Supporting Information

Mechanism of photocatalytic activity improvement of AgNPs/TiO_2 by oxygen plasma irradiation

Yingcui Fang[a]*, Bing Zhang[a], Liu Hong[a], Kang Zhang[a], Gongpu Li[b], Jun Jiang[b*], Rong Yan[c], Junling Chen[c]*

[a] Department of Vacuum Science and Technology, Hefei University of Technology, Hefei, 230009.

[b] Hefei National Laboratory for Physical Sciences at the Microscale, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), and School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, 230026, China.

[c] Institute of Plasma Physics, Chinese Academy of Sciences, Hefei, 230031, China.

1. The sketch of photocatalysis setup.

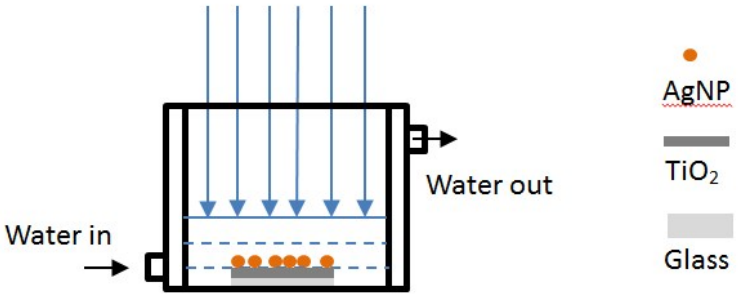

Figure S1 The sketch of photocatalysis setup.

2. Photocatalytic efficiency (k_t) under UV and visible lights of samples 10sAgNPs/TiO_2, 30sAgNPs/TiO_2, 60sAgNPs/TiO_2 without OPI (k_0) and with OPI for 2 s (k_2), and the corresponding PAIs (η).

Table S1

	UV light			Visible light		
Samples	k_0	k_2	η	k_0	k_2	η
10sAgNPs/TiO2	0.021	0.03	43%	0.03	0.035	17%
30sAgNPs/TiO2	0.024	0.041	71%	0.047	0.059	26%
60sAgNPs/TiO2	0.016	0.023	44%	0.035	0.042	20%

3. Photocatalytic efficiencies (k_t) under UV and visible lights of sample 30sAgNPs/TiO_2 (t=0), and the ones with OPI for 2, 5 and 10 s, and the corresponding PAIs (η)

Table S2

	UV light		Visible light	
t (s)	k_t	η	k_t	η
0	0.024		0.047	

2	0.041	71%	0.059	26%
5	0.052	117%	0.074	57%
10	0.036	52%	0.063	34%

4. Histograms of 10sAgNPs(a), 30sAgNPs(b), 60sAgNPs(c), 30sAgNPs-OPI-2s (d)，and 30sAgNPs-OPI-5s (e).

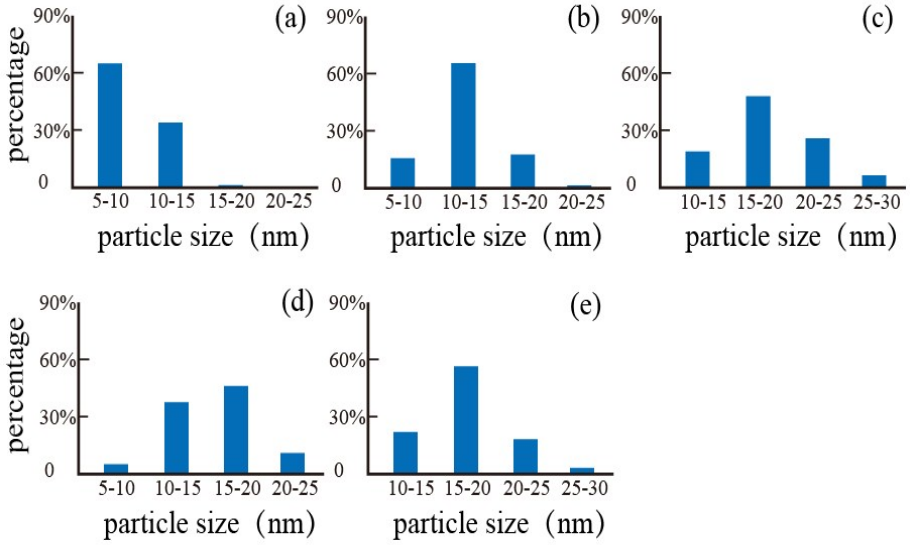

Figure S2　The histograms of 10sAgNPs(a), 30sAgNPs(b), 60sAgNPs(c), 30sAgNPs-OPI-2s (d)，and 30sAgNPs-OPI-5s (e).

5. Percentage (%) of metallic silver (368.2 eV) and oxidized silver (367.8 eV) of samples 30sAgNPs-OPI-2s，30sAgNPs-OPI-5s and 30sAgNPs-OPI-10s calculated by the component's peak area of the XPS spectra of Ag $3d_{5/2}$.

