# Supporting Information

## Construction of Laccase/$CeO_2$/attapulgite nanocomposite for photoenzymatic catalytic $CO_2$ reduction coupled with biomass oxidation

Huaimin Tian, Yao Xiao, Chao Yao, Taoli Huhe*, and Xiazhang Li *

## Experimental Details

**Materials.** Attapulgite (ATP) was obtained from Nanda Zijin Co, Ltd. Hydrochloric acid, cerium nitrate hexahydrate, hexamethylenetetramine ($C_6H_{12}N_4$), melamine ($C_3H_6N_6$), glutaraldehyde ($C_5H_8O_2$), laccase(Coriolus versicolor), and benzyl alcohol were purchased from Shanghai Aladdin Co. Ltd..

**Materials Synthesis.** In this work, photoenzyme catalysts were synthesized by homogeneous precipitation and covalent cross-linking. In a typical synthesis, Lac/$CeO_2$/ATP was prepared by the following steps:

**1. Preparation of acid modified $CeO_2$/p-ATP.** Firstly, 5 g ATP was mixed with 200mL deionized water at 80 °C for 12 h in 3 M hydrochloric acid solution, then washed three times with deionized water and ethanol solution respectively, and finally dried in the oven. 1 g of the above acid-modified ATP was subjected to ultrasonic treatment for 15 min. $Ce(NO_3)_3\cdot 6H_2O$ and $C_6H_{12}N_4$ (HMT) with a molar ratio of 1:5 were added under magnetic stirring and heated at a higher temperature for 2 h. After the reaction solution was cooled, it was vacuum filtered and dried overnight in a drying oven for later use. Finally, the samples were calcined at 400 °C for 2 h in a muffle furnace.

**2. Preparation of Lac/$CeO_2$/ATP.** 0.6 g of melamine (MEL) was added to 20 mL of ethanol solution, and the above samples were added at the same time. The samples were stirred at room temperature for 24 h, and then dried at 50 °C until the solvent evaporated. 0.4 g MEL modified

$CeO_2$/p-ATP was added to 10mL glutaraldehyde solution (0.5% V/V), stirred for 30min at room temperature, centrifuged at 3000 rpm/min after the reaction was completed, and washed three times. Then 40 mL of different content of Lac solution (1 mg/mL) was added for enzyme immobilization, which was used to prepare composite materials with different loadings from 0.5-2.0. Then it was stirred at room temperature for 5 h, centrifuged at 3000 rpm/min, washed three times with water, and the first supernatant was taken to test its absorbance (530 nm) to determine the enzyme immobilization rate. Finally, it was dried at room temperature for later use.

Samples with different Lac loadings were prepared by the same method: 0.5-Lac/$CeO_2$/ATP, 1.5-Lac/$CeO_2$/ATP, 2.0-Lac/$CeO_2$/ATP.

**Photocatalytic $CO_2$ reduction coupled with benzyl alcohol oxidation.** The photocatalytic $CO_2$ reduction coupled biomass conversion experiment was carried out in a 100 mL photochemical high-pressure reactor. First, 100 mg of catalyst and 0.5 mmol of benzyl alcohol were added to a photochemical high-pressure reactor containing 40 ml of deionized water and stirred evenly. An ultrapure $CO_2$ of 110 kPa (99.9999 %) is continuously injected into the reactor until a pure $CO_2$ atmosphere is established, and then the reactor gas is discharged until the pressure in the reactor is consistent with the atmosphere. In order to ensure that the reactor is filled with pure $CO_2$, the above steps were carried out three times. Then the reactor was pressurized for 15 min to maintain the pressure in the reactor at 0.1 MPa. Before irradiation, the dark adsorption reaction was carried out by stirring for half an hour through a continuous circulating water bath system. The filter was placed in front of the lamp source to filter the stray light, and the transparent window (diameter 30-40 mm) at the top of the visible reaction was irradiated vertically for 5 h using a 300 W xenon lamp. The GC system thermal conductivity detector (TCD) and hydrogen flame ionization detector (FID) were used to analyze the product (model GC-7860 Plus). Triplicate experiments were carried out for each test with a relative deviation generally less than 5%.

