

Supporting materials

## **TiO<sub>2</sub> topotactic transformation assisted trapping atomically dispersed Pt catalyst for low temperature CO oxidation**

Yunping He, Xue-Zhi Song, Feng Ding, Xiaolan Kang, Feifei Sun, Qiaofeng Su and Zhenquan Tan \*

State Key Laboratory of Fine Chemicals, School of Petroleum and Chemical Engineering, Dalian University of Technology, Panjin, Liaoning 124221, China.

E-mail: tanzq@dlut.edu.cn; Tel: +86-427-2631808

### **1. Experimental section**

#### **1.1 Material**

Titanium butoxide (TBOT, 98%), Chloroplatinic acid hydrate (H<sub>2</sub>Cl<sub>6</sub>Pt·xH<sub>2</sub>O, 99.95%) was supplied by Aladdin Chemicals (Shanghai, China). Ammonium fluoride (NH<sub>4</sub>F), absolute ethyl alcohol (EtOH, 99.7%) and glacial acetic acid (HAc, 99.5%) were purchased from Tianjin Great Mao Co.Ltd. Isopropanol (99.7%) and boric acid were all obtained from Sinopharm Chemical Reagent Co.Ltd (Shanghai,China). Unless otherwise noted, all chemicals were used without further purification.

#### **1.2 Synthesis of the NH<sub>4</sub>TiOF<sub>3</sub> precursor**

NH<sub>4</sub>TiOF<sub>3</sub> precursor was prepared using solvothermal method. Firstly, 0.77 mL of TBOT was added into 40.0 mL of HAc under vigorous stirring to form a white suspension. 0.333 g of NH<sub>4</sub>F was added in the above suspension and then kept stirring for 15 min. Subsequently, the mixture solution was moved to a Teflon-lined autoclave with 100 mL capacity and kept in 150 °C for 12 h. After the autoclave cooling quickly to room temperature, the white precipitate was separated by centrifugation and washed with deionized water and ethanol for several times, respectively. Finally, NH<sub>4</sub>TiOF<sub>3</sub> mesocrystals were obtained after dried at 60 °C overnight under vacuum.

### 1.3 Synthesis of Pt/TiO<sub>2</sub> catalysts

The as-prepared NH<sub>4</sub>TiOF<sub>3</sub> mesocrystals (0.3g) were evenly dispersed in 5 mL of deionized water, followed the newly prepared H<sub>2</sub>PtCl<sub>6</sub> (1.81mL, 0.016mol/L) was added under stirring for 5 minutes and then stored away from light for 2 hours. The suspension was mixed with boric acid solution (40 mL, 0.5 M) under stirring and kept at 60 °C for 4 hours. The product was collected by centrifugation, washed several times with deionized water and ethanol, and then dried at 60 °C overnight. The product was recorded as 1% Pt/TiO<sub>2</sub>-T that means the mass ratio of Pt to TiO<sub>2</sub> is 1%. Other Pt/TiO<sub>2</sub>-T samples were prepared by the same method with a various mass ratio of 0.1%, 0.5%, and 3%. The as-prepared catalysts were calcined in N<sub>2</sub> at 450 °C for 4 h and the obtained samples were labeled as Pt/TiO<sub>2</sub>-TC. As a comparison, we prepared Pt/TiO<sub>2</sub> catalyst by a conventional method. In which approach, the precursor NH<sub>4</sub>TiOF<sub>3</sub> was firstly converted into TiO<sub>2</sub> by boric acid treatment, and then TiO<sub>2</sub> was impregnated with H<sub>2</sub>PtCl<sub>6</sub> solution. The preparation conditions were the same as above, and the obtained sample was recorded as Pt/TiO<sub>2</sub>-NC.

