

Supplementary Materials: Carbon-Modified Mesoporous Anatase/TiO₂(B) Whisker for Enhanced Activity in Direct Synthesis of Hydrogen Peroxide by Palladium

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1. Materials

Benzenephosphonous acid (C₆H₇O₂P, Maya Reagent, Zhejiang, China), dichloromethane (CH₂Cl₂, Shanghai Linfeng Chemical Reagent Co., Ltd, Shanghai, China), Palladium chloride (PdCl₂, Sigma-Aldrich, Shanghai, China), acetone (C₃H₆O, Suzhou Henghuixiang Chemical, Suzhou, China), hydrochloric acid (HCl, Shanghai Linfeng Chemical Reagent Co., Ltd, Shanghai, China), sulfuric acid (H₂SO₄, Shanghai Linfeng Chemical Reagent Co., Ltd, Shanghai, China). All chemicals were used without refinement.

2. Catalysts Characterization Results

2.1 Scanning Electron Microscope (SEM)

Figure S1 shows the morphology of pristine mb-TiO₂ and carbon modified mb-TiO₂. The whisker is fiber-like with a uniform diameter of 300–400 nm, and the length varies from 1 to 10 μm [1]. The structure of whisker has barely changed after the carbon decoration.

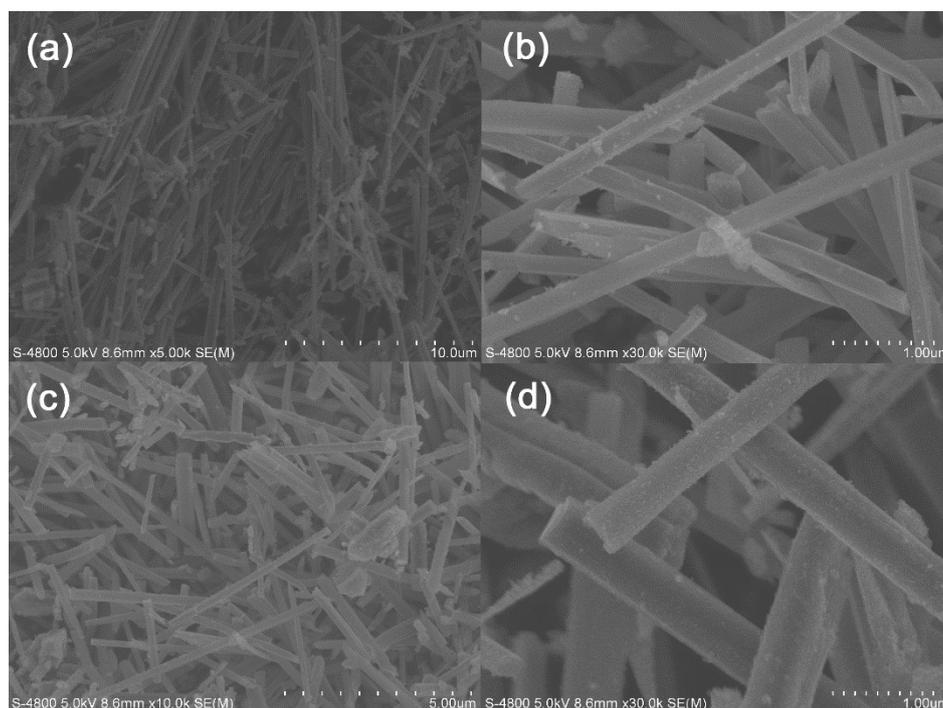


Figure S1. SEM images of (a,b) mb-TiO₂ and (c,d) C-mb-TiO₂.

2.2 TG Analysis

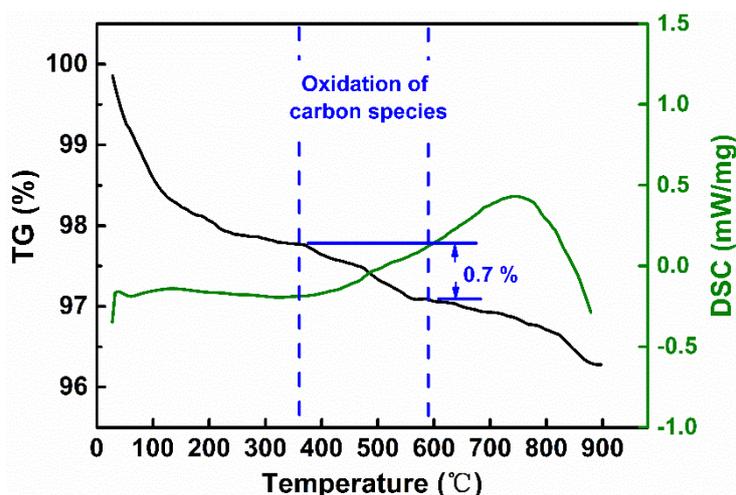


Figure S2. TG and DSC curves of C-mb-TiO₂.

As shown in Figure S2, a distinct exothermic peak is observed in the DSC curve, ranging from the temperature of 360 °C to 900 °C. This interval contains the oxidation of phosphorus species, oxidation of carbon species, volatilization of phosphorus oxide, and so on. These processes may occur simultaneously or overlap, therefore, it is difficult to separate them accurately. Generally, the oxidation of carbon species occurs at 400–600 °C [2]. The TG curve shows that the mass loss of carbon species at 400–600 °C is less than 1 wt% (about 0.7 wt %). Thus, we can qualitatively confirm the content of carbon species of C/mb-TiO₂ is less than 1 wt %.

