Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Photocatalytic Methane Conversion Coupling with Hydrogen Evolution from Water over Pd/TiO_2

*Linhui Yu, Danzhen Li**

State Key Laboratory of Photocatalysis on Energy and Environment, Research Institute of Photocatalysis, Fuzhou University, Fuzhou 350002, P. R. China

Corresponding author Tel & Fax: (+86)591-83779256, E-mail: dzli@fzu.edu.cn.

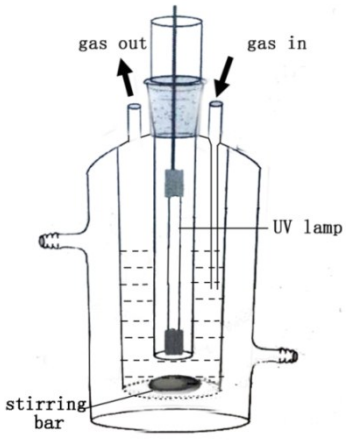

Figure S1. Schematic photocatalytic reactor.

1. The analysis of possible H_2 origin

$$2H_2O \rightarrow 2H_2 + O_2 \quad \text{(S1)}$$

$$2\,CH_4 \rightarrow C_2H_6 + H_2 \quad \text{(S2)}$$

Table S1 The account of H_2 in experiment and calculation

H_2 / μmol with CH_4	H_2 / μmol without CH_4	C_2H_6 / μmol	H_2 / μmol calculated by eq. S2
55.4[a]	21.9 [a]	12.8[a]	12.8[b]

[a] the experiment results, [b] calculated amount of H_2 from CH_4 by equation S2.

The equation S1 presents the H_2 origin of photocatalytic water splitting, and the amount of H_2 production is detected to be 21.9 μmol in the result of Figure 7(a) without CH_4. Equation S2 represents contingent coupling of CH_4 into C_2H_6 together with the production of H_2, of which C_2H_6 is the main product in this reaction. With a high degree of probability, the calculated amount of H_2 from CH_4 is 12.8 μmol according to the 1:1 of C_2H_6 to H_2 by equation S2. The H_2 production increases 33.5 μmol in the presence of CH_4, which is much more than the 12.8 μmol. It is inferred the large increasing amount of H_2 is ascribed to the water splitting after the participation of CH_4, which increases the electron availability for H_2 production.

2. Quantum Efficiency calculation

The quantum efficiency (QE) of H_2 production is calculated using the following equation: $QE = \frac{2 \times N(H2)}{I} \times 100\%$, where $N(H_2)$ and I represent the number of evolved H_2 molecules and the incident photons, respectively.[1]

The quantum efficiency (QE) for CH_4 conversion is calculated using the equation of QE = $\frac{2 \times N(CO) + 8 \times N(CO_2) + 4 \times N(C_2H_4) + 2 \times N(C_2H_6)}{I} \times 100\%$, in which N represents the molecule number of corresponding carbonous products and I represent the incident photons, respectively. It is considered a molecule of C_2H_6 consumes 2 holes, while a molecule of C_2H_4 consumes 4 holes. It is known that the overall water oxidation to O_2 is a four-electron (corresponds to 4 holes) process. The formation of a molecule of CO hence encounters 2 holes. Referring the $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, the reverse reaction of CO_2 reduction[2-4], and the reported CH_4 reacting with H_2O to CO_2,[5] a molecule of CO_2 is considered encountering 8 holes.

The all quantum efficiencies above are calculated as apparent quantum efficiency, which is assumed that all incident photons are absorbed by photocatalyst. The number of the incident photons is measured by using an ILT 950 spectroradiometer (International Light Technologies Inc., USA), and the spectra is shown in Figure S2. And the estimated quantum efficiency of H_2 production is 2.83%, while quantum efficiency of CH_4 conversion is 2.76%.

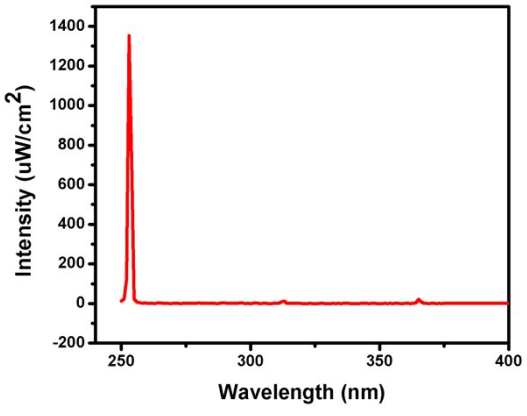

Figure S2. The spectrum of the UV lamp.

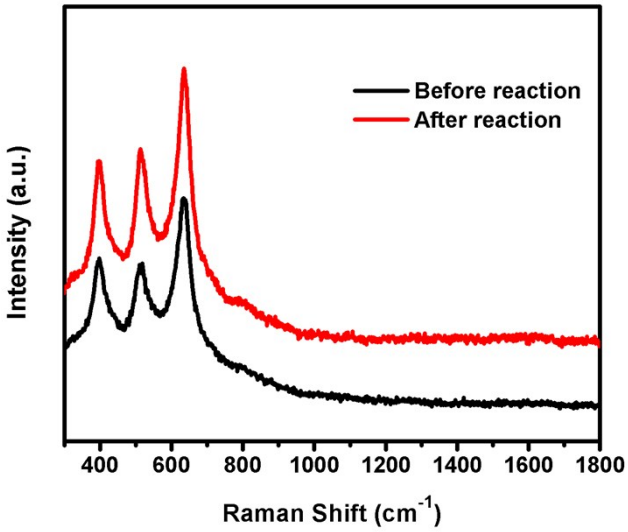

Figure S3. The Raman spectra of 1.5%-Pd/TiO_2 before and after reaction.

