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Electronic Supporting Information

Enhanced Selectivity of Methane Production for Photocatalytic Reduction by Piezoelectric Effect

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Sample Preparation. In the synthesis progress, all the chemicals were of analytical grade and used as received without further purification. ZnO NRs were prepared by a solvothermal method [1]. In a typical preparation process, 10 mL of 0.1 M of zinc acetate stock solution in ethanol was mixed with 20 mL of 0.5 M NaOH solution in ethanol to get a clear solution which was transferred to a Teflon-lined stainless steel autoclave and heated at 150 °C for 24 hours. The final products were washed with DI water to remove impurities and dried at room temperature. The non-rod-like ZnO particles were synthesized as following steps: 1 mmol ZnCl₂ and 2 mmol KOH were dissolved into small amount of distilled water respectively. Then a white floccule immediately appeared as soon as they were mixed. Then the system was transferred into a Teflon-lined stainless steel autoclave of 40 ml and filled by distilled water up to 80% volume. Hydrothermal treatments were carried out at 120 °C for 5 h. After that, the autoclave was allowed to cool down naturally. White precipitates were collected and washed with distilled water and ethanol several times to remove impurities. Finally, the precipitates were dried at 60 °C for 12 hours. Anatase TiO₂ was directly used without further purification purchased in Aladdin Industrial Corporation.

Evolution tests of gas-phase products. In the test progress, 20 mg catalyst was firstly

dispersed in 10 ml deionized water and then evenly dipped on the bottom of a glass container followed by vacuum drying at 60 °C for 1 h. After that, the reactor was filled with carbon dioxide with one atmosphere pressure and then sealed, 50 µl DI water was injected into the reactor and heated to the vapor. Finally, the reduction progress of carbon dioxide was conducted under differently experimental conditions. When the experiment was conducted for one hour, 4 ml gas-phase products were extracted into chromatography, the productive yields of carbon monoxide and methane were determined. The selective percentages of CO and CH₄ have been

$$\text{CO percentage (\%)} = \frac{\text{CO production}}{\text{CO production} + \text{CH}_4 \text{ production}} \times 100$$

$$\text{CH}_4 \text{ percentage (\%)} = \frac{\text{CH}_4 \text{ production}}{\text{CO production} + \text{CH}_4 \text{ production}} \times 100$$

given below.

Characterization. The X-ray diffraction data were detected via a Bruker D8-Advance X-ray diffractometer using K_{Cu} radiation. The operated conditions were controlled at 40 × 10³ V and 40 × 10⁻³ A with a step width of 0.02 and the scan range was 20–80°. The morphology and microstructure of the as-prepared samples were analyzed by field-emission scanning electron microscope (FESEM, FEI Nova NanoSEM-230) and transmission electron microscope (TEM, Tecnai G2F20 S-TWIN, FEI Company). The optical properties of the samples were collected via diffuse reflection spectra (DRS) on a Varian-Cary-500 spectrophotometer. The Fourier transform infrared spectroscopy (FTIR) data were collected with a resolution of 4 cm⁻¹ using a Nicolet Nexus-670 FTIR spectrophotometer. The yields of carbon monoxide and methane were detected by GC 7900 Techcomp chromatography and the type of chromatographic column was GDX-102. The Raman scattering measurement was measured on a Renishaw instrument with a 532 nm laser at ambient temperatures. The collection of the scattered light and laser beam were obtained by a 50× microscope objective lens. The time of obtained spectra was 5 s, and the spot radius of samples was 0.5 µm under the focused laser-beam irradiation. Electrochemical analysis was measured by a Zennium electrochemical system equipped with a common three-electrode system. The counter electrode is Pt plate and the reference electrode is Ag/AgCl. The electrolyte is 0.2 mol/L Na₂SO₄ solution (pH = 6.8). ZnO NRs (5 mg) were dispersed in the mixed solution of 700 µl H₂O, 250 µl ethanol and 50 µl Nafion. The slurry was spread on FTO glass substrate that served as the working electrode. The light source was a 300 W xenon lamp with full arc light irradiation.

Reference

[1] Q. Wang, B. Geng, S. Wang, Y. Ye and B. Tao, Chem. Commun., 2010, **46**, 1899-1901.

