

## Supplementary Information for “Ultrathin Titania Coating for High-Temperature Stable SiO<sub>2</sub>/Pt Nanocatalyst”

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### Synthesis of Hybrid Nanoparticles

The silica supported Pt nanoparticles were synthesized using the method reported by Zhang et al.<sup>1-3</sup>. Silica nanospheres were synthesized using a modified Stöber method. Typically, 5 mL of tetraethyl orthosilicate (TEOS, Aldrich) was mixed with 100 mL of anhydrous ethanol solution containing aqueous ammonia (1.55 mL, 28% v/v) and millipore water (4 mL) in a 250 mL round bottom flask. The reaction mixture was stirred magnetically for 24 h at room temperature. The silica colloids were collected by centrifugation and washed with ethanol, and dispersed in isopropanol (20 mL), to which APTES (50 μL, Aldrich) was added by ultra-sonication (5 min). The resultant mixture was heated at 80°C for 2 h to form amine-functionalized silica (f-SiO<sub>2</sub>). The f-SiO<sub>2</sub> was centrifuged and washed with ethanol, and finally dispersed in ethanol (3 mL). In a separate reaction, Pt nanoparticles were synthesized by injecting sodium citrate (5 mL, 38.8 mM) into a boiling H<sub>2</sub>PtCl<sub>6</sub> solution (50 mL, 1 mM, Kojima Chemical Co., Korea) under reflux. The reaction mixture was further refluxed for 2 h. Citrate capped Pt nanoparticles thus formed were immobilized on f-SiO<sub>2</sub> by adding excess citrate-stabilized Pt colloids (10 mL) to the f-SiO<sub>2</sub> in ethanol (1.5 mL) under sonication for 30 min. The resultant SiO<sub>2</sub>/Pt hybrid colloids were centrifuged and washed three times with ethanol to separate unbound Pt nanoparticles. Finally, these colloids were dispersed in ethanol (3 mL) under sonication for further analysis and titania coating.

Titania coating of the SiO<sub>2</sub>/Pt hybrid nanoparticles was performed by hydrolyzing titanium-butoxide (TBT, Ti-(OBu)<sub>4</sub>, 97 %, Kanto Chemical Co., Korea) in anhydrous ethanol<sup>2</sup>. In a typical synthesis, 1.5 mL of SiO<sub>2</sub>/Pt (from the above stock) solution was added to the titania sol (10 mL, volume ratio TBT/EtOH, 1/9) and subjected to ultrasonic treatment (30 min) followed by incubation for 16 h at room temperature. The mixture was centrifuged to remove excess titania sol then washed with ethanol. The separated hybrid colloids were condensed with ethanol:water (1:1) under magnetic stirring for 2 h. The titania coating process was repeated two times. Finally, the hybrid colloids were dispersed in ethanol for further characterization and catalytic measurements.

### Characterization

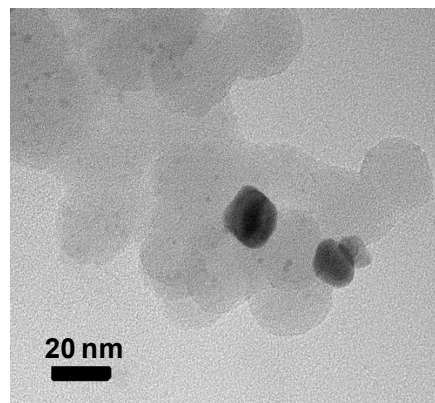
The particle size and shape of the hybrid catalysts were determined using TEM (FE-TEM, Tecnai F20, 200KV). High-resolution TEM images and EDS line mapping were taken (JEM-ARM200F). The morphologies of the 2D array of hybrid nanoparticles on a silicon wafer made by the LB technique were characterized by scanning electron microscopy (SEM, JSM-7600F). X-ray photoelectron spectroscopy (Sigma Probe, Thermo VG Scientific) was used to determine the elemental composition and oxidation state of the constituent species in the hybrid catalyst.

