

Supporting Information

Self-doped Ti³⁺-TiO₂ as Photocatalyst for the Reduction of CO₂ into Hydrocarbon Fuel under Visible Light Irradiation

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❖ Experimental Section:

➤ *Synthesis*

All chemicals, including titanium powder (Aldrich, 99%) and hydrochloric acid (Fisher scientific, 37.1%), were used as received without any further purification. In a typical synthetic procedure, titanium powder (0.300 g) and hydrochloric acid (10 mL, 2m) were mixed in a 50 mL beaker and magnetically stirred for 30 min. This mixture was then transferred to the Teflon-lined stainless-steel autoclave (23 mL capacity) and hydrothermally treated for a night under 220⁰ C. The sample was then collected and washed by distilled water and ethanol few times.¹

➤ *Characterization*

X-ray diffraction patterns (XRD) were recorded on a D8 advance diffractometer (Bruker AXS, Germany) with CuK α radiation. Transmission electron microscope (TEM) images were obtained on a JEM-2010 transmission electron microscope at an acceleration voltage of 200 kV. N₂ adsorption-desorption measurements were carried out at 77 K on a Micromeritics ASAP 2020 analyzer. Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Axis Ultra DLD using C 1s (284.8 eV) as a reference to correct the binding energy. A Hitachi ST-4800 scanning electron microscope (SEM) was used to determine the morphology.

➤ *Flat-band potential measurement*

Mott–Schottky plots were recorded on an electrochemical workstation (CHI650E, Chenhua, Shanghai) by using the Impedance-Potential technique. The working electrode was prepared on fluorine-doped tin oxide (FTO) glasses, which was cleaned by sonication in chloroform, acetone and ethanol for 30 min, respectively. The glass was then rinsed with millipore water and kept in isopropanol (or ethanol). 5 mg ultrafine powder was mixed with 0.5 mL dimethyl formamide under sonication for 2 h to get slurry. The slurry was spreading onto FTO glass whose side part was previously protected using Scotch tape. A copper wire was connected to the side part of the FTO glass using a conductive tape. Uncoated parts of the electrode were isolated with epoxy

resin, and the exposed area of the electrode was 0.25 cm². Electrochemical measurements were performed in a conventional three electrode cell, using a Pt plate and a saturated Ag/AgCl electrode as counter electrode and reference electrode, respectively. The working electrodes were immersed in a 0.2 M Na₂SO₄ aqueous solution (pH ~6.9) without additive for 30 s before measurement was carried out. For Mott-Schottky experiments, the potential ranged from -0.4 to 1.2 V (vs. Ag/AgCl), and the perturbation signal were 10 mV with the frequency from 1.25 to 0.5 kHz. The potential was swept at a sweep rate of 10 mV s⁻¹ or 20 mV s⁻¹.²

Data treatment

$$C_s = -1/(2*\pi*Z''*F)$$

where C_s is the capacitance of the self-supported film electrodes; Z'' is the virtual resistance; F is the given frequency.

Mott–Schottky plot: 1/(C_s*Cs) ~ Potential

From figure 2, the flatband potential of Ti⁺³-TiO₂ is ~-0.65 vs. Ag/AgCl. To convert the potential to be against the normal hydrogen electrode (NHE), +0.197 V has to be added according the following equation²:

$$E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.197$$

Hence, the flat band potential of Ti⁺³-TiO₂ is -0.45 vs. NHE.

Mott–Schottky plot: 1/(C_s*Cs) ~ Potential

➤ Photocatalyst Reaction

Photocatalytic reduction of CO₂ in the presence of H₂O was carried out in a lab bench reactor (volume, ~400 mL) with a quartz window on the top of the reactor. The light source was a 300 W Xe lamp with a 400 nm cut-on filter (Newport Corp.). The photocatalytic reaction was performed in a gas (vapor)-solid heterogeneous reaction mode. Typically, 100 mg of solid catalyst was placed on a Teflon catalyst holder in the upper region of the reactor. Liquid water

with a volume of 4 mL was pre-charged in the bottom of the reactor. It should be noted that the catalyst was not immersed into the liquid water. Instead, the catalyst was surrounded by H₂O vapor and CO₂. The pressure of CO₂ was typically regulated to 1 atm. The photocatalytic reaction was typically performed for 6 h. The amounts of CH₄ formed were analyzed by gas chromatography. We adopted a flame ionization detector (FID) for quantifying the amounts of CH₄ formed from CO₂ to ensure high sensitivities. Argon was used as the carrier gas. We performed the same experiment (including both reaction and detection) for at least 3 times for each catalyst, and the relative error was <5%.