Table S3

Peak BE (eV)	367.8	368.2
OPI-2s	27.8	72.2
OPI-5s	34.2	65.8
OPI-10s	57.4	42.6

6. **Determine the substance according to TEM images**

According to PDF-2004, we attribute the left part of figure 4 in the manuscript as hexagonal crystal system silver, the crystal face with an inter-planar spacing between 0.243-0.244 is Ag (004), between 0.207-0.211 is Ag (1-12), and with d=0.196 is Ag (103). Then we calculate the angles between two neighboring faces and compare them with the corresponding measured angles.

The angle is calculated by the following formulae (for hexagonal crystal system)

$$\cos\emptyset = \frac{h_1h_2 + k_1k_2 + \frac{1}{2}(h_1k_2 + h_2k_1) + \frac{3a^2}{4c^2}l_1l_2}{\sqrt{(h_1^2 + k_1^2 + h_1k_1 + \frac{3a^2}{4c^2}l_1^2)(h_2^2 + k_2^2 + h_2k_2 + \frac{3a^2}{4c^2}l_2^2)}}$$

Here, a=b=0.28862, c=1;

For the Ag (004) and Ag(1-12), h_1=0, k_1=0, l_1=4, h_2=1, k_2=-1, l_2=2, the calculated angle is 63.4° and the measured one is 68°. The angles between two other faces are calculated in the same way and the results are listed in Table S4. The errors are smaller than 7% thus the results are acceptable.

Table S4 Comparison of the calculated and measured angles between two faces

Faces	Calculated	Measured	Error
Ag(004) and Ag(1-12)	63.4°	68°	7%
Ag(1-12) and Ag(103)	51.24°	51°	0%
Ag(004) and Ag(103)	53.15°	57°	7%

It is difficult to determine the component of the right part of figure 4, since only one dimension inter-planar spacing can be measured. We suppose that another inter-planar spacing is 0.244, which is same as the left part, and at the same time suppose that the right part is Ag, Ag_2O and AgO, respectively, and try to calculate the angles and compare them with the measured ones. It is found that Ag_2O fits best. We thus attribute the right part to Ag_2O.

7. The XPS spectra of O1s lines and their fittings of AgNPs/TiO_2 after OPI for 2, 5 and 10 seconds.

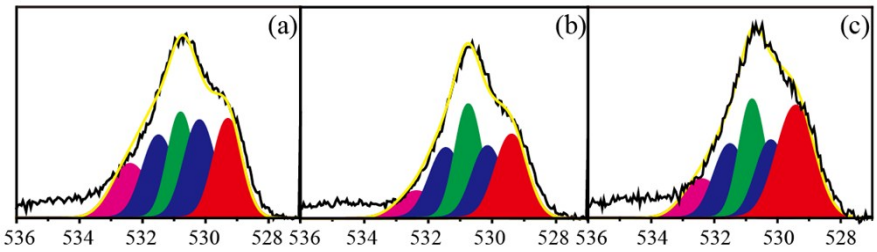

Figure S3 The O1s lines and their fittings of 30sAgNPs/TiO_2 after OPI for 2s (a), 5s (b) and 10s (c).

Table S5 The content and the FWHM of each component with binding energies at 529.4, 530.2, 530.8, 531.5 and 532.4 eV of the sample 30sAgNPs/TiO_2, after OPI for 2, 5 and 10 seconds.

Table S5

	529.4 eV		530.2 eV		530.8 eV		531.5 eV		532.4 eV	
	%	FWHM eV	%	FWHM eV	%	FWHM eV	%	FWHM eV	%	FWHM eV
OPI-2s	21.5	0.9	22.4	0.8	20.4	0.8	20	1	15.7	1.2
OPI-5s	24.2	1	19.8	0.95	26.4	0.8	20.4	1	9.3	1.2

OPI-10s	31.8	1.2	17.4	0.95	22.4	0.8	17.4	1	11	1.2	

8. The energy levels sketch describing the Schottky barrier Δ (a), and the transferring of the excited electrons (b). The electrons are excited from the VB of TiO_2 to its CB, among which energetic electrons will jump to AgNPs, due to its energy larger than the Schottky barrier; while those with energy smaller than the Schottky barrier stay in the CB of TiO_2. Holes transfer to AgNPs no matter the energy of the electrons is low or high; however, the migration speed depends on the interface and the Schottky barrier.

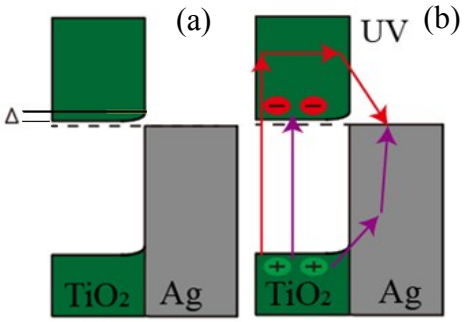

Figure S4 The sketch of energy levels describing the Schottky barrier Δ (a), and the transferring of the excited electrons (b).