### Catalytic Activity Measurements

The CO oxidation reaction was performed in an ultrahigh-vacuum batch reactor (1L) with a base pressure of 5.0 x 10<sup>-8</sup> torr. The thin film of hybrid nanoparticles deposited on a Si wafer (0.7x1.1 cm<sup>2</sup>) by the LB technique was mounted in the reaction chamber. The catalyst was calcinated at 300°C for 2 h, followed by reduction using diluted H<sub>2</sub> at 250°C for 1 h. The reaction chamber was evacuated and isolated with a gate valve before it was charged with 40 torr CO, 100 torr O<sub>2</sub> and 620 torr He at room temperature. The reaction mixture was circulated continuously through the reaction line by a metal-bellows recirculation pump at a rate of 2 L min<sup>-1</sup>. The CO conversion was monitored as a function of reaction temperature (200 to 340°C). After equilibrating for 20 min, the reaction mixture was continuously analyzed through an online gas chromatograph (GC). The reaction mixture was separated for analysis using a DS 6200 gas chromatograph equipped with a thermal conductivity detector and a 15' long stainless steel 60/80 mesh size carboxen-1000 (Supelco) column. CO conversion was reported in terms of TOFs and was calculated based on the product molecules of CO<sub>2</sub> produced per metal surface site per second of reaction time. The number of active metal sites was determined by the geometry seen in SEM images of the hybrid catalyst LB film used for the reaction study.

### Effect of thermal treatment of Pt/SiO<sub>2</sub> without titania coating

Fig. S1 shows that sintering of Pt nanoparticles occurred upon calcination of Pt/SiO<sub>2</sub>, after heating at 600°C. Hence, the role of titania coating on Pt/SiO<sub>2</sub> is significant to provide thermal stability. The thickness of titania can be tuned



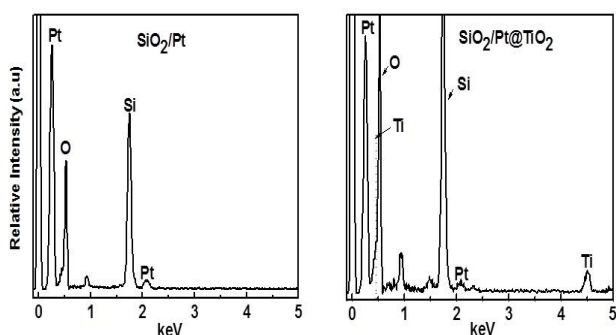
**Figure S1** TEM images of SiO<sub>2</sub>/Pt after heating at 600 °C in air for 2 h.

by repeating the titania coating cycles, depending on the size of

metal nanoparticles, during the synthesis of the hybrid catalyst. Likewise, the amount of Pt on SiO<sub>2</sub> can also be controlled by varying the concentration of the Pt colloid solution, as reported elsewhere<sup>3</sup>.

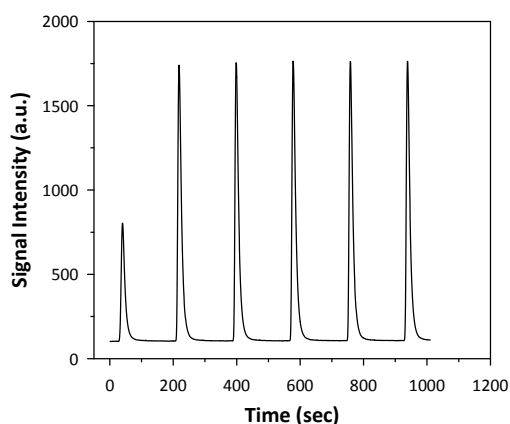
### Energy Dispersive Spectroscopy (EDS) of SiO<sub>2</sub>/Pt and SiO<sub>2</sub>/Pt@TiO<sub>2</sub>

Figure S2(a) shows EDS data for the elemental composition of SiO<sub>2</sub>/Pt, indicating predominant peaks of Si, Pt and O. Obviously, the Pt peaks can be attributed to the Pt nanoparticles on the silica spheres. Figure S2(b) shows EDS data of titania-coated SiO<sub>2</sub>/Pt nanoparticles. Peaks corresponding to Ti in addition to Si, Pt and O are present. The presence of Ti peaks can be ascribed to the formation of a titania layer.