**Materials Characterization.** The crystal phases of the samples were examined using an X-ray diffractometer (D/Max 2500 PC, Rigaku Corporation, Japan) coupled with Cu Kα radiation. Transmission electron microscopy (TEM, JEM-2100, Japan) operated at 200 kV was employed for morphological studies. Diffuse reflectance UV-Vis spectra were measured using a UV-Vis spectrophotometer (UV-2700, Japan). The group analysis of the samples was characterized by an FT-IR spectrometer (IS-20). Transient photocurrent responses were recorded using a CHI 1030B electrochemical workstation under a 500 W Xe lamp and a standard three-electrode system. All in situ DRIFTS results were performed on a Frontier FTIR spectrometer (Thermo Fisher iS20, USA).

**In situ DRIFTS characterization.** In-situ DRIFTS (diffuse reflectance infrared spectrometer) experiments were performed using an in-situ FT-IR spectrometer (Nicolet iS20 FT-IR), using a MCT detector with a resolution of 4 $cm^{-1}$ and 64 scans. In situ DRIFTS measurements were performed on a Fourier transform infrared spectrophotometer. Firstly, the catalyst was activated in pure $CO_2$ atmosphere (purity > 99.999 %) for 30 min. The background spectra were collected in a 50 °C $CO_2$ flow environment. In addition, the mixture of $CO_2$ and benzyl alcohol aqueous solution was transported to the reaction chamber through a bubbling tank at a rate of 30 mL $min^{-1}$. In addition, the samples were placed in a dark environment of $CO_2$ and $H_2O$ for 30 min and exposed to a 300 W xenon lamp for 180 min.

**Photoelectrochemical measurements.** The transient photocurrent response was recorded by CHI1030B electrochemical workstation under 500 W Xe lamp and standard three-electrode system. The Pt wire was used as the counter electrode and the saturated Ag/AgCl was used as the reference electrode. The F-doped tin oxide glass after cleaning was used as the working electrode. The corresponding photocatalyst and Nafion (5 %) 20 μL were added into 980 μL ethanol to form a uniform slurry. The uniform slurry was ultrasonically treated for 30 minutes and then coated on FTO glass. The obtained system was dried at room temperature for 60 min, supported electrolyte was $Na_2SO_4$ solution (0.5 M), and pH value was 6.8. The incident visible light source is a 500 W xenon lamp. The photocurrent time of xenon lamp irradiation at a bias potential of 0.5 V vs. Ag / AgCl was studied. EIS was detected by 10 mV AC voltage amplitude in the frequency range of 100,000 Hz to 0.01 Hz at -0.3 V vs. Ag / AgCl.

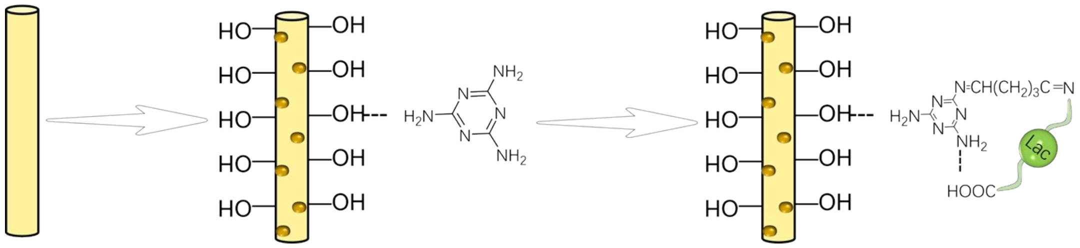

Fig. S1 The preparation process of Lac/$CeO_2$/ATP composite material.

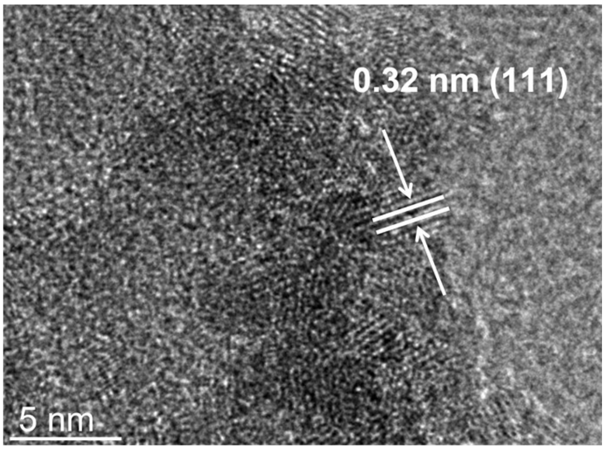

Fig. S2 The HRTEM image of $CeO_2$/ATP composite.

