Supplementary Information

SiO_2-Ag-SiO_2-TiO_2 multi-shell structures: plasmon enhanced photocatalysts with wide-spectral-response

Juan Zhou[a], Feng Ren*[a], Shaofeng Zhang[a], Wei Wu[b], Xiangheng Xiao[a], Ying Liu[a], Changzhong Jiang*[a]

[a] School of Physics and Technology and Center for Electron Microscopy, Wuhan University, Wuhan 430072, P. R. China.

[b] School of Printing and Packaging and College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, P. R. China.

* Corresponding author.

E-mail address: fren@whu.edu.cn; czjiang@whu.edu.cn.

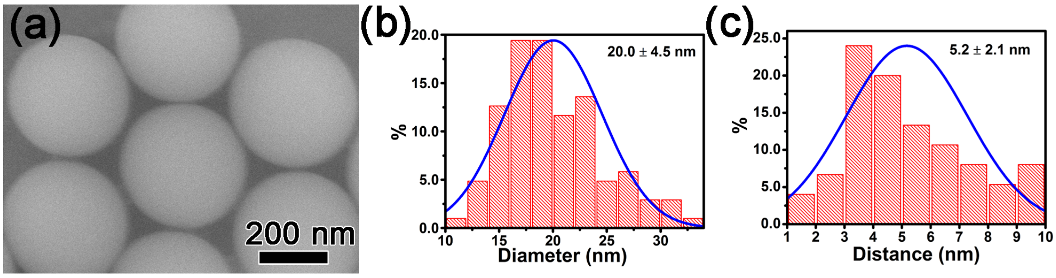

Figure SI 1. (a) SEM micrographs of 368nm uncoated SiO_2 spheres, (b) size distribution histograms of the Ag NPs coated on SiO_2 spheres, and (c) distance distribution histograms of the Ag NPs.

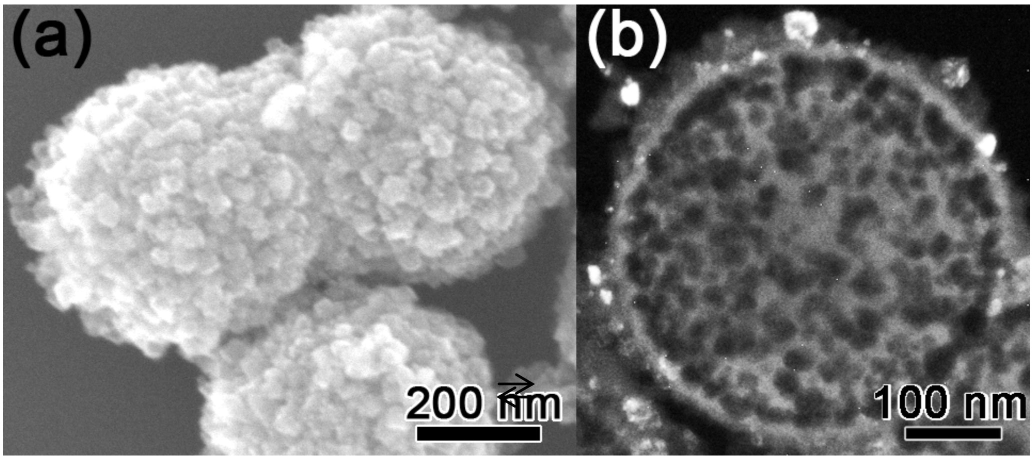

Figure SI 2. SEM image (a) and dark-field TEM image (b) of the SiO_2-Ag-SiO_2 (5 nm)-TiO_2 multi-shell structure.

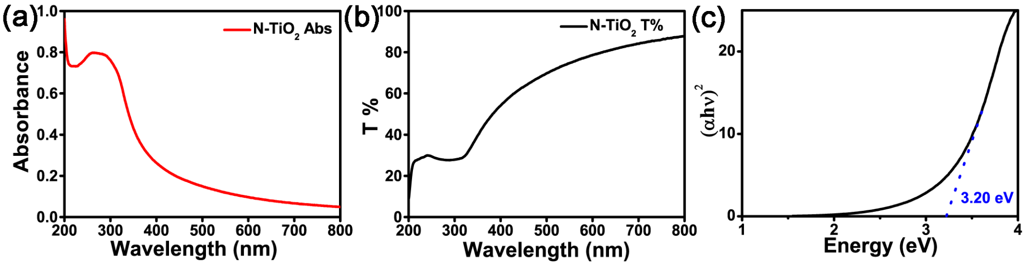

Figure SI 3. (a) UV-vis absorption spectrum, (b) UV-vis transmission spectrum of TiO_2 NPs; and (c) the analysis of direct transitions.

