Supporting Information

Facet-Dependent Evolutions of Sizes, Structures and Catalytic Activity of Au Nanoparticles on Anatase TiO_2 Nanocrystals

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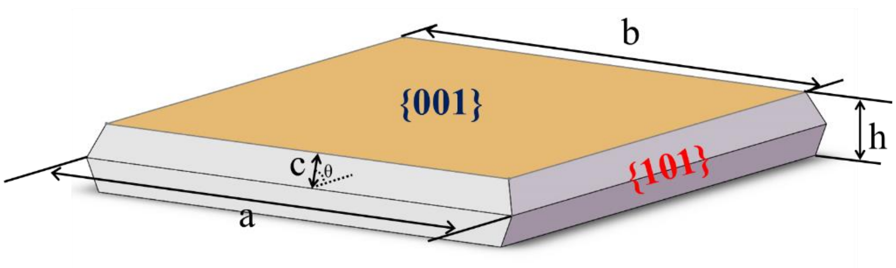
Calculation method of the percentages of different crystal planes in these TiO_2 nanocrystals:

Based on Wulff Construction, we can built the ideal crystal models, by the TEM images and results of previous reports we can get the geometrical parameters of different TiO_2 nanocrystals.[1-3]

(1) TiO_2 {001}

There are two kinds of crystal planets exposed in TiO_2 {001}: {001} and {101}. The figure below is the geometrical models of TiO_2 {001} nanocrystals.



a= 55 nm

b= 52 nm

h= 6 nm

θ = 68.3°

$$c = \frac{h}{2 \times \sin\theta}$$

$$S_{001} = 2 \times b^2$$

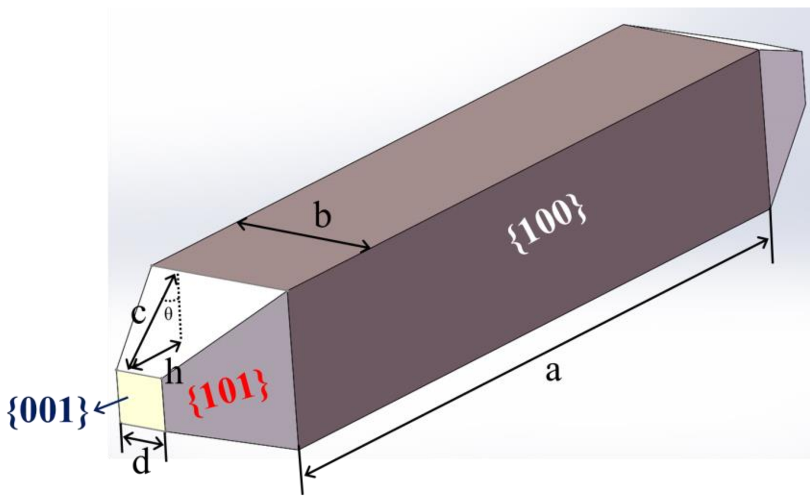
$$S_{101} = 8 \times \frac{1}{2}(a + b) \times c$$

$$P_{001} = \frac{S_{001}}{S_{001} + S_{101}} = 80\%$$

$$P_{101} = \frac{S_{101}}{S_{001} + S_{101}} = 20\%$$

(2) TiO_2{100}

There are three kinds of crystal planets exposed in TiO_2{100}: {100}, {001} and {101}. The figure below is the geometrical models of TiO_2{100} nanocrystals.



a= 50 nm

b= 14 nm

d= 4 nm

h= 11 nm

θ= 68.3°

$$c = \frac{h}{\sin\theta}$$

$$S_{001} = 2 \times d^2$$

$$S_{100} = 4 \times (a \times b)$$

$$S_{101} = 8 \times \frac{1}{2}(b + d) \times c$$

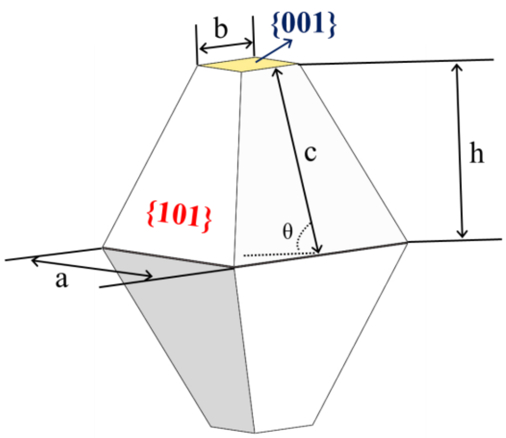
$$P_{001} = \frac{S_{001}}{S_{001} + S_{100} + S_{101}} = 1\%$$

$$P_{100} = \frac{S_{100}}{S_{001} + S_{100} + S_{101}} = 76\%$$

$$P_{101} = \frac{S_{101}}{S_{001} + S_{100} + S_{101}} = 23\%$$

(3) TiO_2\{101\}

There are two kinds of crystal planets exposed in TiO_2\{101\}: \{001\} and \{101\}. The figure below is the geometrical models of TiO_2\{101\} nanocrystals.