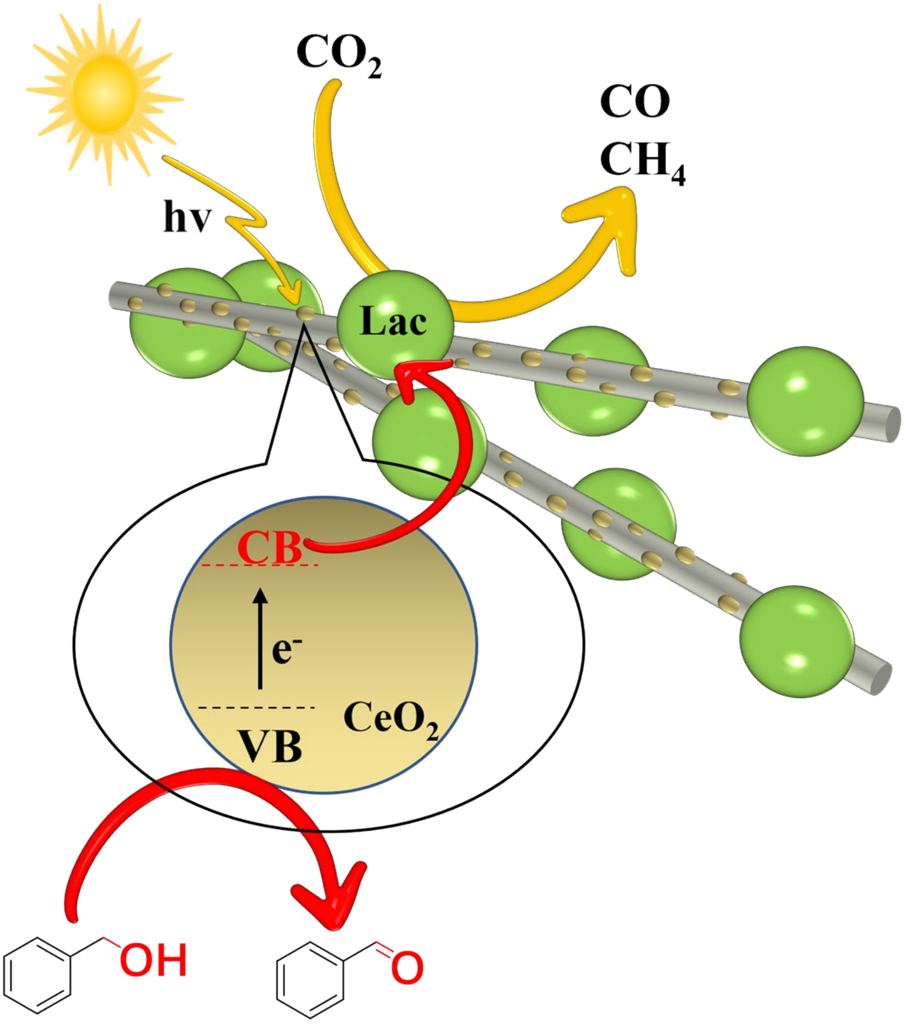

Fig. S3 The photocatalytic mechanism diagram of Lac/$CeO_2$/ATP composite.