The HMTA reactions during the formation of TiO_2 are as following:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \qquad \text{(SI 1)}$$

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^- \qquad \text{(SI 2)}$$

The relationship between the absorption coefficient (α) and the photon energy (hυ) can be expressed by Equation (SI 3):

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \qquad \text{(SI 3)}$$

Where A is a constant, E_g is the band gap, and the exponent, n, depends on the nature of the transitions. The value of n may be 1/2, 2, 3/2 and 4, corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. The absorption coefficient close to the band edge can be calculated from the transmission measurements as the Lamberts formula shown by Equation (SI 4):

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \qquad \text{(SI 4)}$$

Where t is the path length of the TiO_2 colloidal solution, and T is the transmittance (which can be directly obtained from Figure SI 3b).[1-3] After conversion to the absorption coefficient, the intercept of the tangent to the plot $(\alpha h\upsilon)^2$ versus hυ (Figure SI 3c), is 3.20 eV, which is the same as the accepted bandgap of 3.2 eV for TiO_2.

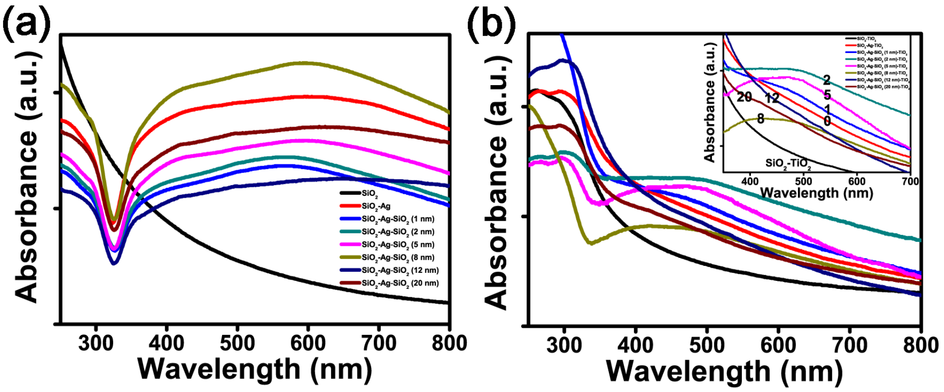

Figure SI 4. UV-visible absorption spectra of the multi-shell NPs before (a) and after (b) TiO_2 coating.

After being coated with TiO_2, when the thickness of SiO_2 interlayer increases from 1 to 8 nm, the intense plasmon resonance peaks of Ag NPs shells in the SiO_2-Ag-SiO_2-TiO_2 appear obviously. For the SiO_2-Ag-SiO_2-TiO_2 with the thickness of SiO_2 interlayer of 12 nm and 20 nm, the absorption spectra of the two samples have the same trend with that of the SiO_2-Ag-TiO_2.

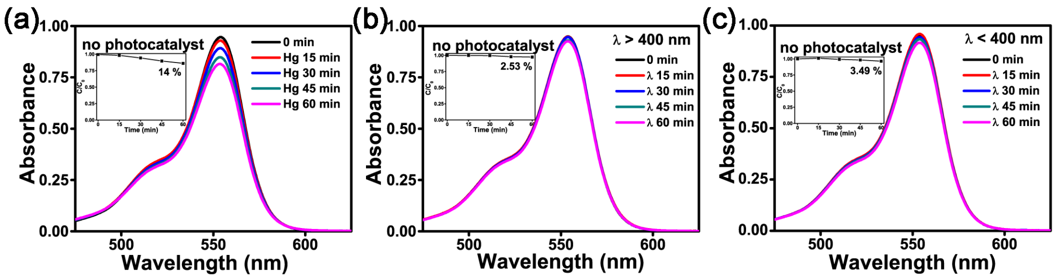

Figure SI 5. UV-vis absorption spectra of concentration changed RhB solution versus reaction time with no photocatalyst under a 300 W high-pressure mercury lamp without any filer (a), with a cutoff filer to get the visible light (b), and with a cutoff filer to get the ultraviolet light (c) (the inners are the corresponding self-degradations of RhB).

