

# Enhanced charge separation of rutile TiO<sub>2</sub> nanorods by trapping holes and transferring electrons for efficient cocatalyst-free photocatalytic conversion of CO<sub>2</sub> to fuels

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## Electronic supplementary information (ESI):

### SI-Experimental procedures

All substances used in this study were of analytical grade and used without further purification. Deionized water was used in all experiments.

**Synthesis of materials.** Rutile TiO<sub>2</sub> was synthesized by a low-temperature hydrothermal process in the presence of 2.0 M hydrochloric acid (HCl). Tetrabutyl titanate was used as the main starting material. Initially, this reagent was dropwise added to a desired concentrated HCl solution, maintained below 10 °C by an ice-water bath. Then, the mixture was heated in a water bath for 4 h at 80 °C so as to produce white suspension. Subsequently, the suspension was placed in Teflon-lined hydrothermal reactors and heated at 160 °C for 6 h. After that, a white precipitate was collected and washed repeatedly with isopropanol and distilled water. Finally, the rutile TiO<sub>2</sub>, which has modified-Cl on its surfaces referred to as Cl-R, was obtained by drying the white precipitate at 100 °C for 12 h. Moreover, the rutile TiO<sub>2</sub>, which did not have modified-Cl on its surfaces referred to as R, was obtained by treating Cl-R in the NaOH-containing hydrothermal process.

The phosphoric acids modified Cl-R was synthesized by a simple wet-chemical process. 0.5 g of Cl-R powder was dissolved into 20 mL of different molar concentration of H<sub>3</sub>PO<sub>4</sub> solution. Then, the resulting suspension was stirred for 2 h, centrifuged, and washed with water. Finally, the phosphoric acids modified Cl-R was obtained by drying at 100 °C for 12 h and calcining at 450 °C for 0.5 h. The sample was defined as XP'Cl-R, P in XP means the modified phosphate, X in XP is the concentration of used phosphoric acid solution. To further couple

XP'Cl-R with CNTs, 0.5 g of XP'Cl-R samples were dissolved into 30 mL distilled water, then 2% (2% means the mass ratio percentage of CNTs to Cl-R) of CNTs (The CNTs were pretreated in a reflux system containing nitric acid and sulfuric acid) were taken and dissolved in the mixed solution above. The mixture was heated to 80 °C and the temperature was maintained under vigorous stirring. After evaporation of the solvent, the residual mixture was dried at 80 °C. Thus, CNT-coupled XP'Cl-R composites were obtained referred to 2C/XP'Cl-R. C in 2C means the coupled CNTs, and 2 is the mass ratio percentage of C to Cl-R.

To synthesize the CNT-coupled rutile TiO<sub>2</sub>, 0.5 g of Cl-R samples were dissolved into 30 mL distilled water, and then a certain amount of CNTs was taken and dissolved in the mixed solution above. The mixture was heated to 80 °C and the temperature was maintained under vigorous stirring. After evaporation of the solvent, the residual mixture was dried at 80 °C. Thus, the CNT-coupled rutile TiO<sub>2</sub> were obtained referred to as YC/Cl-R, C in YC means the coupled CNTs, and Y is the mass ratio percentage of C to Cl-R. In addition, the phosphoric acids modified CNTs were also prepared in order to measure the change of the banding energy of [PO<sub>4</sub>]<sup>3-</sup> groups by a simple wet-chemical process same as the method of phosphoric acids modified Cl-R.