❖ Figures :

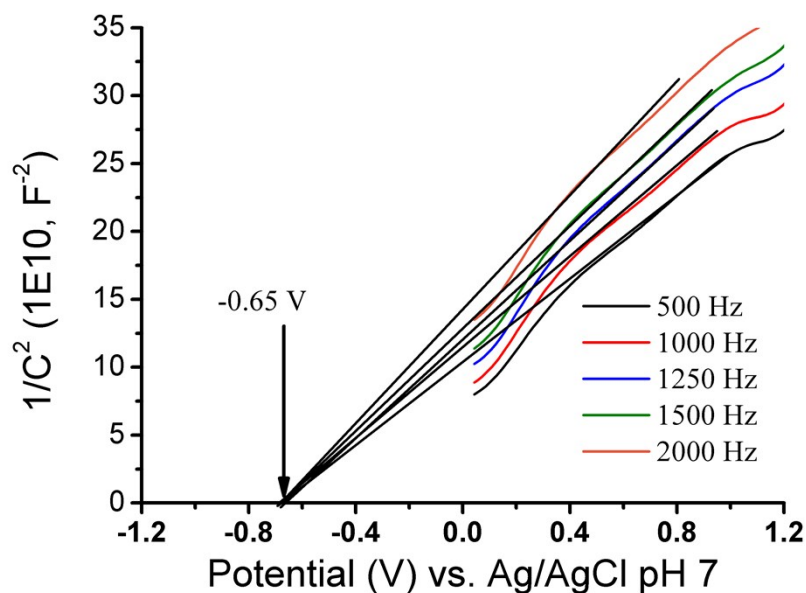


Figure 1. Mott-Schottky plot obtained at different frequencies for Ti³⁺-TiO₂.

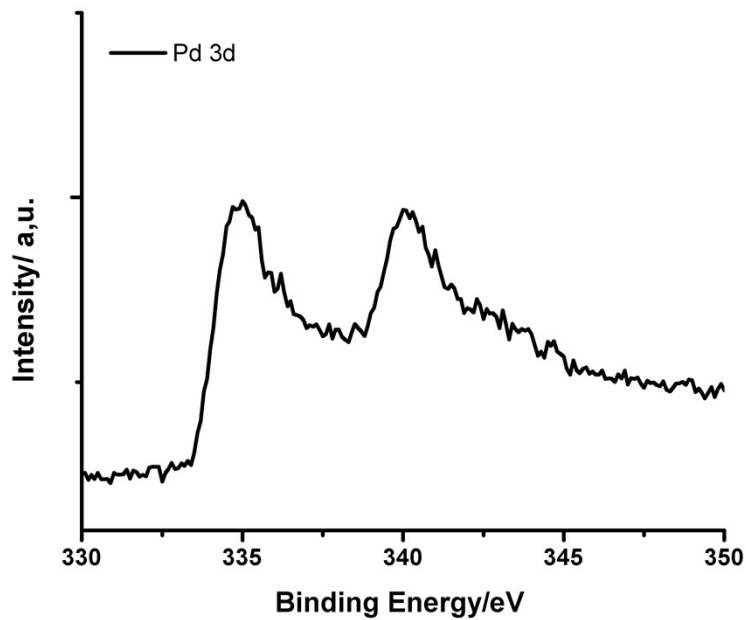


Figure 2. The Pd 3d XPS spectra of the Pd/Ti³⁺-TiO₂.