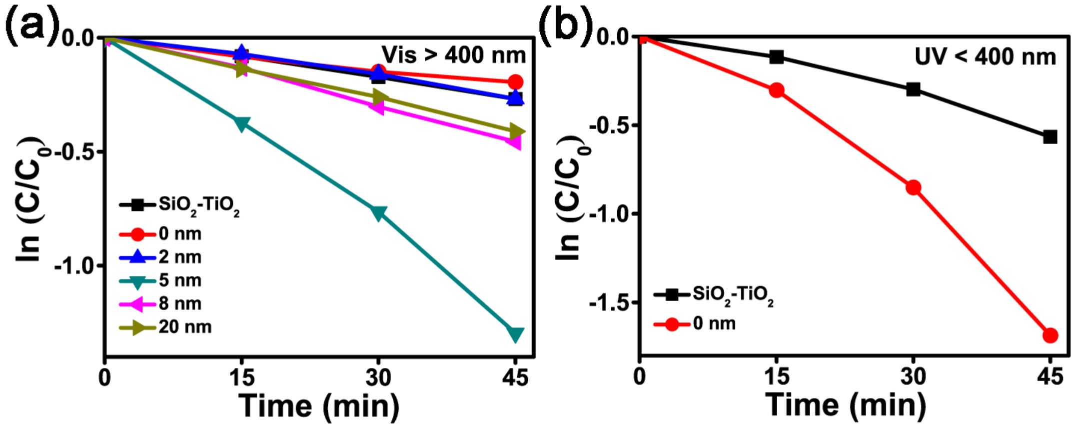

Figure SI 6. (a) ln (C/C_0) versus time line under the visible light ($\lambda > 400$ nm), and (b) ln (C/C_0) versus time line under the ultraviolet light ($\lambda < 400$ nm).

It should be noted, the activity of the same sample under UV light or visible light is lower than that of Hg lamp without any filer, which is because the intensity of lights is decreased after filtered and the photocatalytic reaction rate has a linear dependence on light intensity.[4]

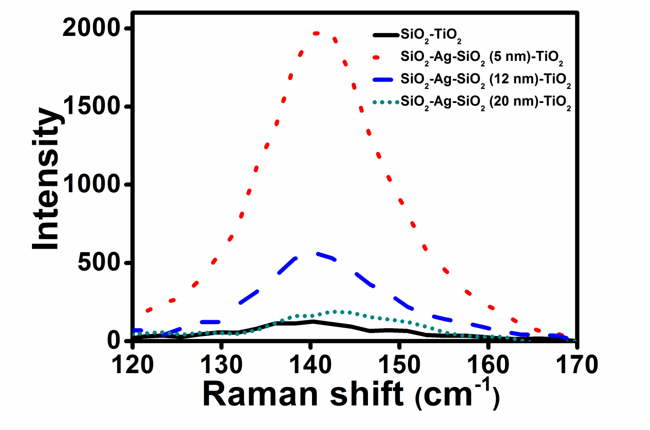

Figure SI 7. Normalized Raman peak corresponding to 143.4 cm^{-1} for the SiO$_2$ -TiO$_2$ and the SiO$_2$-Ag-SiO$_2$-TiO$_2$ with the SiO$_2$ interlayer thicknesses of 5 nm, 12 nm, and 20 nm, respectively.