a= 13.5 nm

b= 3.5 nm

h= 12.5 nm

θ= 68.3°

$$c = \frac{h}{\sin\theta}$$

$$S_{001} = 2 \times b^2$$

$$S_{101} = 8 \times \frac{1}{2}(a + b) \times c$$

$$P_{001} = \frac{S_{001}}{S_{001} + S_{101}} = 2\%$$

$$P_{101} = \frac{S_{101}}{S_{001} + S_{101}} = 98\%$$

Table S1. Au particle-size distributions, Au content and the apparent activation energies (E_a) of various Au/TiO_2 catalysts.

Catalysts	Size＜2nm	Size:2-5nm	Size＞5nm	Au content (wt. %)	E_a (kJ/mol)
0.2%- Au/TiO_2{001}	34%	54%	12%	0.19	28.4±1.6
0.5%- Au/TiO_2{001}	40%	47%	13%	0.48	29.0±3.1
1%- Au/TiO_2{001}	40%	45%	15%	0.99	28.1±3.9
2%-Au/ TiO_2{001}	38%	22%	40%	1.96	30.6±3.3
5%-Au/ TiO_2{001}	4%	41%	55%	5.10	29.9±1.7
0.2%- Au/TiO_2{100}	34%	66%	0	0.21	44.6±4.6
0.5%- Au/TiO_2{100}	33%	67%	0	0.50	47.1±2.5
1%-Au/ TiO_2{100}	32%	68%	0	0.90	47.8±3.9
2%-Au/ TiO_2{100}	44%	56%	0	1.80	43.2±2.9
5%-Au/ TiO_2{100}	36%	64%	0	4.73	44.4±4.6
0.2%- Au/TiO_2{101}	55%	45%	0	0.21	45.1±2.6
0.5%- Au/TiO_2{101}	58%	42%	0	0.51	48.0±3.0
1%-Au/ TiO_2{101}	62%	38%	0	0.92	48.2±4.2
2%-Au/ TiO_2{101}	36%	64%	0	1.84	47.0±3.5
5%-Au/ TiO_2{101}	35%	60%	5%	4.6	38.0±0.6

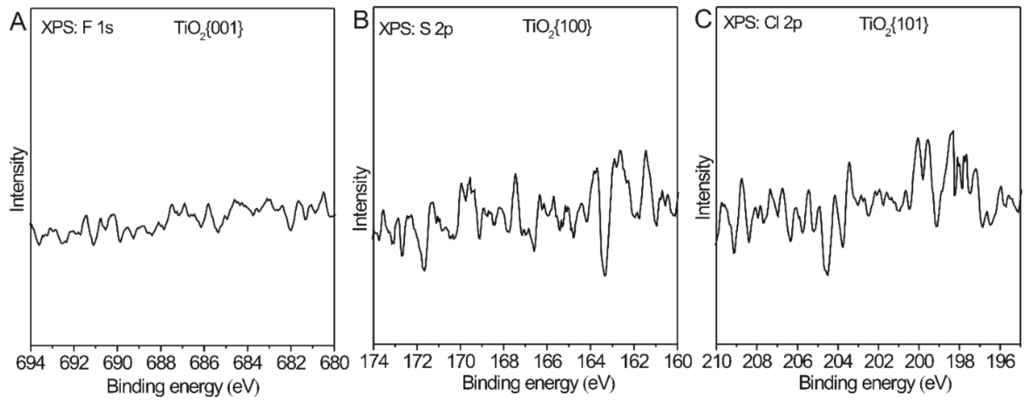


Figure S1. F 1s, S 2p and Cl 2p XPS spectra of (A) TiO_2\{001\}; (B) TiO_2\{100\}; (C) TiO_2\{101\}.