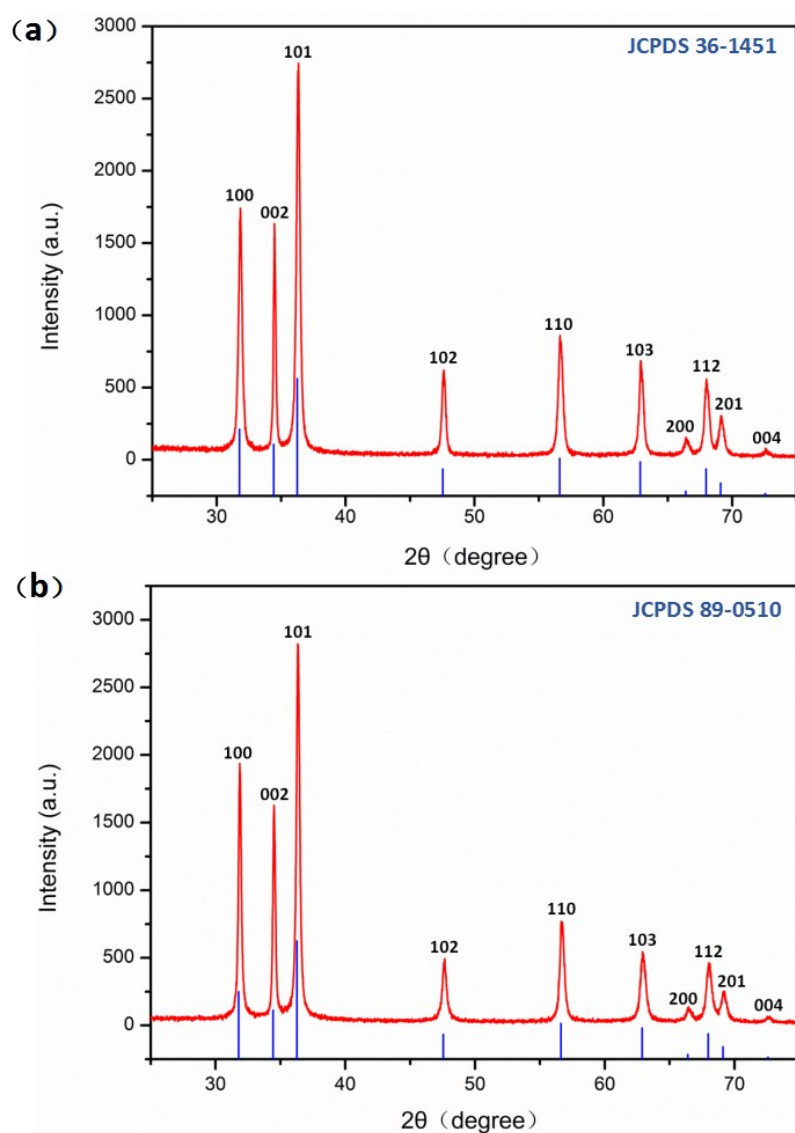


Fig. S1 XRD patterns of (a) ZnO NRs and (b) particles.

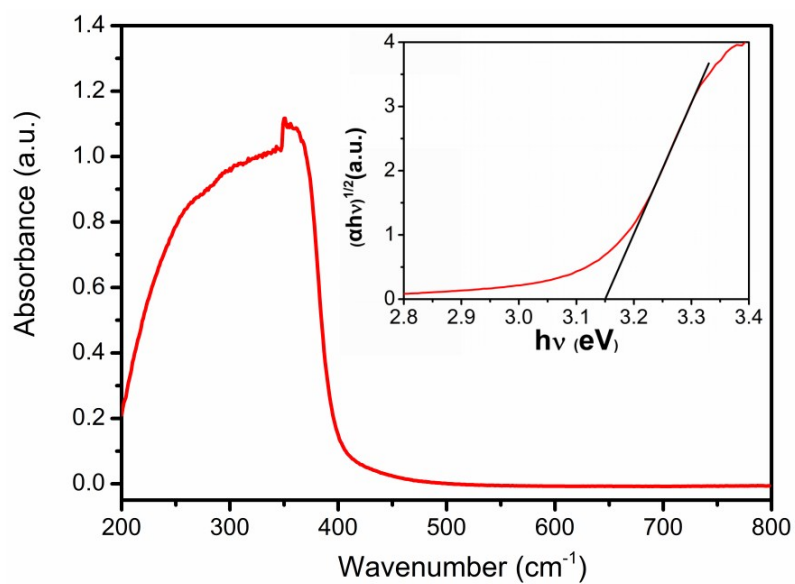


Fig. S2 UV-visible absorption spectra of ZnO NRs. Inset is the $(\alpha hv)^{1/2}$ versus $h\nu$ curve.