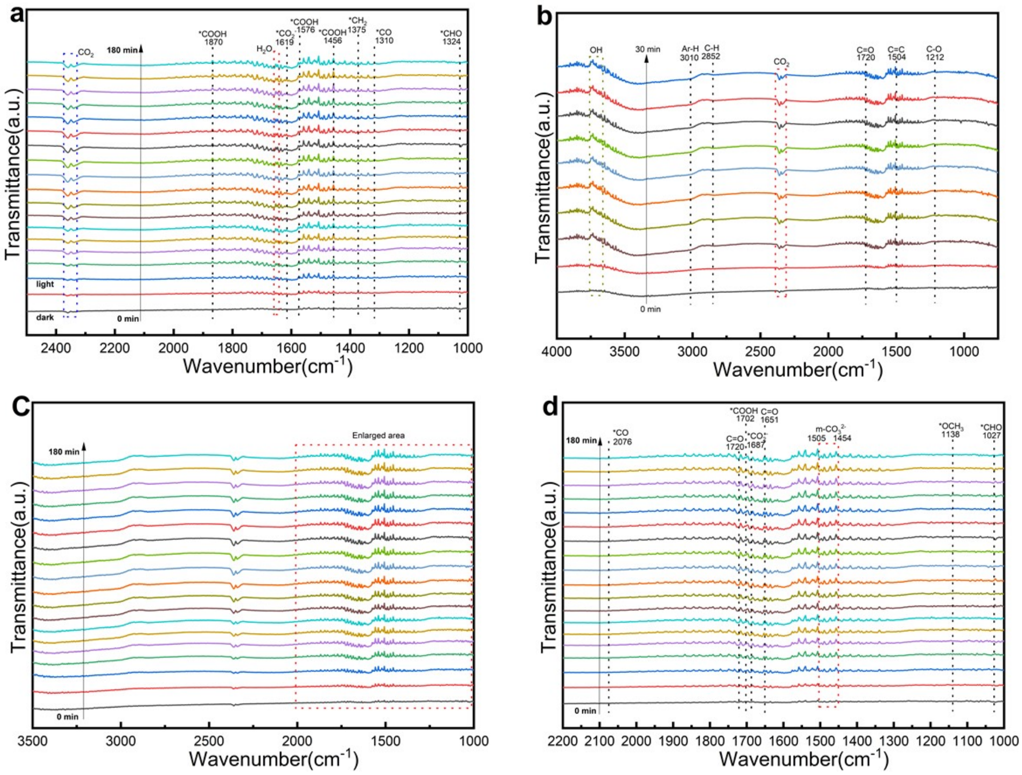

Fig. S4 *In-situ* FTIR spectra of Lac/CeO$_2$/ATP photocatalytic coupling reaction of CO$_2$ reduction and benzyl alcohol oxidation.

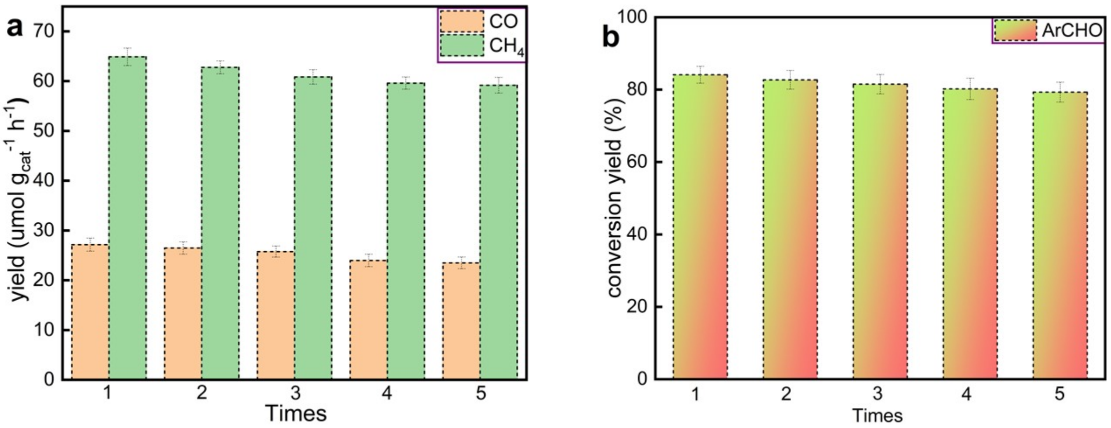

Fig. S5 Cycle experiment of 1.0-Lac/$CeO_2$/p-ATP for five runs.

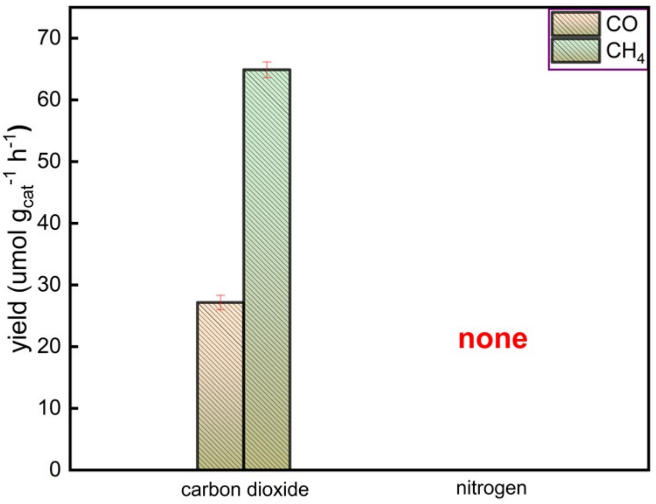

Fig. S6  Gaseous production yield under $CO_2$ and $N_2$ atmosphere of 1.0-Lac/$CeO_2$/p-ATP