G/BVNS, 4ZnPc/BVNS and 1ZnPc/BVNS in N_2 atmosphere assisted with 660 nm monochromatic beam.

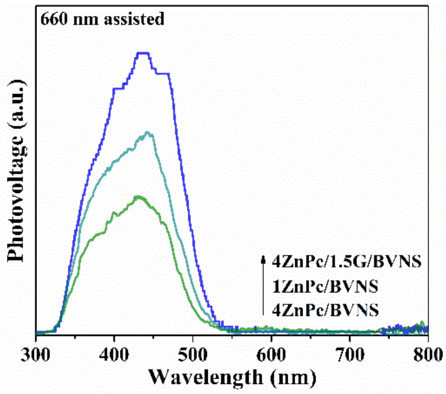


Fig. S14 FS spectra of 4ZnPc/1.5G/BVNS, 4ZnPc/BVNS and 1ZnPc/BVNS nanocomposites under double excitation (520 nm and 660 nm).

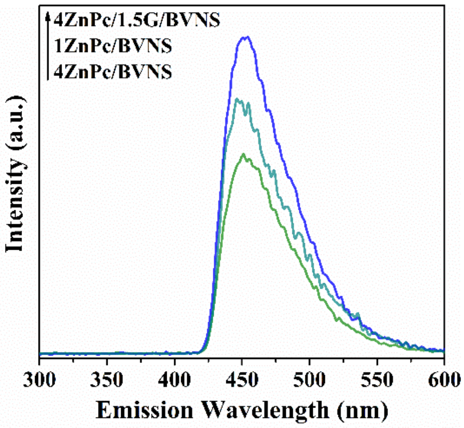


Fig. S15 Normalized photocurrent action spectra of BVNS, ZnPc, 4ZnPc/BVNS and 4ZnPc/1.5G/BVNS under different monochromatic light irradiation.

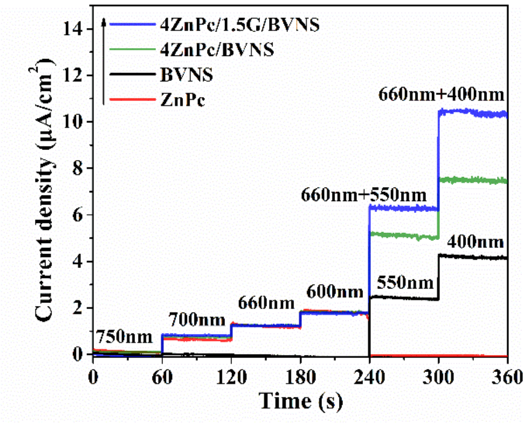


Fig. S16 Electrochemical reduction curves of 4ZnPc/1.5G/BVNS, 4ZnPc/BVNS, 1.5G/BVNS and BVNS in N_2-bubbled system.

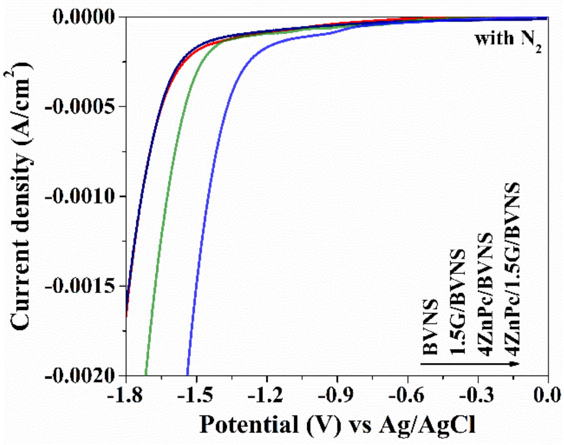
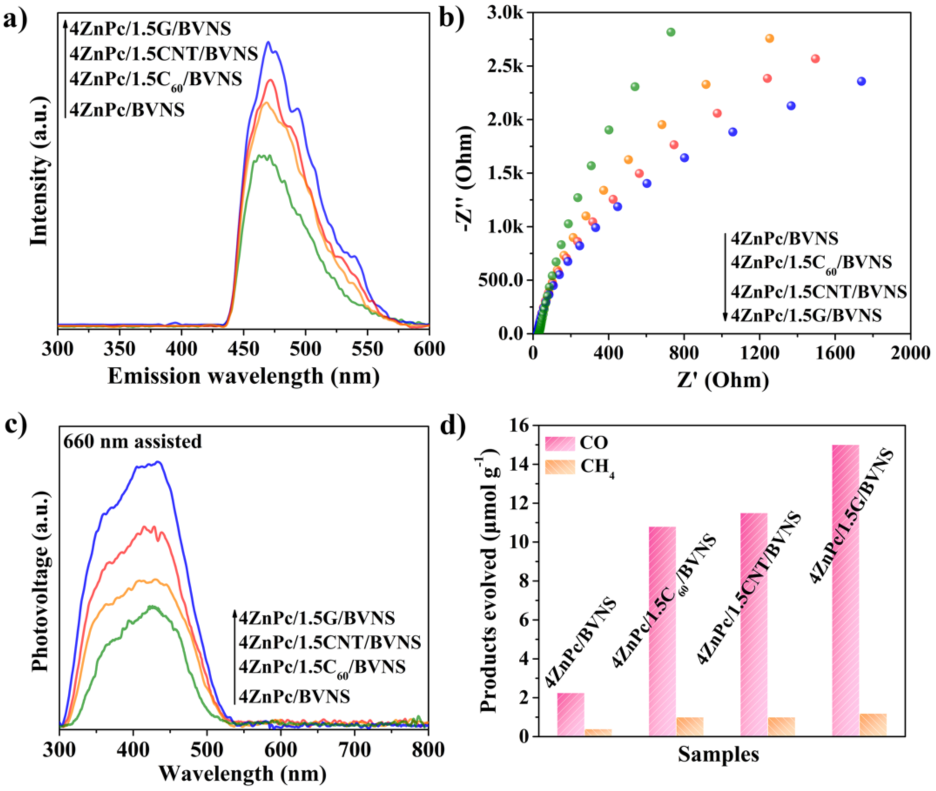


Fig. S17 (a) FS spectra, (b) EIS spectra, (c) SPS responses in N_2 atmosphere assisted with 660 nm monochromatic beam and (d) photocatalytic activities for CO_2 reduction under visible-light irradiation of 4ZnPc/BVNS, 4ZnPc/1.5G/BVNS, 4ZnPc/1.5CNT/BVNS and 4ZnPc/1.5C_{60}/BVNS.



References

1. L. Wang, C. Tian, H. Wang, Y. Ma, B. Wang and H. Fu, *The Journal of Physical Chemistry C*, 2010, 1**14**, 8727.