9. The spectrum of Xe lamp

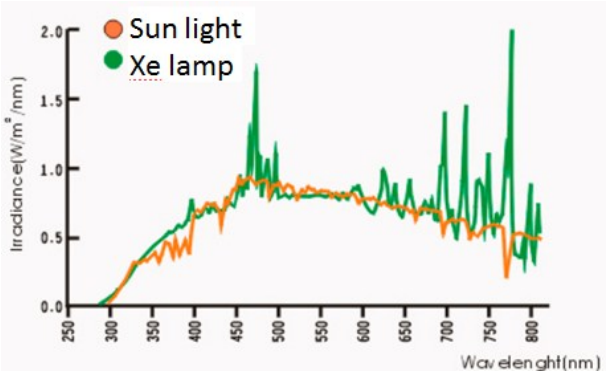

Figure S5 The absorption spectra of Xe lamp and sun light.

10. Photodegradation of AgNPs/TiO_2

Rhodamine 6 G (R6G) with concentration of 10^{-5} mol/l was chosen to be degraded under UV light and visible lights, respectively. The light source is a PL-X500D Xenon lamp with power of 300W. The lamp is set at a distance about 135 mm above the solution and illuminates the solution evenly from the top for 1hrs. The photocatalytic efficiency of AgNPs/TiO_2 can be expressed as k_t=-ln (C_t/C), where C is the initial concentration of R6G before degradation, and C_t is the final concentration after 1 hrs degradation under UV or visible light, where t is the deposition time of Ag. The results are shown in figure S6. With the increasing of silver content, the degradation efficiency increases at first and then decreases.

The photocatalytic activity improvement (PAI) can be calculated with the formulae $\eta=(k_t-k_0)/k_0$, k_0 refers to t=0s (without Ag deposition), and the results are shown in Table S6. Under UV light, after 10 s deposition of silver, the improvement is about 24%, and it increases to 41% when Ag content reaches 30s, however, it decreases to -6% when the content of Ag increases to 60s. Under visible light, After 10 s deposition of silver, the improvement is 67%, and it increases to 161 % when the content of AgNPs reaches 30 s, while it decreases to 94% when the content of Ag increases to 60s.

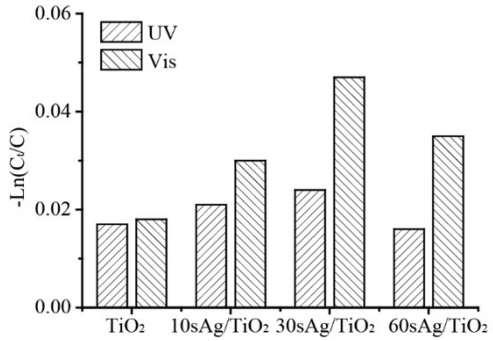

Figure S6 Photocatalytic efficiency (k_t) under UV light and visible lights of samples TiO_2,

10sAg/TiO_2, 30sAg/TiO_2, and 60sAg/TiO_2, t is the deposition time of Ag.

Table S6 Photocatalytic efficiency (k_t) and improvements (η) under UV and visible lights of samples TiO_2, 10sAg/TiO_2, 30sAg/TiO_2 and 60sAg/TiO_2, t is the deposition time of Ag.

	UV-light		visible-light	
Samples	k_t	η	k_t	η
TiO_2	0.017		0.018	
10sAg/TiO_2	0.021	24%	0.030	67%
30sAg/TiO_2	0.024	41%	0.047	161%
60sAg/TiO_2	0.016	-6%	0.035	94%

11. The model of AgNP oxidation

The left sample (a) in figure S7 has a configuration of Ag_2O (top)/AgNPs (middle) /TiO_2 (bottom), this is what exactly described in figure 5b in the manuscript. The middle sample (b) in figure S7 has a configuration of Ag_2O (shell)/Ag (core)/TiO_2, which seems to be the most

possible case in our experiments. We discuss this situation.

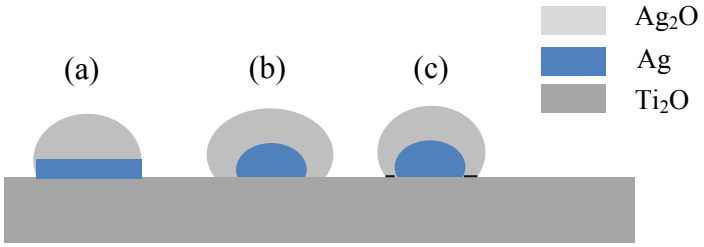

Figure S7 The models of the oxidization of AgNP/TiO_2

Since Ag_2O grows from silver thus the binding between Ag_2O and Ag is definitely strong, but there is no binding between Ag_2O and TiO_2 and there might be lane between them if the intension makes Ag_2O shrink, as shown in figure S7 (c). Under this circumstance, the contact between Ag_2O and TiO_2 is not good, thus figure 5d is still suitable.

12. Photocatalytic efficiency (k_t) under UV, visible, and UV-visible lights of sample 30sAgNPs/TiO_2 without and with OPI for 2s and the corresponding PAIs (η).

Table S7

	UV light		Visible light		UV-Visible light	
t (s)	k_t	η	k_t	η	k_t	η
0	0.023		0.044		0.03	
2	0.052	126%	0.064	45%	0.057	90%