### 1.4 Characterization

The morphology and microstructure of the prepared samples were recorded on a FEI Nova Nano SEM 450 field emission scanning electron microscope with an accelerating voltage of 18 kV. The transmission electron microscopy (TEM) images and the corresponding energy dispersive spectroscopy (EDS) mapping analysis were implemented on a TECNAI G2 F-30 equipped with an EDAX detector operating at 200 kV. Atomic-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were gained on a FEI Titan Cube 60-300 STEM/TEM equipped with a probe spherical-aberration corrector with a high spatial resolution of 0.07 nm. The X-ray diffraction (XRD) profiles were collected by a SHIMADZU XRD-7000S diffractometer equipped with a Cu K $\alpha$ 1 radiation source in a 2 $\theta$  range of 10-70° with a scan speed of 2°/min. The X-ray photoelectron spectra (XPS) were performed using a Thermo Fisher ESCALABTM 250Xi electron spectrometer. N<sub>2</sub> adsorption-desorption studies were performed by JW-BK132F operating at -196 °C. The surface areas of the samples were measured using the

Brunauer-Emmett-Teller (BET) method. The pore diameter distributions were derived by the Barrett-Joyner-Halenda (BJH) method using the adsorption branch of the isotherm.

### 1.5 CO oxidation test

The experiment for performance of the catalysts was carried out in custom-built flow reactor. Powders of catalyst (30 mg) were carefully loaded into a quartz tube (i.d. = 3 mm) and fixed by glass wool on both ends. A standard reaction gas comprising 1% CO and 21% O<sub>2</sub> and 78% N<sub>2</sub> gas was acted as the source to form a required gas mixture, which was introduced into the reactor using mass-flow controllers at a rate of 30 mL/min. The tube reactor was fixed into a heating furnace to control reaction temperature. After 10 minutes of stable operation, the performance of the catalyst was recorded and analyzed. The reaction temperature was regulated by a thermocouple fixed on the middle outside of the tube. The composition (CO content) of the out gas from the reaction quartz tube was monitored via online gas chromatography (GC) provided with a FID under steady-state conditions. The conversion of CO ( $X_{CO}$ ) as a function of temperature was calculated as following Equation 1:

$$X_{CO} \text{ conversion (\%)} = ([CO]_{in} - [CO]_{out})/[CO]_{in} \times 100 \quad (1)$$

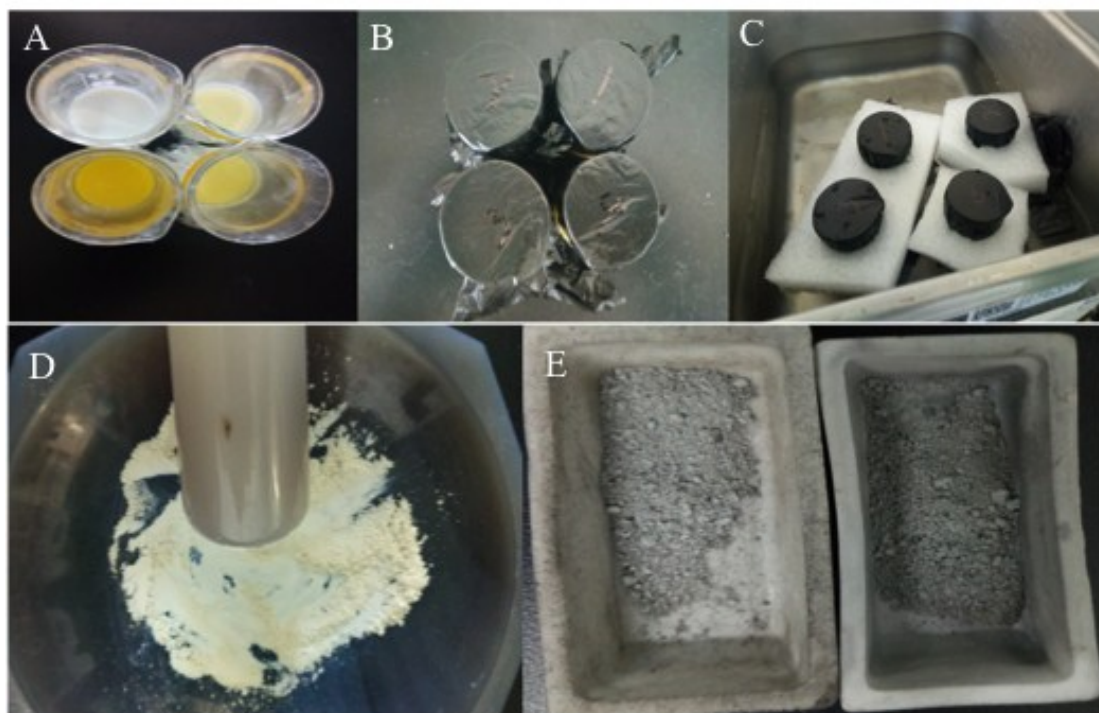
Where  $[CO]_{in}$  and  $[CO]_{out}$  are the amount of CO in the reaction gas before and after oxidation reaction.

