## Supporting Information

## Surface States Modulation for Size-Controllable Photodeposition of Noble Metal Nanoparticles on Semiconductors

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Sample	Designed loading amount	Loading amount	
	(wt.%)	estimated by ICP (wt.%)	
Ag/TiO <sub>2</sub> (A)-9	2.5	2.50	
Ag/TiO <sub>2</sub> (A)-2	2.5	2.49	
<b>Pt/TiO<sub>2</sub>(A)-6</b>	2.5	2.48	
Au/TiO <sub>2</sub> (A)-6	2.5	2.47	
Pd/TiO <sub>2</sub> (A)-6	2.5	2.47	

Table S1. The designed and ICP estimated loading amount

Sample	TiO <sub>2</sub>	Metal precursor	pH values	Size distribution
1	Anatase	AgNO <sub>3</sub>	2.0	4.2-72 nm
2	Anatase	AgNO <sub>3</sub>	4.5	10.3-39.6 nm
3	Anatase	AgNO <sub>3</sub>	9.0	0.6-2.3 nm, 2.9-16.9 nm
4	Rutile	AgNO <sub>3</sub>	2.0	7.9-128 nm
5	Rutile	AgNO <sub>3</sub>	6.0	0.7-2.3nm, 8-30.8 nm
6	Rutile	AgNO <sub>3</sub>	9.0	0.71-37.6 nm
7	Anatase	H <sub>2</sub> PtCl <sub>6</sub>	2.0	1.3-20.2 nm
8	Anatase	H <sub>2</sub> PtCl <sub>6</sub>	4.5	1.7-4 nm
9	Anatase	H <sub>2</sub> PtCl <sub>6</sub>	9.0	1.1-13 nm
10	Rutile	H <sub>2</sub> PtCl <sub>6</sub>	6.0	1.3-6 nm
11	Anatase	HAuCl <sub>4</sub>	4.5	2.4-34.4 nm
12	Rutile	HAuCl <sub>4</sub>	6.0	5.3-44.2 nm
13	Anatase	PdCl <sub>2</sub>	4.5	3-20.2 nm
14	Rutile	PdCl <sub>2</sub>	6.0	0.3-1.7nm, 2.3-9.4 nm

 Table S2 A summary of size distribution of different metal nanoparticles based on

 the size statistics results.

Samples	Surface charge	<b>Metal Precursors</b>	Size distribution
Ag/TiO <sub>2</sub> (R)-2.0	44.6	AgNO <sub>3</sub>	7.9-128 nm
Ag/TiO <sub>2</sub> (R)-6.0	-22	AgNO <sub>3</sub>	0.7-2.3 nm,
			8-30.8 nm
Ag/TiO <sub>2</sub> (R)-9.0	-38	AgNO <sub>3</sub>	0.71-37.61 nm
Pt/ TiO <sub>2</sub> (R)-6.0	-22	$H_2PtCl_6$	1.3-6 nm
Au/ TiO <sub>2</sub> (R)-6.0	-22	HAuCl <sub>4</sub>	5.3-44.2 nm
Pd/ TiO <sub>2</sub> (R)-6.0	-22	PdCl <sub>2</sub>	0.3-1.7nm,
			2.3-9.4 nm
Ag/TiO <sub>2</sub> (A)-4.5	4.5	AgNO <sub>3</sub>	10.3-39.6 nm
Pt/ TiO <sub>2</sub> (A)-4.5	4.5	H <sub>2</sub> PtCl <sub>6</sub>	1.7-4 nm
Au/ TiO <sub>2</sub> (A)-4.5	4.5	HAuCl <sub>4</sub>	2.4-34.4 nm
Pd/ TiO <sub>2</sub> (A)-4.5	4.5	PdCl <sub>2</sub>	3-20.2 nm

Table S3 A summary of size distribution of different metal nanoparticles obtained with different surface charge and metal precursors.



**Figure S1.** The XRD patterns (a) and UV-vis spectra (b) of anatase, rutile and P25. The inset in (b) is the amplified UV-vis spectra.



**Figure S2**. XRD patterns of different samples: (a)  $Ag/TiO_2(A)$  prepared at different pH and (b) different metals on  $TiO_2(A)$ -4.5.



Figure S3. TEM and HRTEM images of (a-b)  $Ag/TiO_2(R)-2$ , (c-d)  $Ag/TiO_2(R)-6$ , (e-f)  $Ag/TiO_2(R)-9$  and corresponding particle size distribution.



Figure S4. TEM images of  $TiO_2(A)$  impregnation in the AgNO<sub>3</sub> solution (pH=9) without irradiation.



**Figure S5.** HRTEM images of (a-b)  $Pd/TiO_2(R)$ -6.0, (c-d)  $Au/TiO_2(R)$ -6.0, (e-f)  $Pt/TiO_2(R)$ -6.0 and corresponding particle size distribution. The yellow circles and the arrows indicate the type I and type II nanoparticles, respectively.



Figure S6. The evolution of Ag concentration in the solution during photodeposition on  $TiO_2(A)$ -2.0 and  $TiO_2(A)$ -9.0.



**Figure S7.** TEM and HRTEM images of (a, b) Ag/TiO<sub>2</sub>(P25), (c, d) Ag/TiO<sub>2</sub>(anatase rod). The yellow cycles and the arrows are indicating the type I and type II Ag nanoparticles, respectively.



**Figure S8.** TEM images of Pt photodeposited on anatase TiO<sub>2</sub> at the pH of 2.0 (a, b) and 9.0 (c, d). (e-g) are the size distribution of Pt nanoparticles at the pH of 2.0, 4.5 and 9.0, respectively.



Figure S9. TEM image and size distribution of Pt on  $TiO_2$  for different samples: (a) and (d) for 0.5 wt.% Pt/TiO<sub>2</sub>(A)-6.0, (b) and (e) for 1.0 wt.% Pt/TiO<sub>2</sub>(A)-6.0, (c) and (f) for 2.5 wt.% Pt/TiO<sub>2</sub>(A)-6.0.



Figure S10. The influence of Pt loading amount for  $Pt/TiO_2(A)$  at pH 6.0 on HCHO conversion at room temperature.



**Figure S11** The longevity of 0.3wt.% Pt/TiO<sub>2</sub>(A)-9 for 90 h at a total gas flow rate of 250 mL min<sup>-1</sup> and the concentration of HCHO is 300 ppm.