Supporting Information for

Ultra-thin TiO_2 nanosheets decorated with Pd quantum dots for high-efficiency hydrogen production from aldehyde

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Synthesis of TiO_2 nanosheets

All the reagents were of analytical grade and were used without further purification. TiO_2 nanosheets with exposed different ratios (001) facets were prepared by the hydrothermal method similar to that reported by Xie.[1] In a typical experimental procedure, 25 mL of $Ti(OC_4H_9)_4$ and 1, 2, 4 and 6 mL of hydrofluoric acid solution (with a concentration ca. 40 wt %) were mixed in a dried Teflon autoclave with a capacity of 100 mL at ambient temperature, followed by hydrothermal treatment of the mixture at 180 ^oC for 24 h. After being cooled to room temperature, the white precipitate was separated by high-speed centrifugation, washed with ethanol and distilled water for three times, and then dried in an oven at 70 °C for 6 h. The prepared samples were denoted as TiO_2-HF1, TiO_2-HF2, TiO_2-HF4 and TiO_2-HF6, corresponding to the amount of hydrofluoric acid solution added.

Synthesis of Pd/TiO_2 nanosheets

The Pd/TiO_2 nanosheets catalysts were prepared by impregnation reduction of the above-prepared TiO_2 nanosheets powders (1.0 g) into a clean beaker, which contained 200 mL of deionized water were mixed with appropriate amount of H_2PdCl_4 solution, vigorously stirred for another 1 h to disperse them completely, and then 1 M NaOH solution was added to this solution to adjust the pH value of solution to about 9.0. Then the $NaBH_4$ (freshly prepared) was added drop-wise into the solution with a continuous magnetic stirring,[2] the color of the solutions has changed from glassy yellow, brick red, to gray black at last, the reaction solution kept on stirring for 3 h to complete the reduction reaction. The obtained black granules washed with deionized water and dried in a vacuum oven at 70 ^oC for 6 h. For comparison, the Pd/TiO_2 catalysts were also prepared using commercial Degussa P25, and the nominal weight ratios of Pd to TiO_2 were 2 wt %.

Characterizations

Scanning electron microscope (SEM) images were taken using a field-emission scanning electron microscope (JSM-6701F, JEOL) operated at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were obtained on a transmission electron microscope (JEM1200EX, JEOL) equipped with an energy dispersive X-ray detector (EDX) at an acceleration voltage of 100 kV. The powder X-ray diffraction spectra (Power XRD) measurements were performed on a Philips X' pert MPD instrument using Cu Kα radiation(50 kV). X-ray photoelectron spectrometry (XPS) was carried out on an ESCALAB250xi X-ray photoelectron spectrometer using an Al Kα source.

Activity tests

In the catalytic activity of experiments, HCHO and NaOH solution (100 mL) was added to the sealed flask (600 mL) and given an amount of catalysts (15 mg), then the hydrogen production reaction was started while the solution was stirred vigorously. The amounts of hydrogen produced were measured by a GC (gas chromatograph) equipped with a TCD detector and argon as carrier gas. The amounts of the hydrogen produced were measured every five minutes, each experiment was measured at least 3 times to make sure accuracy. There is not carbon monoxide or other gaseous product have detected in all these catalytic processes.