**Characterizations of Materials.** The samples were analyzed by various methods. The X-ray powder diffraction (XRD) was tested with a Rigaku D/MAX-rA powder diffractometer, using Cu K $\alpha$  radiation. Transmission electron microscopy (TEM) observation was performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. UV-vis diffuse reflectance spectra (DRS) was recorded with a Model Shimadzu UV-2550 spectrophotometer, using BaSO<sub>4</sub> as reference. Fourier transform infrared spectra (FT-IR) was collected with a Bruker Equinox 55 Spectrometer, using KBr as diluents. The Raman spectra was recorded with JOBIN YVON HR800 Raman spectrophotometer (France), and the used excitation wavelength was 457.9 nm with an Ar ion laser beam. The X-ray photoelectron spectroscopy (XPS) was examined by using a Model VG ESCALAB apparatus with Mg K Xray source, and the binding energies were calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV). The surface photovoltage measurements of the samples were carried out with a home-built apparatus. Monochromatic light was obtained by passing light from a 500 W xenon lamp (CHFXQ500W, Global Xenon Lamp Power, made in China)

through a double-prism monochromator (Hilger and Watts, D 300, made in England). A lock-in amplifier (SR830, made in U.S.A.), synchronized with a light chopper (SR540, made in U.S.A.), was employed to amplify photovoltage signal. The powder sample was sandwiched between two ITO glass electrodes, and the sandwiched electrodes were arranged in an atmosphere-controlled container with a quartz window for transmitting light. The SPS signals were the potential barrier change of the testing electrode surface between that in the presence of light and that in the dark. PEC experiments were performed in a glass cell with 0.5 M NaClO<sub>4</sub> solution as the electrolyte. In a typical glass cell, the as-prepared film electrode functioned as working electrode, Pt wire (99.9%) functioned as a counter electrode, and a saturated KCl Ag/AgCl electrode functioned as the reference electrode. High purity nitrogen gas (99.999%) was used to bubble through the electrolyte before and during the experiments. Applied potentials were controlled by a commercial computer-controlled potentiostat (LK2006A made in China). Electrochemical impedance spectra (EIS) were performed using a three-electrode configuration with the Princeton Applied Research Versa STAT 3 and carried out over the frequency range from 0.5 to 10<sup>5</sup> Hz with an amplitude of 10 mV (RMS) in a 0.5 M NaClO<sub>4</sub> solution, using a 300 W xenon light as the illumination source.

***Analysis of hydroxyl radical.*** 0.05 g of samples were dispersed in 50 mL of 1×10<sup>-3</sup> mol/L aqueous solution in a quartz reactor. At given irradiation time, a certain amount of the solution was transferred into a Pyrex glass cell for the fluorescence measurement of 7-hydroxycoumarin at around 450 nm under the light excitation of 332 nm with a spectrofluorometer (PerkinElmer LS 55).

***Photocatalytic activities for CO<sub>2</sub> conversion.*** 0.2g of powder samples were dispersed in pH=7 water (3ml) contained in a cylindrical steel reactor with 100 ml volume and 3.5cm<sup>2</sup> areas. A 300W 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 used photocatalyst was allowed to equilibrate in the CO<sub>2</sub>/H<sub>2</sub>O system for 1 hour. During irradiation, about 0.5 ml of gas production was taken from the reaction cell at given time interval for subsequent CH<sub>4</sub> and CO concentration analysis by using a gas chromatograph (GC-2014 with FID and TCD detector, Shimadzu Corp, Japan). In addition, the CO<sub>2</sub> conversion in NaOH solution (pH=9) was also evaluated under identical conditions.

## SI-figures

**Figure S1.** XRD patterns of different samples. (A) Cl-R means the prepared rutile  $\text{TiO}_2$  by a low-temperature hydrothermal process in the presence of 2.0 M HCl. R means the rutile  $\text{TiO}_2$ , which did not have modified-Cl on its surfaces, obtained by treating Cl-R in the NaOH-containing hydrothermal process. P means the modified phosphate. 0.05, 0.1, 0.2, 0.3 and 0.5 means the concentration of used phosphoric acid solution, respectively. (B) C means the coupled CNTs, and 1, 2, 3 means the mass ratio percentage of C to Cl-R respectively. (C) C in 2C means the coupled CNTs, and 2 is the mass ratio percentage of C to Cl-R.