**Figure S2** EDS spectra of as synthesized SiO<sub>2</sub>/Pt and SiO<sub>2</sub>/Pt@TiO<sub>2</sub> hybrid nanoparticles.

### CO-pulse chemisorption on SiO<sub>2</sub>/Pt@TiO<sub>2</sub>

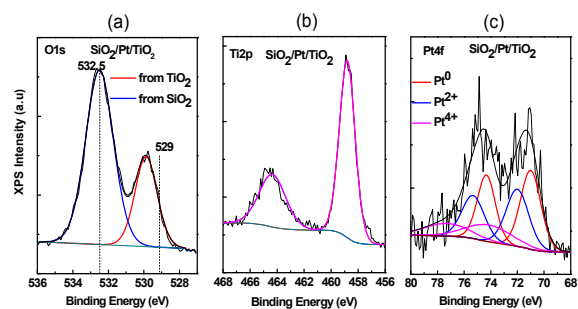


**Figure S3** CO-pulse chemisorption on SiO<sub>2</sub>/Pt@TiO<sub>2</sub> performed at 323 K. He flow is 50 ml min<sup>-1</sup>; pulse is 1 ml (10% CO in He). The sample was reduced for 1 h at 300°C prior to the experiment under hydrogen flow for 30 min and flushed by He at 300°C for 20 min. In order to calculate the metal dispersion, an adsorption stoichiometry of CO/Pt = 1 was assumed. (Pt dispersion is 52.6%)

The CO chemisorption results on SiO<sub>2</sub>/Pt@TiO<sub>2</sub> show that Pt nanoparticles are exposed to the surface and not covered by the titania layer. However, presence of porous titania cannot be ruled out as some of the Pt nanoparticles smaller than the thickness of titania could be buried.

### X-ray photoelectron spectroscopy of SiO<sub>2</sub>/Pt/TiO<sub>2</sub> particles

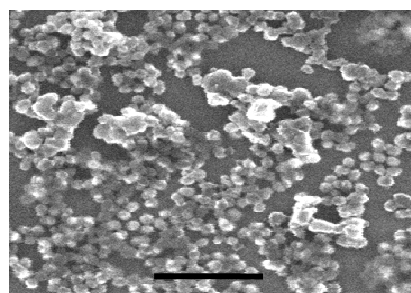
Figure S4 shows XPS data of the SiO<sub>2</sub>/Pt@TiO<sub>2</sub> hybrid nanoparticles. Two peaks for O1s, at binding energies of 532.5 and 529 eV for SiO<sub>2</sub>/Pt@TiO<sub>2</sub> can be ascribed to SiO<sub>2</sub> and TiO<sub>2</sub>, respectively. The Pt peak exhibits the moderate oxidation state (Pt<sup>2+/4+</sup>).



**Figure S4** XPS results of as synthesized SiO<sub>2</sub>/Pt/TiO<sub>2</sub>. For (a) O1s, (b) Ti2p, and (c) Pt4f of SiO<sub>2</sub>/Pt/TiO<sub>2</sub> hybrid catalyst.

### Scanning Electron Microscopy image of 2D SiO<sub>2</sub>/Pt@TiO<sub>2</sub> nanoparticles

The morphology and chemical composition of a two-dimensional LB film of hybrid nanoparticles were investigated using SEM and XPS, respectively. The SEM image of the hybrid catalyst deposited on a Si wafer (Figure S1) revealed that a majority of the nanoparticles formed into a monolayer with a few bare or multilayered patches. For TOF calculations, we assumed one uniform monolayer, considering the bare and multilayered patches to be equivalent.



**Figure S5** SEM image of as synthesized SiO<sub>2</sub>/Pt/TiO<sub>2</sub> nanoparticles deposited on a Si wafer using the LB technique at a surface pressure of 15 mN m<sup>-2</sup>. Scale bar shown represents 200 nm.

### References

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2. M. E. Grass, Y. Zhang, D. R. Butcher, J. Y. Park, Y. Li, H. Bluhm, K.M. Bratlie, T. Zhang, G. A. Somorjai, *Angew. Chem. Int. Ed.* **2008**, *47*, 8893–8896
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