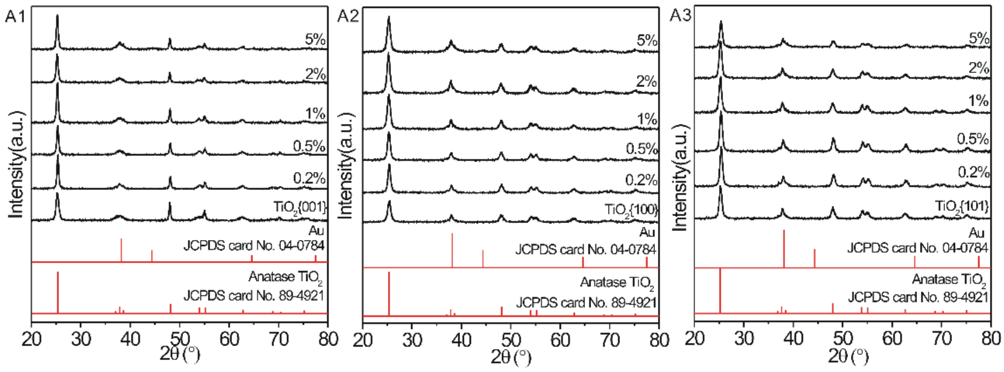


Figure S2. XRD patterns of various Au/TiO_2 and TiO_2 catalysts.

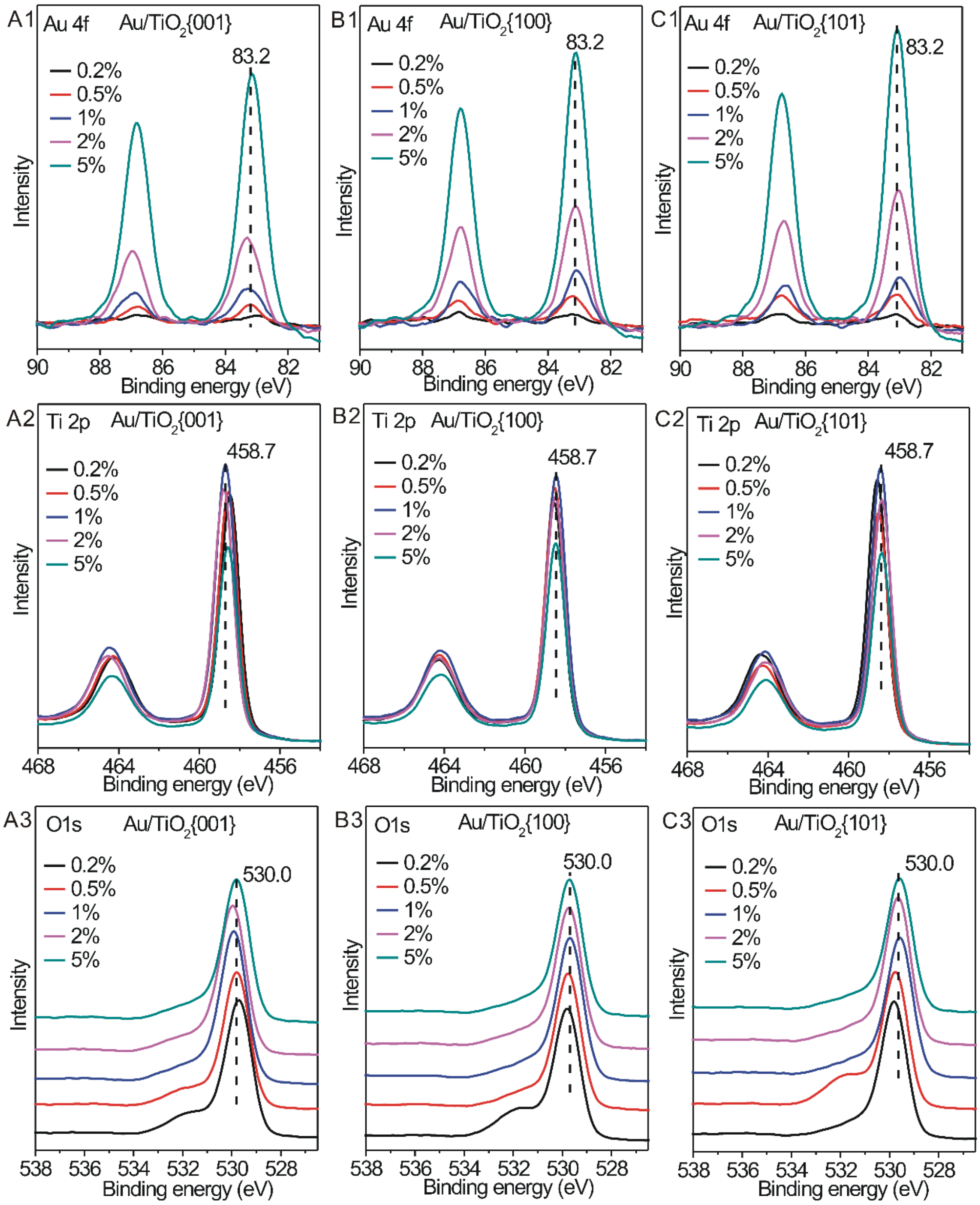


Figure S3. Au 4f, Ti 2p and O 1s XPS spectra of various Au/TiO_2 catalysts: (A) Au/TiO_2{001}; (B) Au/TiO_2{100}; (C) Au/TiO_2{101}.