The turnover frequencies (TOF) for CO oxidation was obtained by using the following Equation 2:

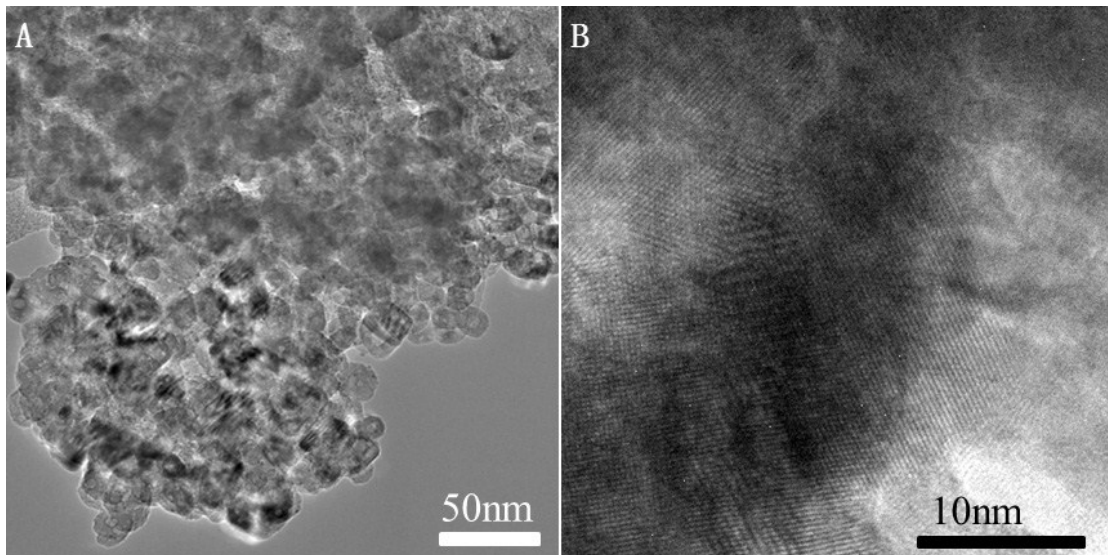
$$TOF = X_{CO} F_{CO} \frac{M_{Pt}}{m_{cat} X_{Pt} D_{Pt}} \quad (2)$$

where  $F_{CO}$  is the flow velocity of CO (mol/s),  $m_{cat}$  is the mass of catalyst (g),  $X_{Pt}$  is the Pt loading content in catalyst,  $D_{Pt}$  is the degree of dispersion for Pt,  $M_{Pt}$  is the molar mass of Pt.