2.3 XPS Analysis

Table S1. Quantified XPS data for the surface Pd atoms.

Catalysts	Pd species	3d _{5/2}		3d _{3/2}		Concentration (%)	
		BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	Pd ⁰	Pd ²⁺
Pd-mb-TiO ₂	Pd ⁰	335.7	1.9	340.8	1.9	66.4	33.7
	Pd ²⁺	337.3	1.7	342.5	1.7		
Pd-C-mb-TiO ₂	Pd ⁰	335.7	1.65	340.8	1.65	65.5	34.5
	Pd ²⁺	337.3	1.9	342.5	1.9		

3. Microcalorimetry Measurement for H₂O₂ Adsorption

The H₂O₂-support interaction was characterized by TAM Air isothermal microcalorimeter (TA instruments, New Castle, DE, USA), two calorimetric channels were used for the sample and a static reference, respectively. The temperature of the channels was kept at 10 °C, 60 mg sample and 2 mL buffer solution (deionized water) were placed in the ampoule and stirred by a micro-motor at 12 V. When the system finally stabilized, 2 mL of H₂O₂ solution (990 ppm) was injected into the ampoule, meanwhile, the same volume of water was added into the reference group. The released energy was calculated by integrating the function of power with time; the slurry was filtered by membrane to separate H₂O₂ and support after the microcalorimetric measurement, the concentration of H₂O₂ was measured by the UV/Vis spectrophotometer. All the results were repeated for three times. The value of the adsorption heat of H₂O₂ is calculated using the following formula [3]:

$$\text{Adsorption heat of H}_2\text{O}_2 = H_{\text{H}_2\text{O}_2} / M_{\text{H}_2\text{O}_2} \quad (\text{S1})$$

$H_{\text{H}_2\text{O}_2}$ and $M_{\text{H}_2\text{O}_2}$ represent the released heat of the adsorption of H_2O_2 and the mole of adsorbed H_2O_2 when the equilibrium is reached, respectively. The detailed data about the adsorption properties of H_2O_2 on the support is shown in Table S2.

Table S2. Calorimetric measurement of H_2O_2 adsorption.

Sample	Total Heat of Adsorption (mJ)	Total Amount of Adsorbed H_2O_2 (mg)	Adsorption Heat of H_2O_2 (KJ/mol- H_2O_2)
mb-TiO ₂	395.6 ± 7.8	1.46 ± 0.09	9.2 ± 0.8
C-mb-TiO ₂	204.6 ± 4.6	1.28 ± 0.08	5.5 ± 0.3

4. Catalysts Testing

The direct synthesis of H_2O_2 from H_2 and O_2 was carried out in the following process (seen in Figure S3). In addition, all the results of our work in Table S2 were collected from the data measured at the first 30 min.

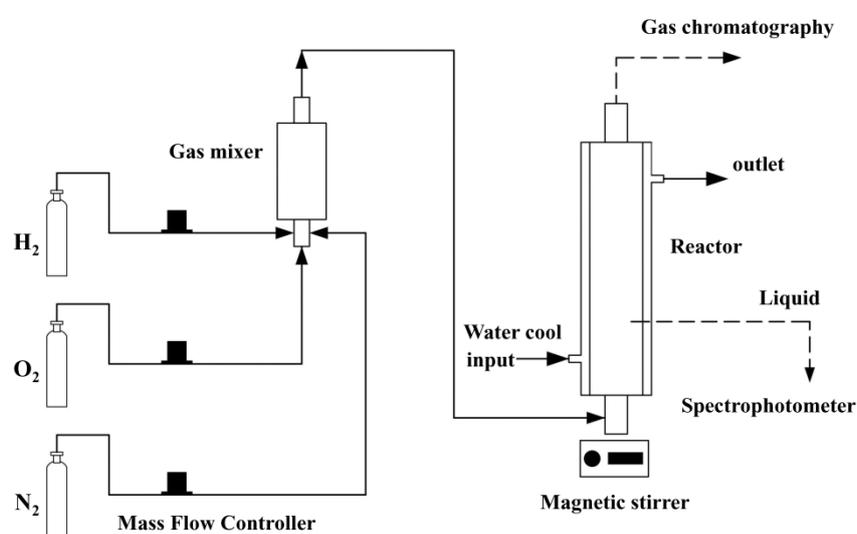


Figure S3. The scheme of reaction process.

Table S3. The performance of Pd catalysts for H_2O_2 synthesis and hydrogenation.

Catalyst	Conversion (%)	Productivity (mmol H_2O_2 /gPd/h)	Selectivity (%)	Hydrogenation (mmol H_2O_2 converted/gPd/h)	Partical size (nm)	Ref
Pd/C-mb-TiO ₂	36	2848	49	2115	11.2	Our work
Pd/mb-TiO ₂	26.6	1933	45	3726	10.5	Our work
Pd-P25	26.8	1857	42.88	2562	2.6	Our work
C-mb-TiO ₂	0	0	0	0	-	Our work
mb-TiO ₂	0	0	0	0	-	Our work
Pd-P25	26.2	1922	44.6	-	2.3	[4]
Pd-TiO ₂	18	1670	31	-	4.8	[5]
Pd-TiO ₂	29	620	21	-	-	[6]

References

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