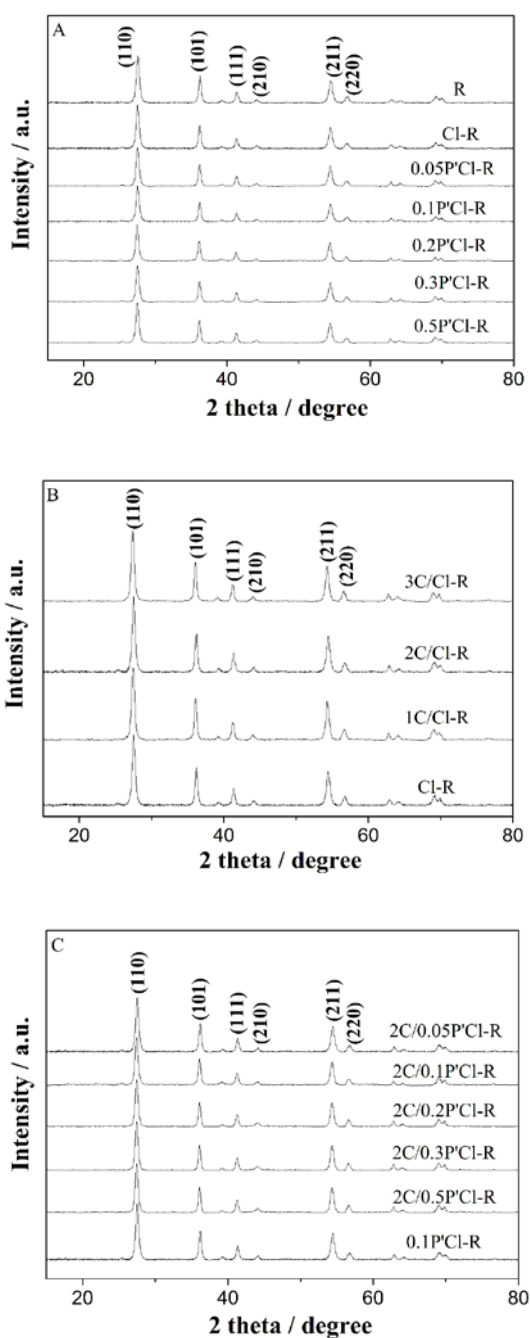
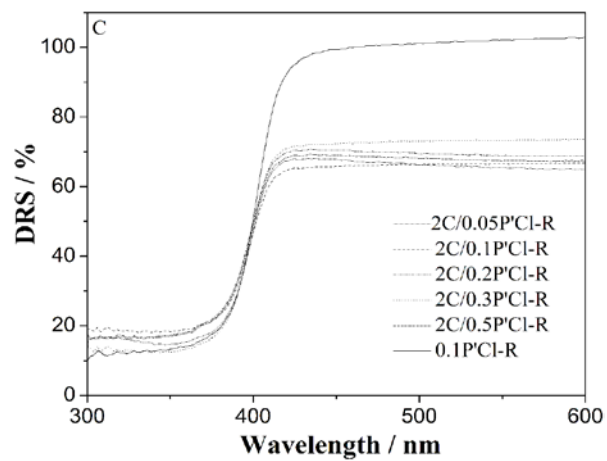
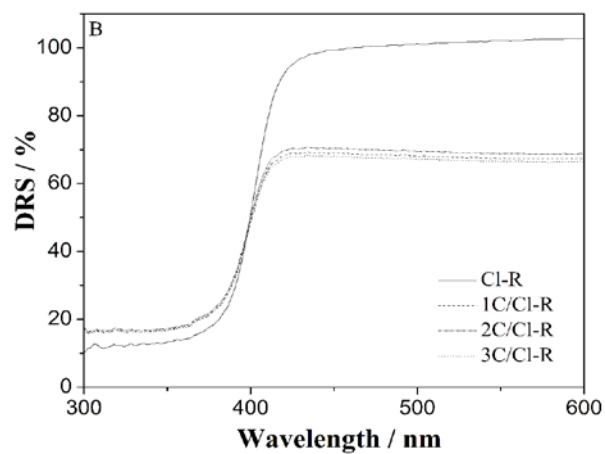