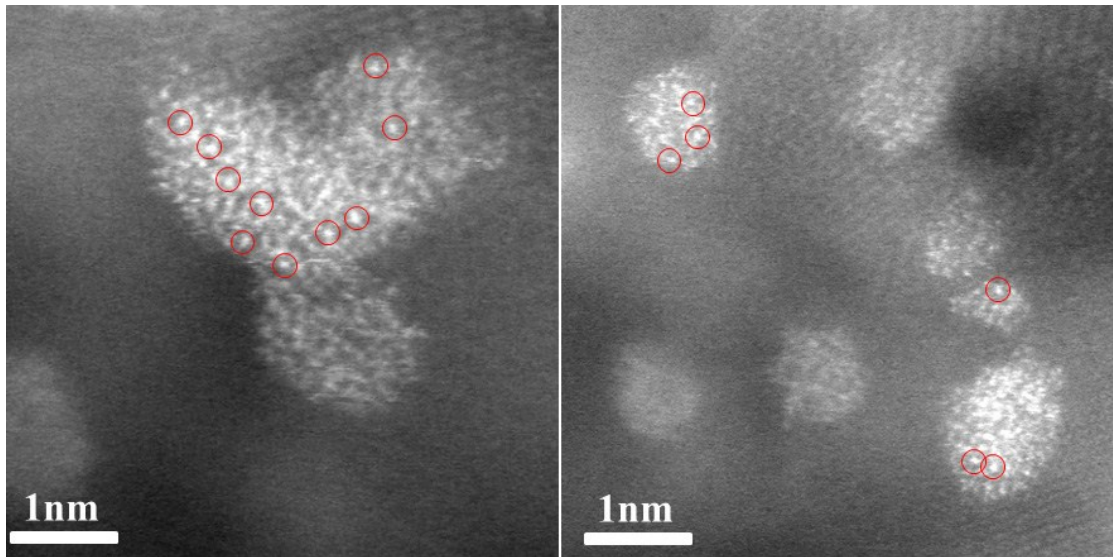
## 2. Supporting figures



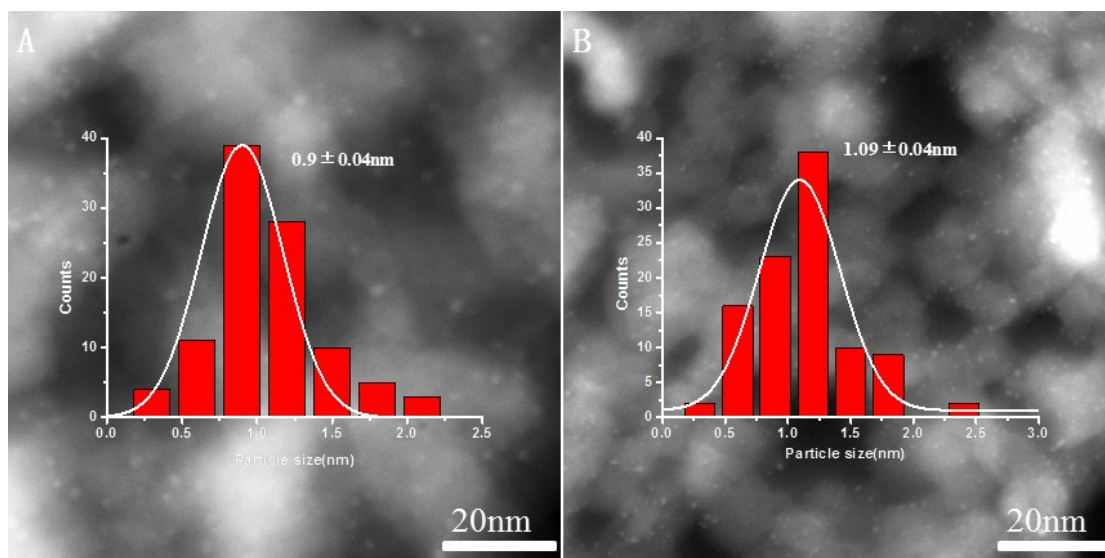
**Figure S1.** Preparation process for Pt/TiO<sub>2</sub> SACs by topological transformation and calcination. (A) NH<sub>4</sub>TiOF<sub>3</sub> mesocrystals mixing with H<sub>2</sub>PtCl<sub>6</sub> solution, (B) keeping away from light, (C) reacting with H<sub>3</sub>BO<sub>3</sub>, (D) washing, drying and grinding, (E) calcinating in N<sub>2</sub> at 450 °C for 4 h.



**Figure S2.** TEM images of 1% Pt/TiO<sub>2</sub>-TC catalysts.



**Figure S3.** High-resolution HAADF-STEM images of 1% Pt/TiO<sub>2</sub>-TC catalysts.



**Figure S4.** HAADF-STEM images and size distribution of (A) 1% Pt/TiO<sub>2</sub> and (B) 3% Pt/TiO<sub>2</sub> catalysts.