The Raman spectrum is a useful method to detect the carbon deposit on the catalyst, and it is carried out on Renishaw inVia-Reflex confocal-micro Raman spectrometer (Renishaw Co. UK) with excitation of 532 nm. The Raman spectra of samples before and after reaction are contrastively shown in Figure S3, and both of them possess three characteristic peaks belonging to antase TiO_2[6, 7]. None of D mode at 1350 cm^{-1}or G mode at 1580 cm^{-1} [8-11] indexed to carbon is observed in the sample after reaction, indicating no carbon deposit existing on the catalyst.

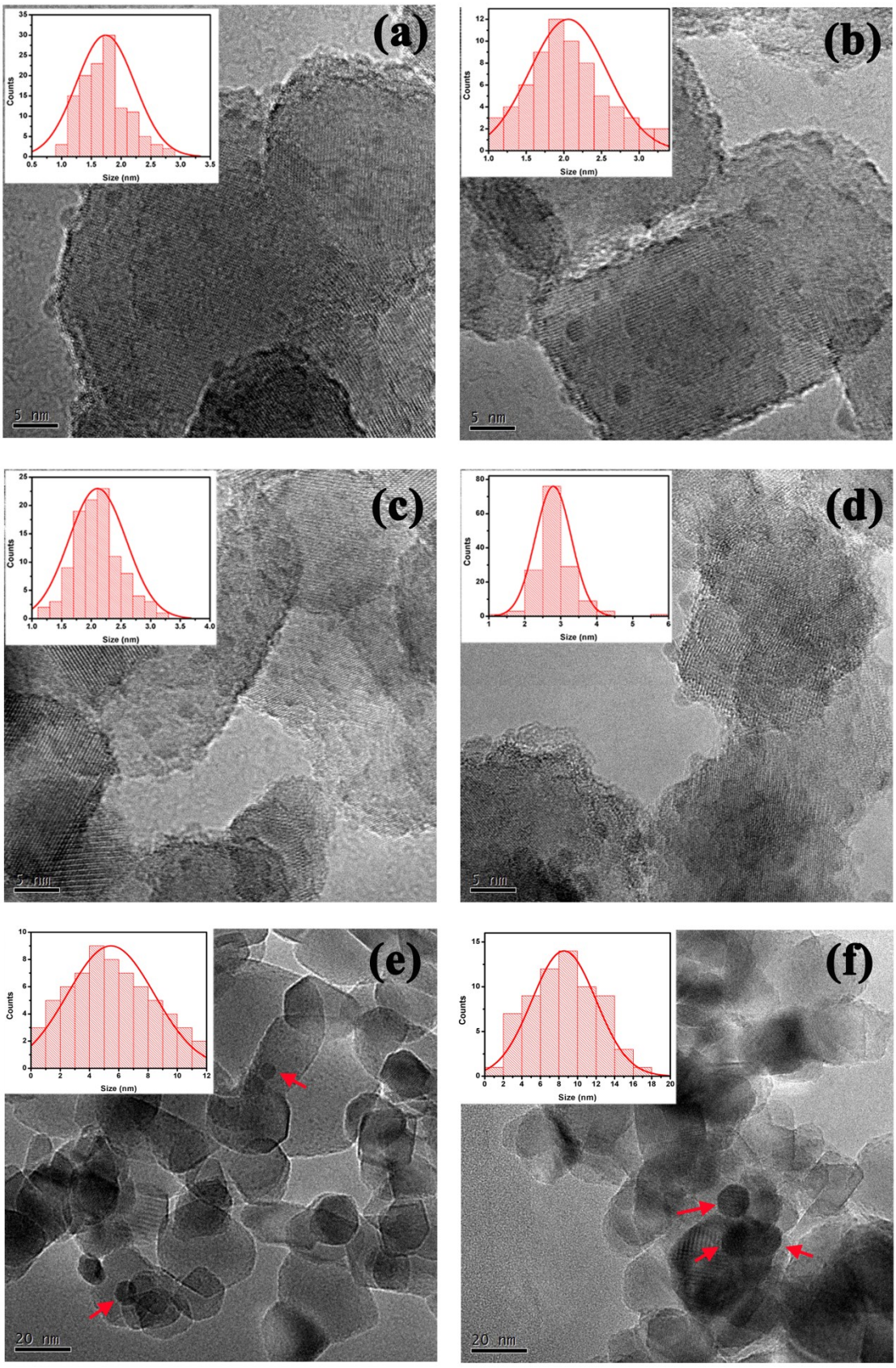

Figure S4. The TEM images of x%-Pd/TiO_2 and their corresponding size distribution inside: (a) 0.1%-Pd/TiO_2, (b) 0.5%-Pd/TiO_2, (c) 1%-Pd/TiO_2, (d) 1.5%-Pd/TiO_2, (e) 2%-Pd/TiO_2, (f) 5%-Pd/TiO_2.

Table S2 The average size of Pd in x%-Pd/TiO_2

Sample	0.1%-Pd/TiO_2	0.5%-Pd/TiO_2	1%-Pd/TiO_2	1.5%-Pd/TiO_2	2%-Pd/TiO_2	5%-Pd/TiO_2
Average size / nm	**1.7**	**2.0**	**2.1**	**2.8**	**5.4**	**8.5**

The average sizes of Pd particle in x%-Pd/TiO_2 are listed in Table S2. According to the photocatalytic activity over x%-Pd/TiO_2 in Figure 5, it is deduced that the increasing amount of small size of Pd makes significant contribution to the increasing of various products, which can be seen from the comparison of 0.1%, 0.5%, 1%, and 1.5%. While more increasing of Pd proportion (up to 2%. 5%) gives rise to the size growth of Pd particles, and it has no contribution the subsequently increasing of various products.

Reference

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