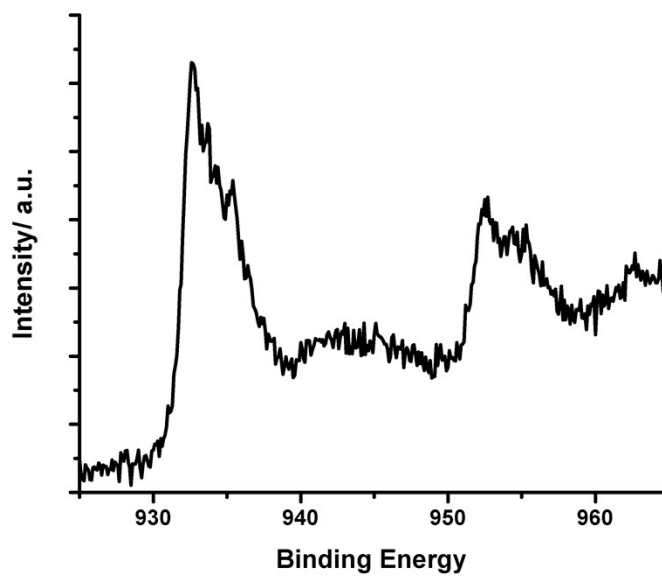


Figure 3. The Cu 2p XPS spectra of the Cu^I /Ti³⁺-TiO₂ and the Cu^I/Pd/Ti³⁺-TiO₂.

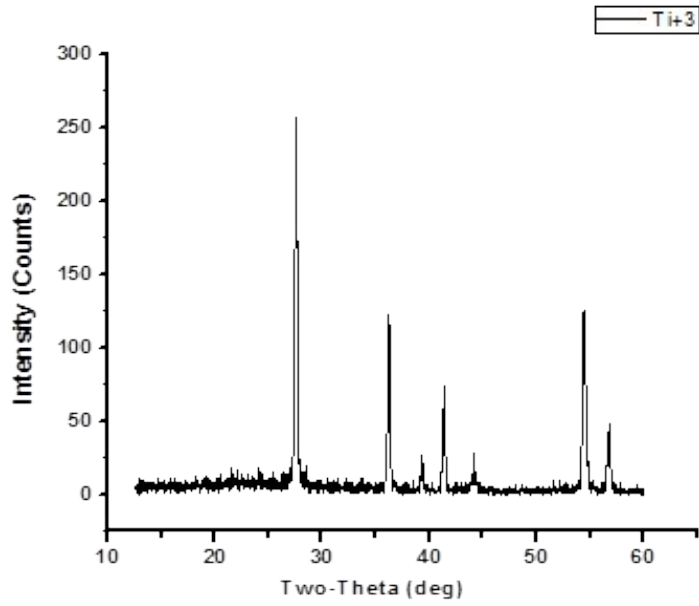


Figure 4. XRD patterns for the Ti^{+3} - TiO_2 .



Figure 5. SEM image of the Ti^{+3} - TiO_2 .

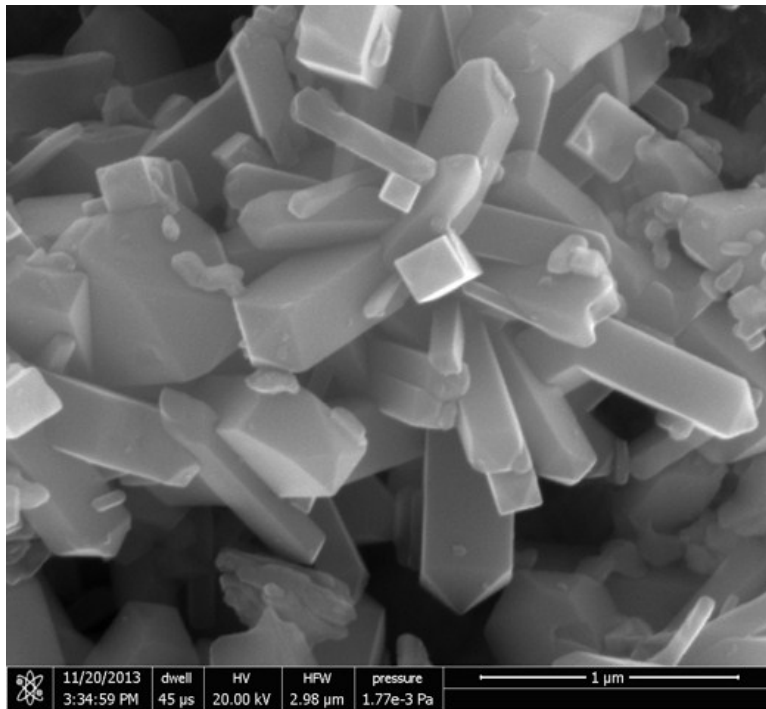


Figure 6. SEM image of the $\text{Ti}^{+3}\text{-TiO}_2$.