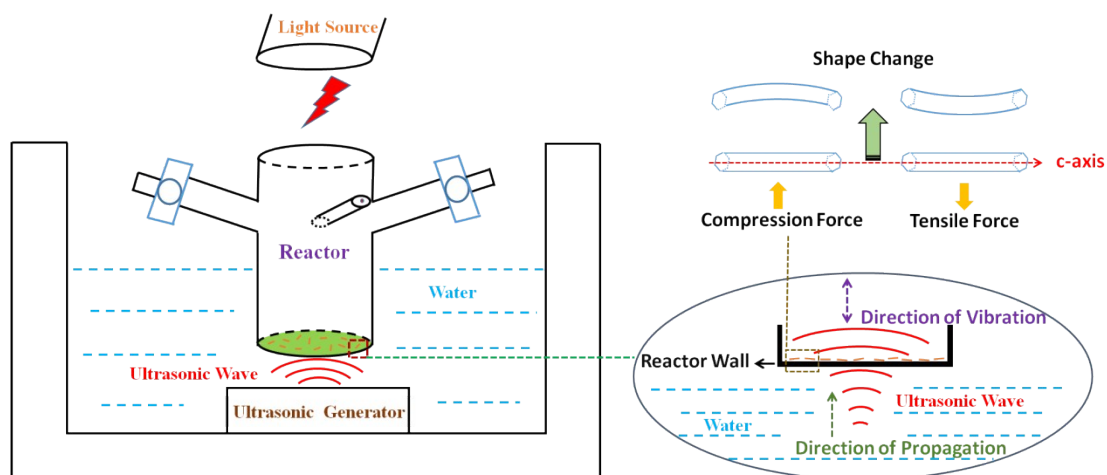


Fig. S3 Schematic diagram of reaction device.

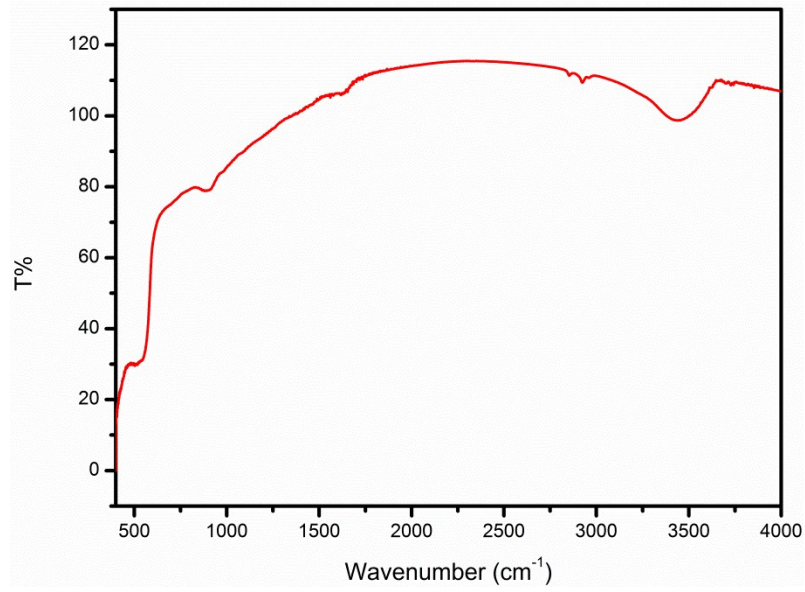


Fig.S4 IR spectrum of ZnO NRs.