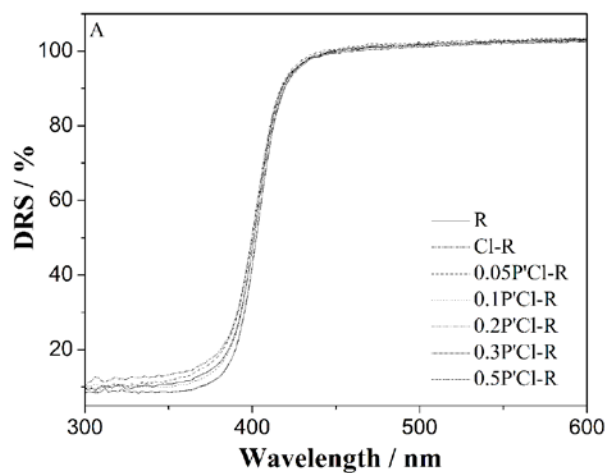
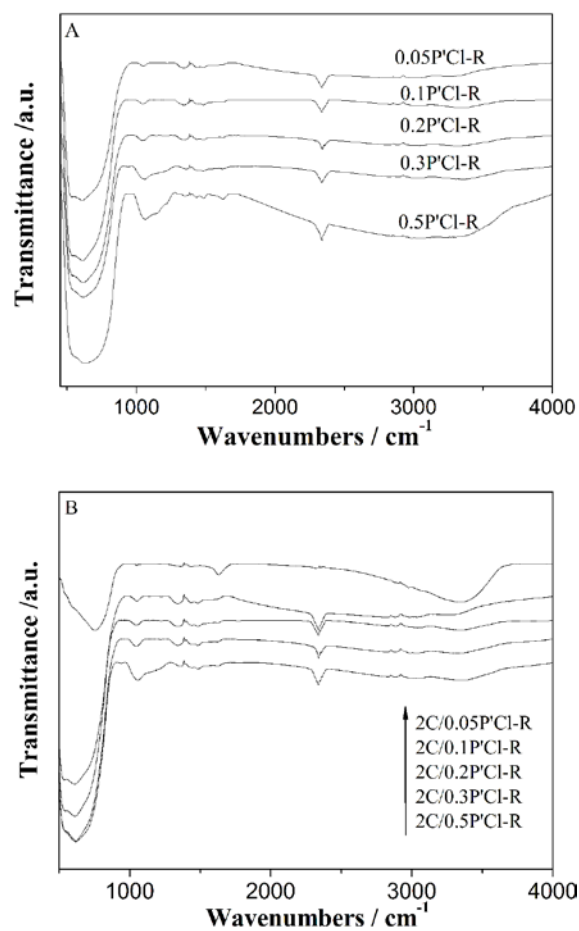