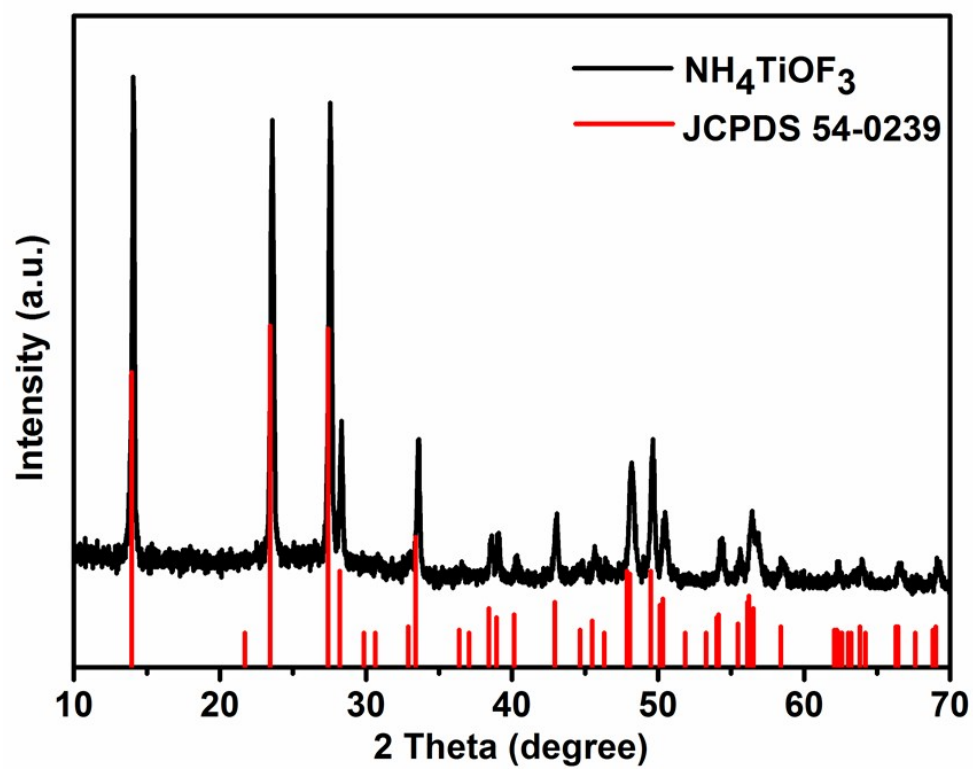


Figure S5. XRD pattern of  $\text{NH}_4\text{TiOF}_3$  mesocrystals.