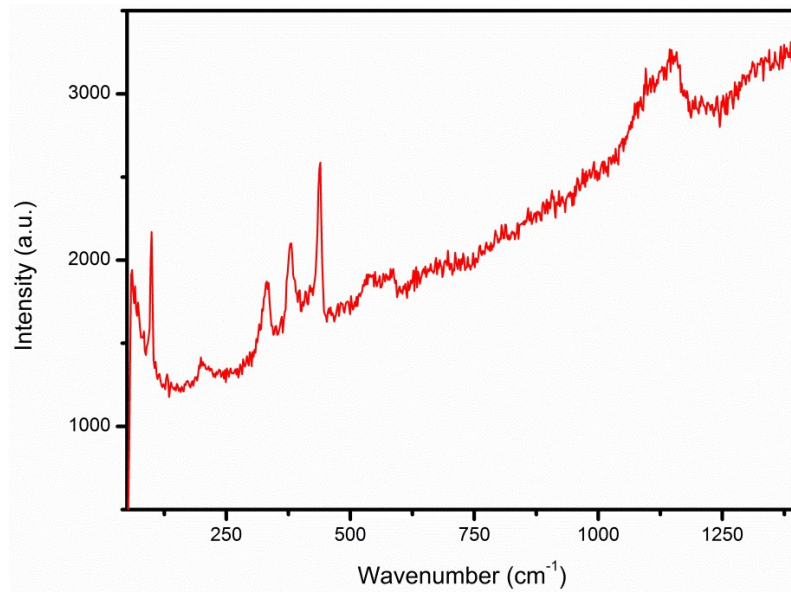


Fig.S5 Raman spectrum of ZnO NRs.

When the light intensity increase from L to L' ($0.142 \text{ W}\cdot\text{cm}^{-2}$ to $0.346 \text{ W}\cdot\text{cm}^{-2}$), the photocurrent density increases greatly as shown in Fig. S6, which means more electrons migrate to the surface of ZnO NRs under L' irradiation. As shown in Fig. S7, the productive rates of CO and CH₄ are $0.492 \mu\text{l}\cdot\text{h}^{-1}$ and $0.0391 \mu\text{l}\cdot\text{h}^{-1}$ respectively under L irradiation ($0.142 \text{ W}\cdot\text{cm}^{-2}$). While under L' irradiation ($0.346 \text{ W}\cdot\text{cm}^{-2}$), the corresponding values turn to $0.727 \mu\text{l}\cdot\text{h}^{-1}$ and $0.215 \mu\text{l}\cdot\text{h}^{-1}$ respectively. Compared with L condition, the selectivity of methane production is increased from 7.36% to 22.8% under the condition of L' irradiation. Hence, the increase in the local density of photo-induced electrons can improve the overall yields and enhance the selectivity of CH₄ production, which is the theoretical basis of our work.

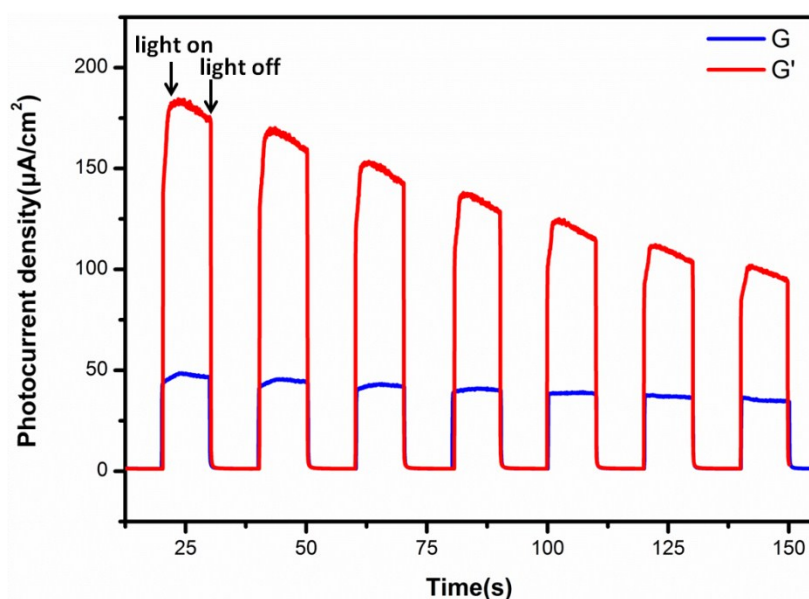


Fig. S6 Photocurrent responses of ZnO NRs in 0.2 M Na₂SO₄ aqueous solutions under full arc light irradiation with different intensity.