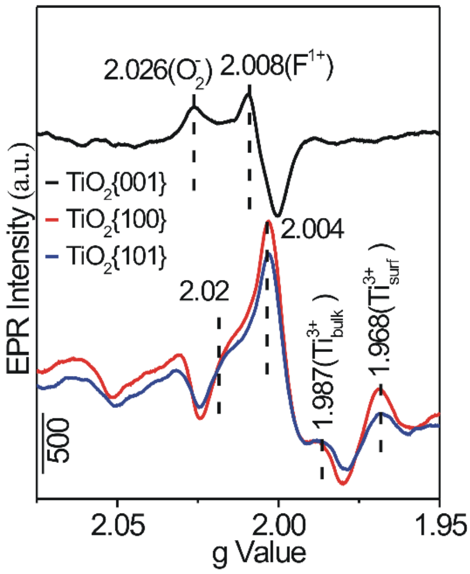


Figure S4. EPR spectra of TiO_2{001}, TiO_2{100} and TiO_2{101}.

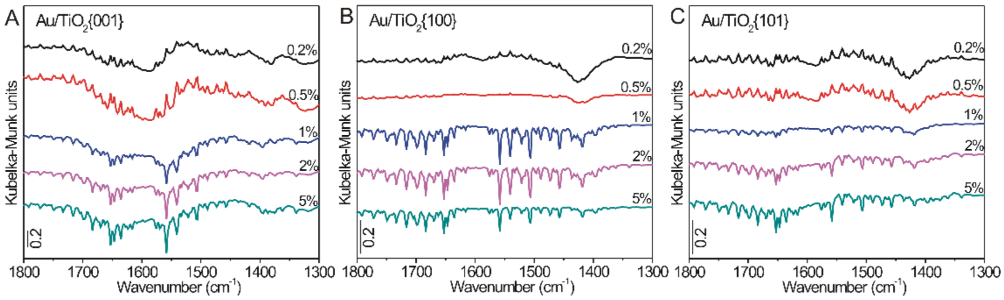


Figure S5. The DFIFTS spectra of as-synthesized Au/TiO$_2$ catalysts.

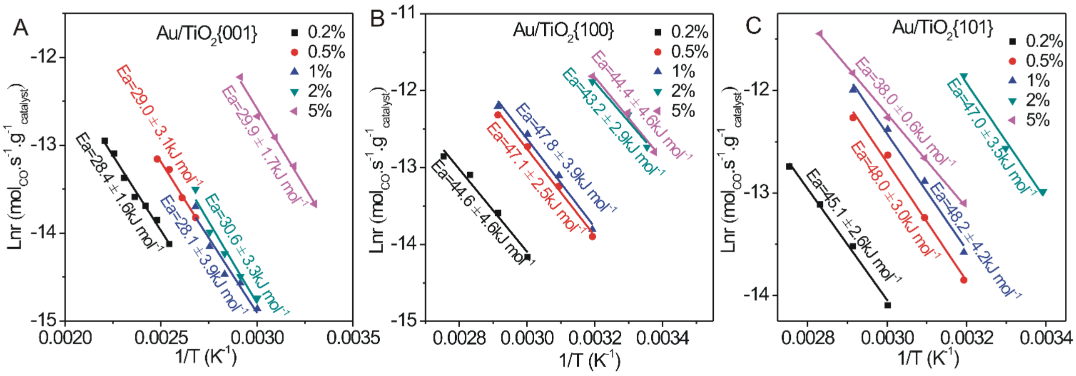


Figure S6. The Arrhenius plots of various Au/TiO_2 catalysts.

References

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(2) Barnard, A.; Curtiss, L. Prediction of TiO_2 Nanoparticle Phase and Shape Transitions Controlled by Surface Chemistry. *Nano lett.* **2005**, *5*, 1261-1266.

(3) Liu, L.; Gu, X.; Cao, Y.; Yao, X.; Zhang, L.; Tang, C.; Gao, F.; Dong, L. Crystal-Plane Effects on the Catalytic Properties of Au/TiO_2. *ACS Catal.* **2013**, *3*, 2768-2775.