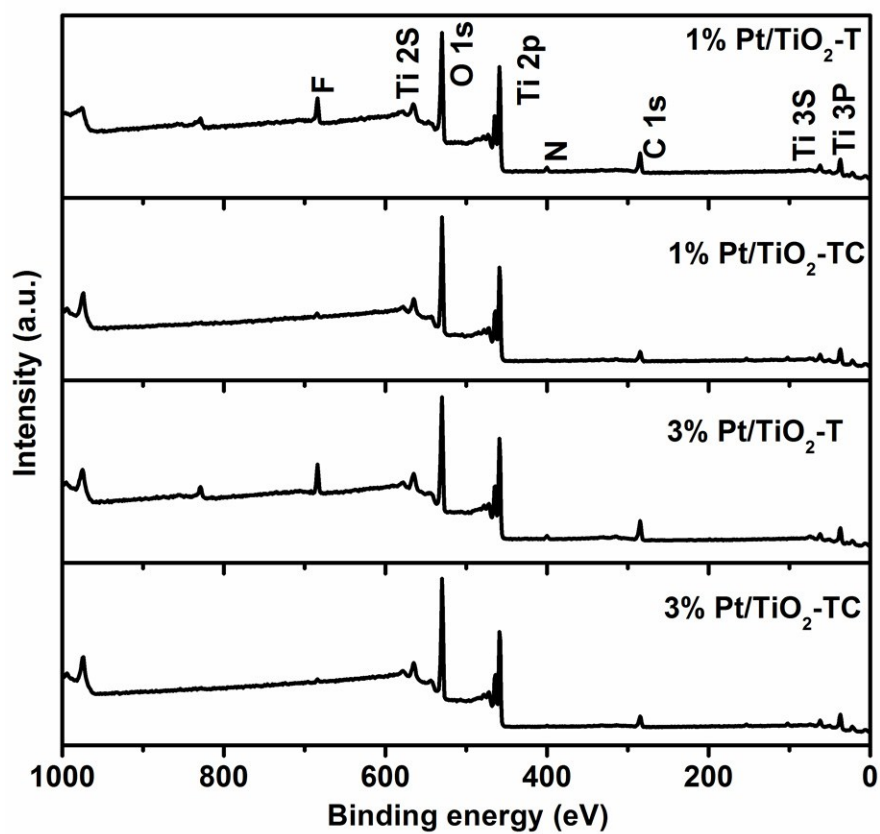
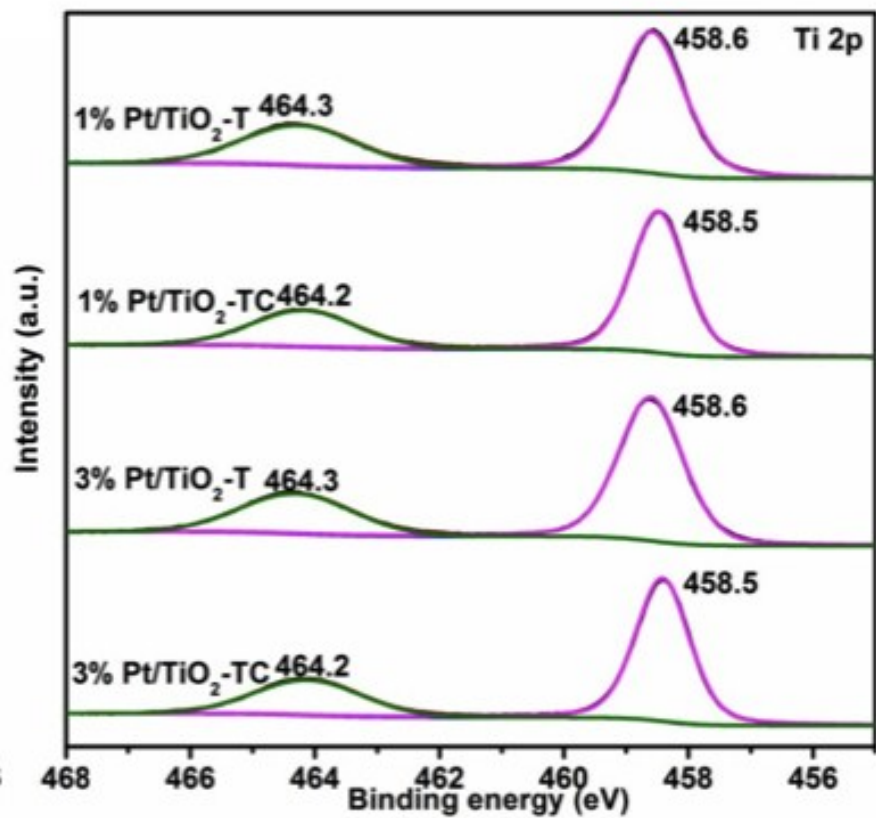
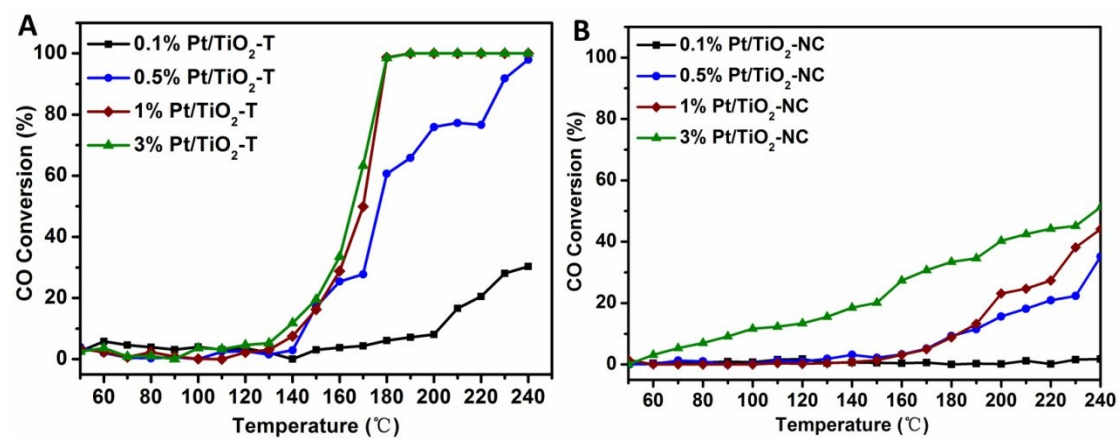