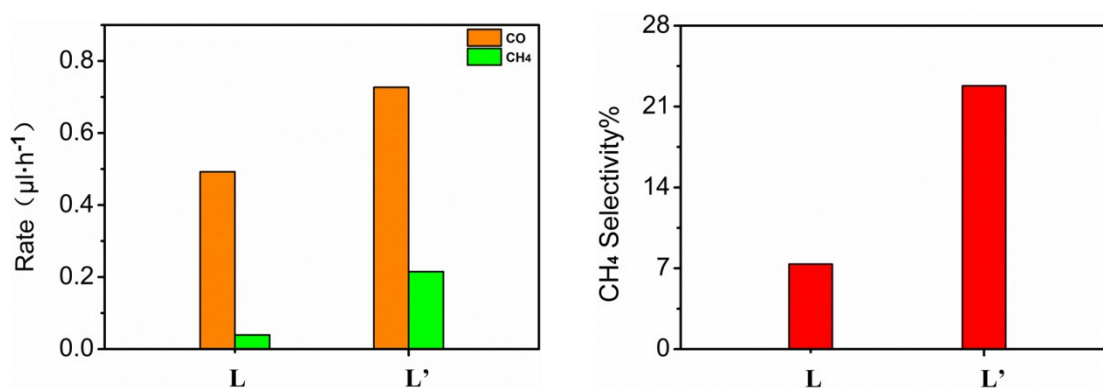


Fig. S7 Reduction of CO₂ by 20 mg ZnO NRs with (a) productive rates of CO and CH₄ and (b) selective percentage of CH₄ under full arc light irradiation with different intensity.

In our experiment, vapour is used as one kind of reactants and the existence of solid-liquid interface is inevitable which means the sonochemical and piezoelectric effects may simultaneously exist in reaction system. In order to differ the sonochemical effect from the piezoelectric effect, we conduct contrastive experiments. Under L and L+S conditions, the yields of CO and CH₄ by anatase TiO₂ (none piezoelectric properties) have been measured. As shown in Fig. S8, the productive rates of CH₄ and CO are 16.96 $\mu\text{l}\cdot\text{h}^{-1}$ and 1.86 $\mu\text{l}\cdot\text{h}^{-1}$ respectively under full arc light irradiation (L). While under the condition of simultaneous irradiation of full arc light and ultrasonic (L+S), the corresponding values turn to 14.91 $\mu\text{l}\cdot\text{h}^{-1}$ and 1.94 $\mu\text{l}\cdot\text{h}^{-1}$ respectively. Compared with L condition, the selectivity of methane production is transformed from 90.1% to 88.5% under the condition of L+S, which almost has no difference under these two conditions. It can be observed that the photocatalytic performance and the selectivity of CH₄ production have not been improved under L+S condition. Hence, the sonochemical effect occur in solid-liquid interface is not the main factor for improving the overall yields and the selectivity of CH₄ production. While for the piezoelectric material ZnO, the photocatalytic performance and the reaction selectivity can be significantly influenced by ultrasonic wave. From these comparisons, we believe that the piezoelectric effect plays a vital impact in reaction system and the sonochemical effect can be minimized. Combined with our original datas, this result further confirms that the enhancement of photocatalytic efficiency arises from the piezo-assistance of piezoelectric material.

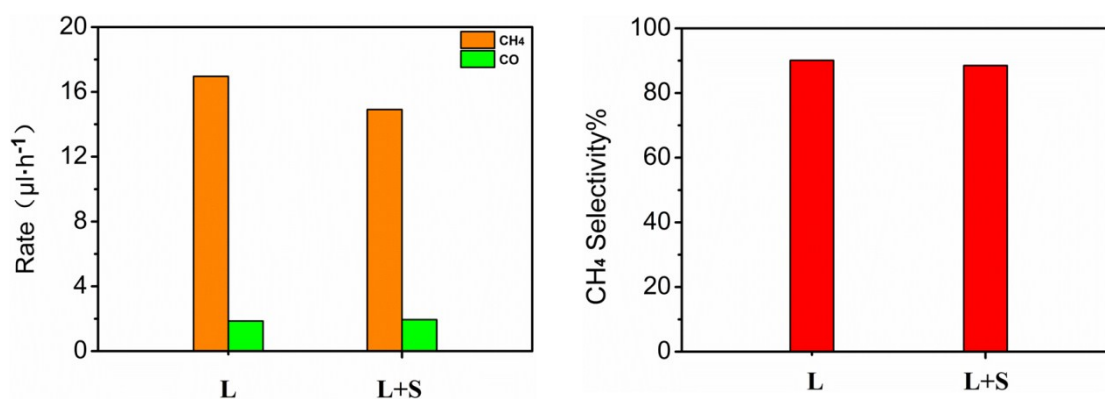


Fig. S8 Reduction of CO₂ by 20 mg anatase TiO₂ with (a) productive rates of CO and CH₄ and (b) selective percentage of CH₄ under different conditions.