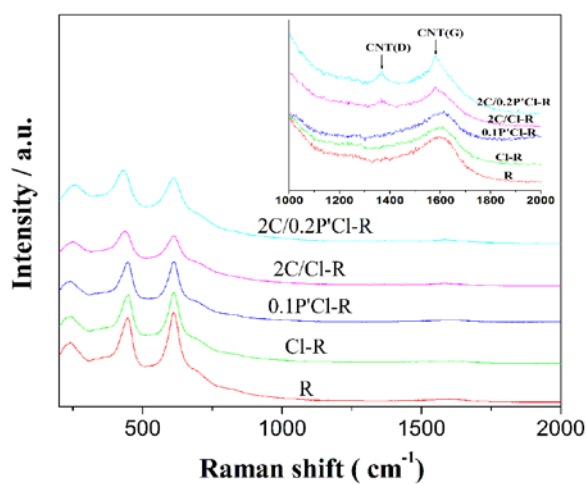
Figure S2. DRS spectra of different samples.



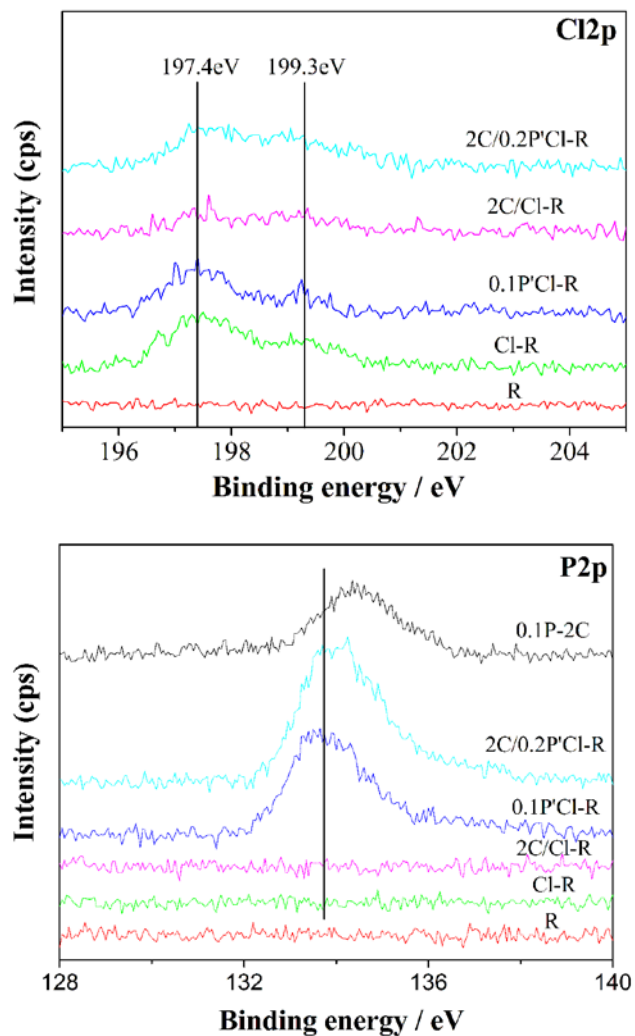
**Figure S3.** FTIR spectra of different samples.



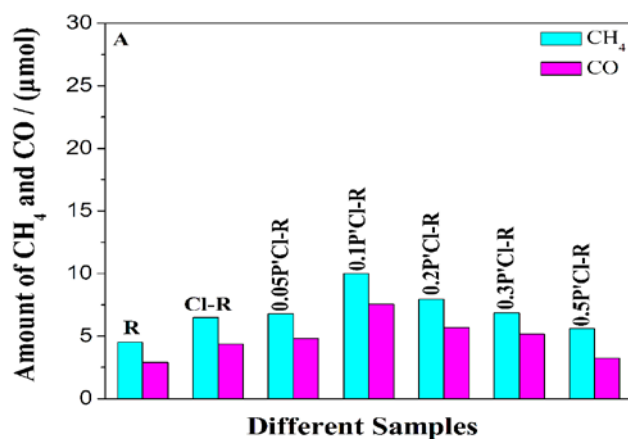
**Figure S4.** Raman spectra of different samples. ( the enlarged region from 1000 cm<sup>-1</sup> to 2000 cm<sup>-1</sup> as an inset )



**Figure S5.** XPS spectra of different samples. For 0.1P-2C, P means the modified phosphate. 0.1 means the concentration of used phosphoric acid solution, C means the coupled CNTs and 2 in 2C means the mass ratio percentage of C to Cl-R.



**Figure S6.** Photocatalytic conversion of CO<sub>2</sub> without co-catalyst for different samples under light irradiation (A) (B) (C) in pH=7 water (D) in NaOH solution (pH=9) under identical conditions.