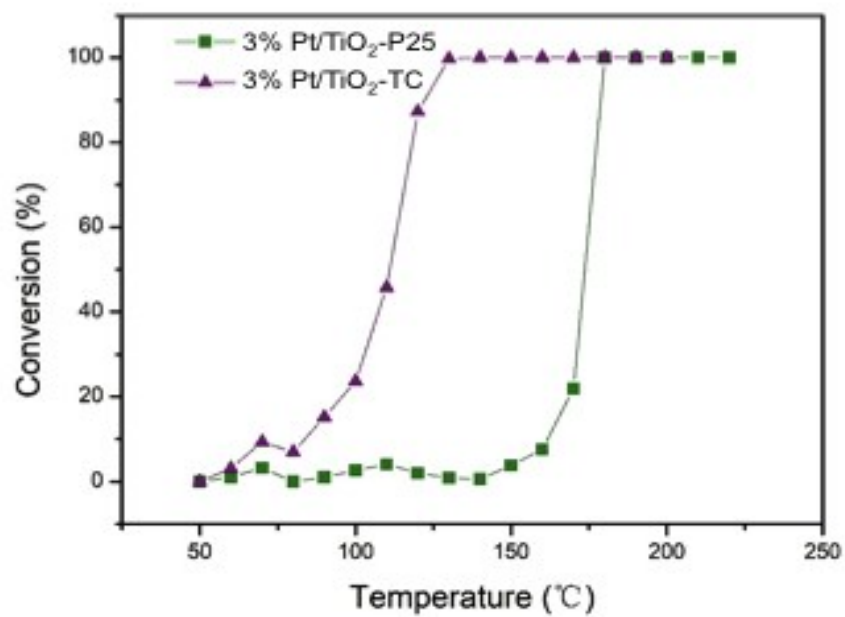
Figure S6. XPS full spectra of Pt/TiO<sub>2</sub>-T and Pt/TiO<sub>2</sub>-TC catalysts.



**Figure S7.** Ti 2p XPS spectra of Pt/TiO<sub>2</sub>-T and Pt/TiO<sub>2</sub>-TC catalysts with and without calcination treatment.



**Figure S8.** Catalytic performance on CO oxidation reaction for (A) Pt/TiO<sub>2</sub>-T and (B) Pt/TiO<sub>2</sub>-NC.



**Figure S9.** Catalytic performance on CO oxidation reaction for 3% Pt/TiO<sub>2</sub>-TC and 3% Pt/TiO<sub>2</sub>-P25.

**Table S1.** Loading content of Pt on the Pt/TiO<sub>2</sub> SACs by EDS and XPS analysis.

catalyst	EDS (Atomic %)	XPS (Atomic %)
1% Pt/TiO <sub>2</sub> -TC	0.1	0.3
3% Pt/ TiO <sub>2</sub> -TC	0.22	0.47

**Table S2.** The reaction temperature of CO oxidation for various Pt/TiO<sub>2</sub> SACs.

catalyst	onset	T <sub>50</sub>	T <sub>100</sub>
0.1% Pt/TiO <sub>2</sub> -TC	90 °C	163 °C	180 °C
0.5% Pt/TiO <sub>2</sub> -TC	60 °C	120 °C	130 °C
1% Pt/TiO <sub>2</sub> -TC	50 °C	108 °C	130 °C
3% Pt/TiO <sub>2</sub> -TC	60 °C	113 °C	160 °C
0.1% Pt/TiO <sub>2</sub> -T	140 °C	> 240 °C	-
0.5% Pt/TiO <sub>2</sub> -T	100 °C	177 °C	>240 °C
1% Pt/TiO <sub>2</sub> -T	100 °C	170 °C	190 °C
3% Pt/TiO <sub>2</sub> -T	70 °C	165 °C	190 °C
0.1% Pt/TiO <sub>2</sub> -NC	-	-	-
0.5% Pt/TiO <sub>2</sub> -NC	120 °C	> 240 °C	-
1% Pt/TiO <sub>2</sub> -NC	130 °C	> 240 °C	-
3% Pt/TiO <sub>2</sub> -NC	50 °C	238 °C	-
3% Pt/TiO <sub>2</sub> -P25	80 °C	168 °C	180 °C

**Table S3.** The reaction temperature of CO oxidation for various SACs.

catalyst	onset	T <sub>50</sub>	T <sub>100</sub>	note
1% Pt/TiO <sub>2</sub> -TC	50 °C	108 °C	130 °C	this work
1% Pt/La-Al <sub>2</sub> O <sub>3</sub>	150 °C	247 °C	261 °C	ref 16
1% Pt/θ-Al <sub>2</sub> O <sub>3</sub>	176 °C	> 230 °C	-	ref 10a
0.5% Pd/La-Al <sub>2</sub> O <sub>3</sub>	25 °C	109 °C	175 °C	ref 10b