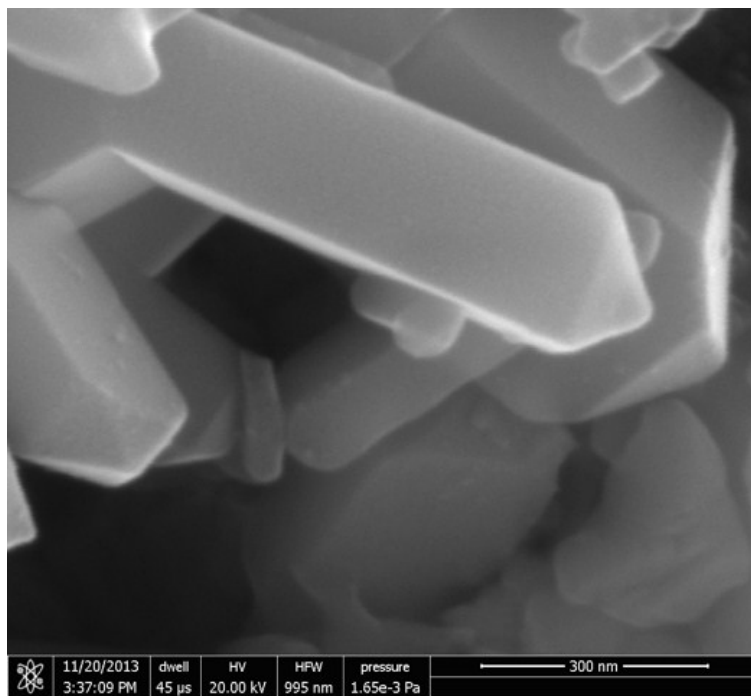


Figure 7. Figure 7. SEM image of the $\text{Ti}^{+3}\text{-TiO}_2$.

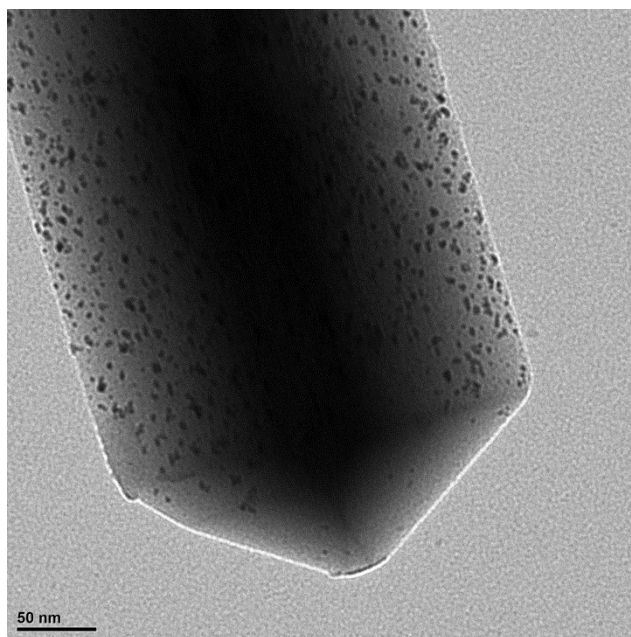


Figure 8. TEM image of the Cu^I/Pd/ Ti³⁺-TiO₂.

References :

1. F. Zuo, K. Bozhilov, R. J. Dillon, L. Wang, P. Smith, X. Zhao, C. Bardeen and P. Feng, *Angewandte Chemie International Edition*, 2012, 51, 6223.
2. X. Tang, Q. Tay, Z. Chen, Y. Chen, G. K. L. Goh and J. Xue, *Journal of Materials Chemistry A*, 2013, 1, 6359.