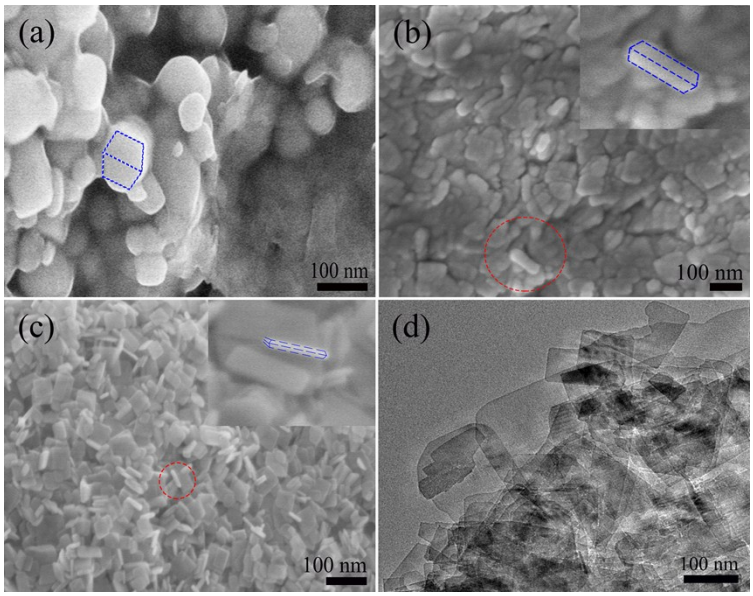

Fig. S1 (a) SEM images of TiO_2-HF1, (b) SEM images of TiO_2-HF2, (c) SEM images of TiO_2-HF4, (d) TEM images of TiO_2-HF6. The insets show the enlarged images of (b) TiO_2-HF2 and (c) TiO_2-HF4.

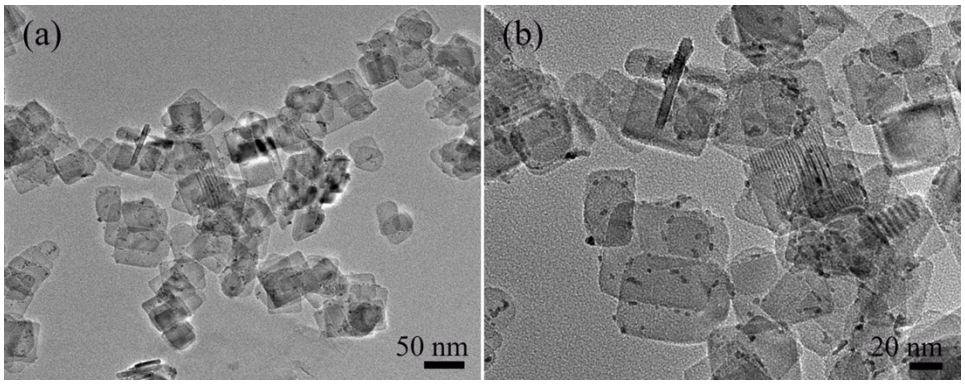

Fig. S2 (a, b) TEM images of Pd/TiO_2(TiO_2-HF4) with different magnifications.

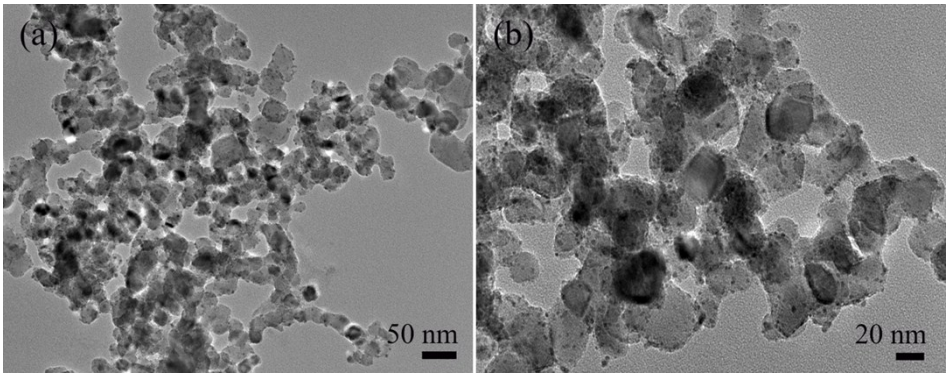

Fig. S3 (a, b) TEM images of Pd/TiO_2-P25 with different magnifications.