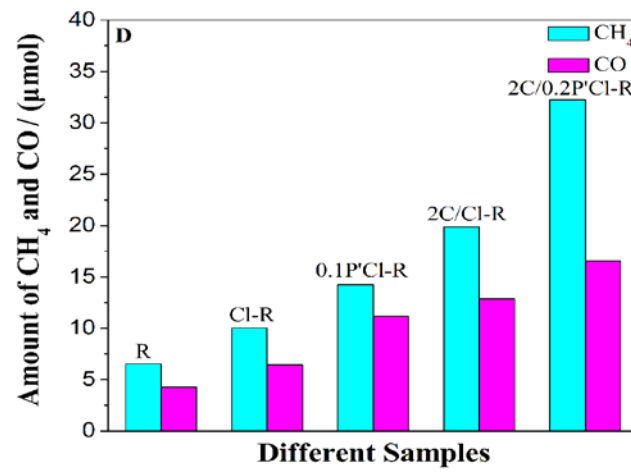
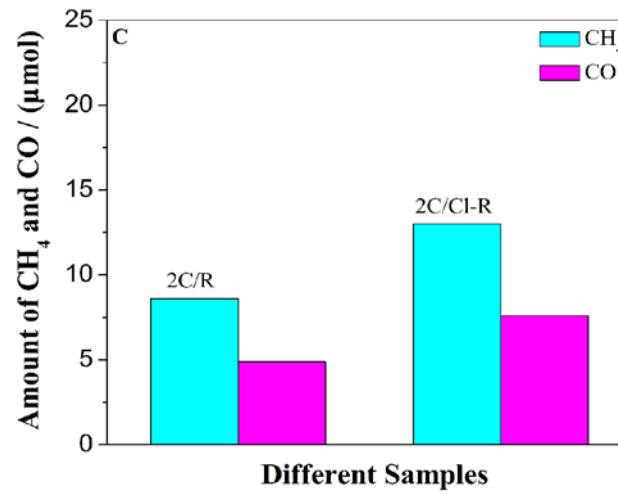
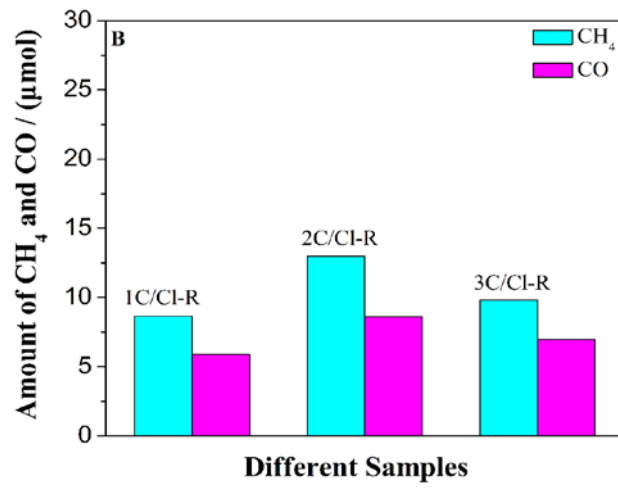
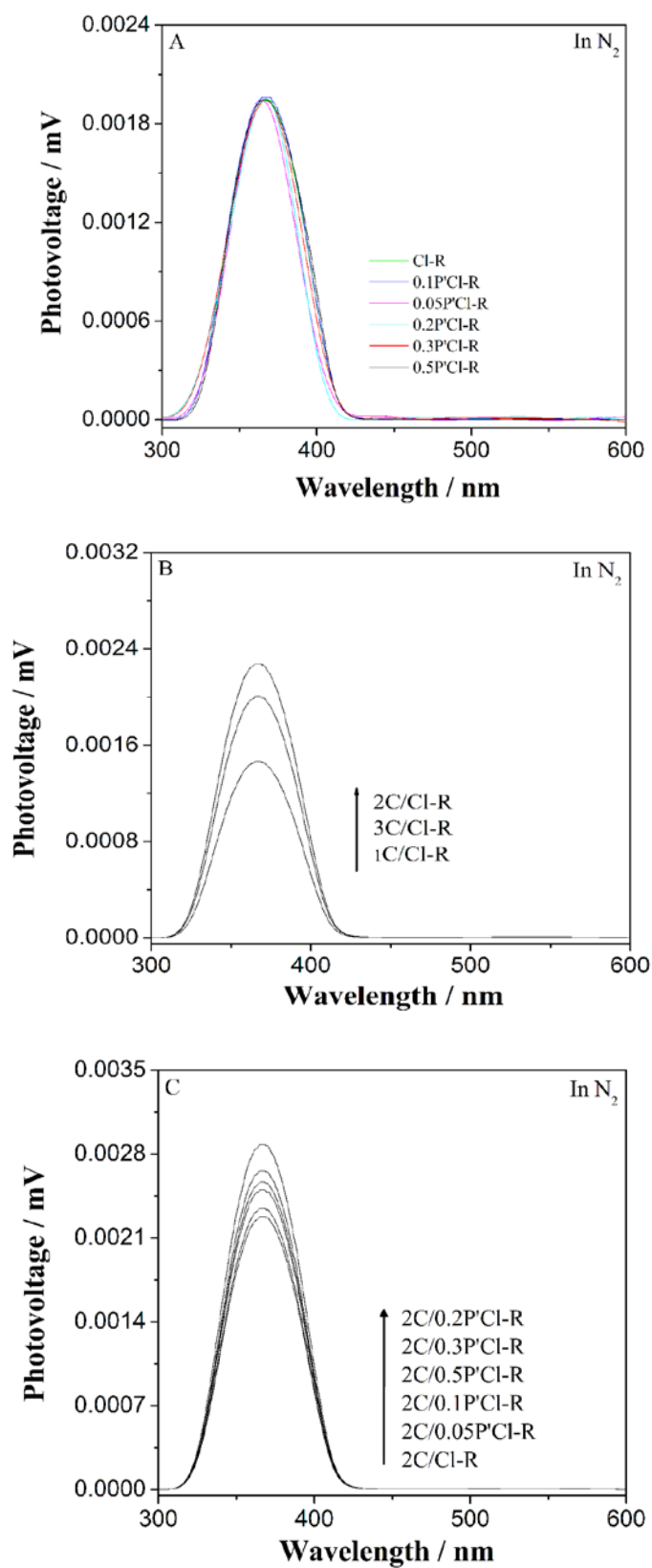
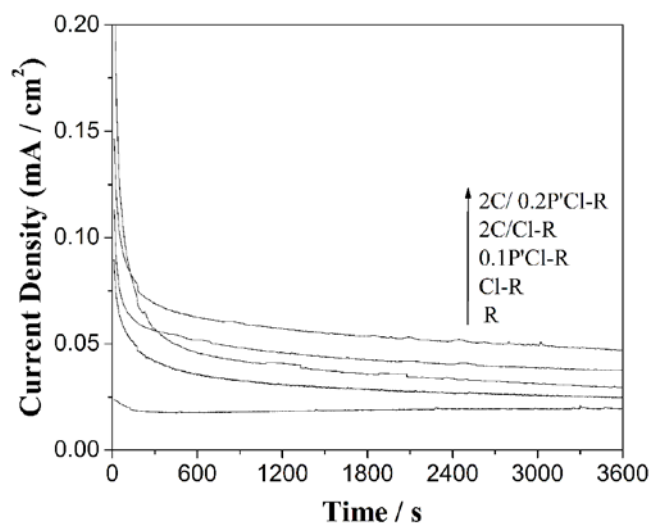




Figure S7. SPS responses in  $N_2$  atmosphere of different samples.



**Figure S8.** I-t curves of different samples after irradiation for 1 hour. Potentials are measured against an Ag/AgCl (saturated KCl solution) reference electrode in a nitrogen purged 0.5 M NaClO<sub>4</sub> solution.



**Figure S9.** Fluorescence spectra related to hydroxyl radicals on different samples after irradiation for 1 h by the widely-used coumarin fluorescent method.