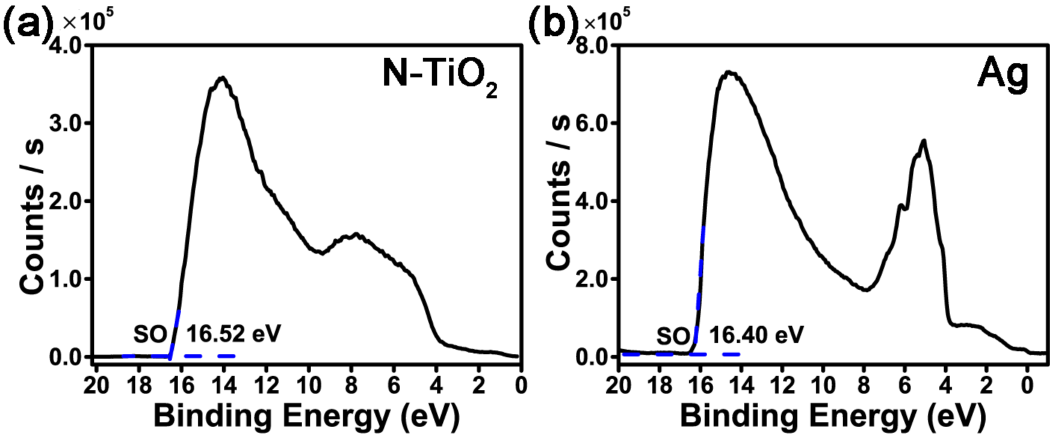

Figure SI 8. UPS (He I) spectrum of (a) the N-doped TiO$_2$, and (b) the surface of Ag, after Ar ion sputtering.

Based on the secondary electron onset (SO, the secondary cutoff energy) we can get the work function of the surface.[5] The SO on the left side of the spectrum in Figure SI 9a is 16.52 eV, and the excitation energy of the He I UPS spectrum is 21.2 eV. Hence, the work function of N-doped TiO$_2$ was calculated to be 4.68 eV. Via the same calculation, the work function of Ag is 4.80 eV from Figure SI 9b on the vacuum level (0 V). The conversion between the absolute potential level E (eV) and the level of normal hydrogen electrode (NHE) is E (NHE) = - 4.50 – E (eV).[6, 7] Hence, the Femi energy of the N doped TiO$_2$ is - 0.18 eV, which is a little higher than that of Ag - 0.30 eV on the NHE scale (pH = 0).

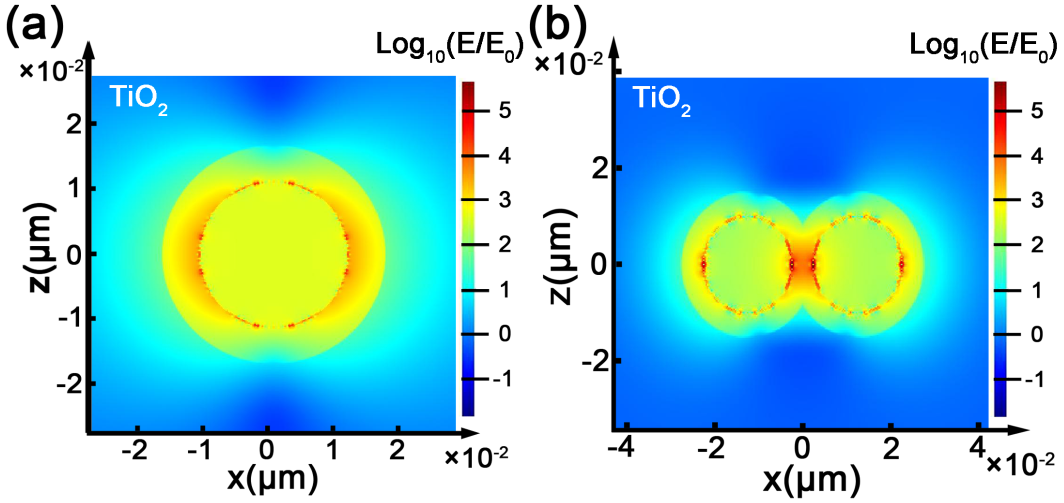

Figure SI 9. FDTD simulated spatial distributions of the SPR-induced enhancement of electric field intensity E/E_0 in the logarithmic scale for an isolated Ag NP at the wavelength of 437 nm (a) and two Ag NPs at the wavelength of 455 nm (b). The size of Ag NPs is 20 nm, the thickness of SiO_2 is 5 nm, and the separation distance is 5 nm. The mesh sizes of 0.1 and 0.3 nm were used for the maximum calculation ability of the PC.

Notes and References

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