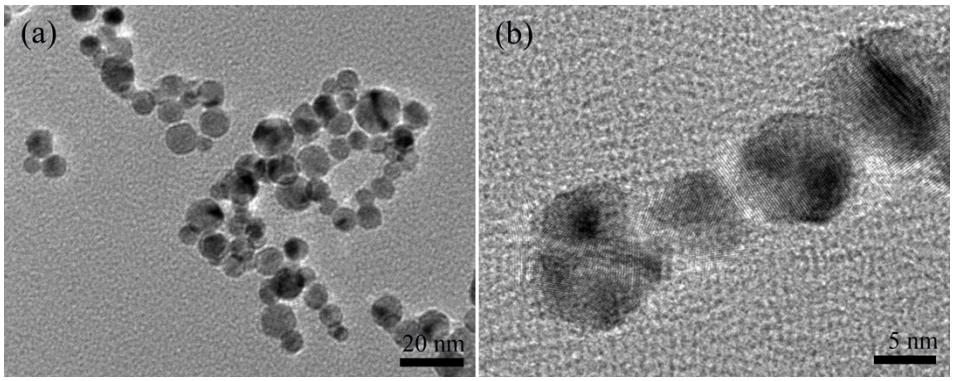

Fig. S4 (a, b) TEM images of Pd nanoparticles with different magnifications.

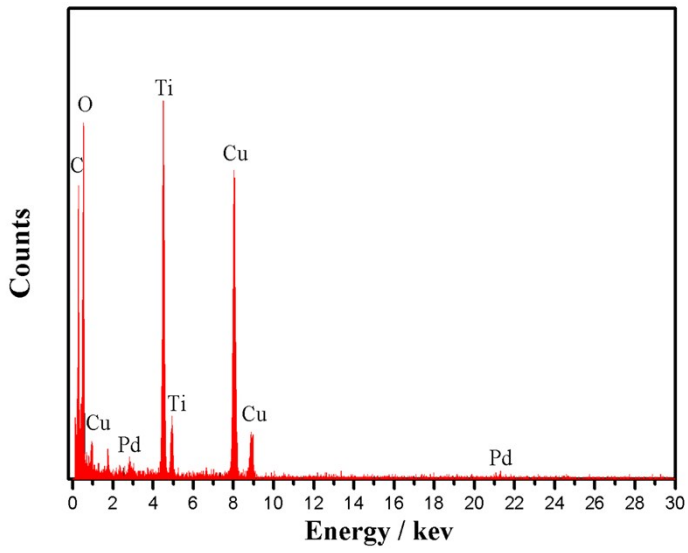

Fig. S5 EDX patterns of as-prepared Pd/TiO_2-HF4.

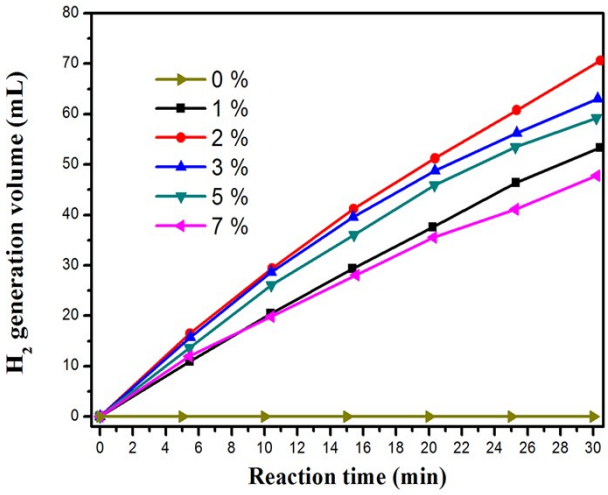

Fig. S6 The effect of Pd and TiO_2 nominal weight ratio on H_2 production, Pd/TiO_2 catalyst: 15 mg, HCHO: 0.6 mol/L, NaOH: 1.0 mol/L, temperature: 25 °C.

Table S1 Comparison of the specific surface areas of different TiO_2 samples

Samples	Crystalline size (nm)	S_{BET} (m^2/g)	Pore volume (m^3/g)	Average pore size (nm)
P25	**30.1**	**50.3**	**0.18**	**13.3**
TiO_2-HF1	**11.3**	**122.6**	**0.07**	**10.8**
TiO_2-HF2	**18.5**	**108.7**	**0.36**	**12.0**
TiO_2-HF4	**25.3**	**94.2**	**0.41**	**14.4**
TiO_2-HF6	**32.6**	**76.5**	**0.21**	**15.8**

References:

1 X. Han, Q. Kuang, M. Jin, Z. Xie and L. Zheng, *J. Am. Chem. Soc.,* 2009, **131**, 3152.

2 L. Nie, J. Yu, X. Li, B. Cheng, G. Liu and M. Jaroniec, *Environ. Sci. Technol.*, 2013, **47**, 2777.