

Supplementary Information

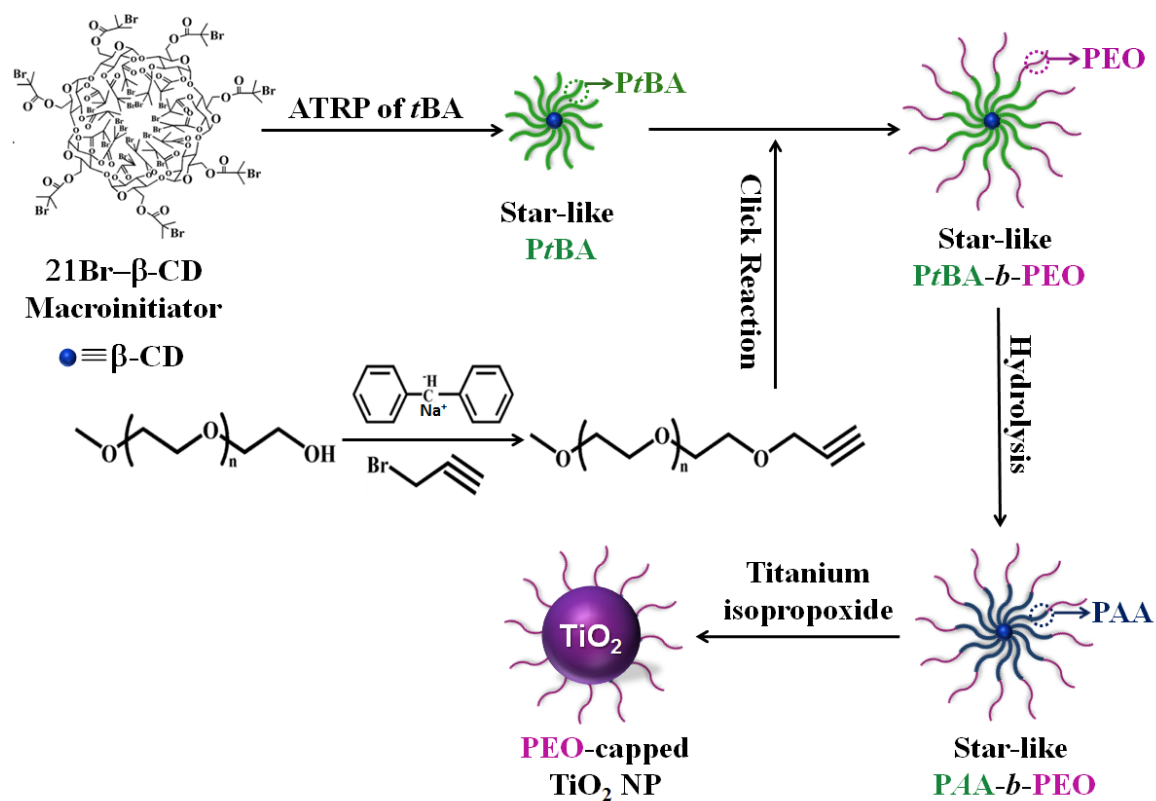
Nonepitaxial Growth of Uniform and Precisely Size-Tunable Core/Shell Nanoparticles and Their Enhanced Plasmon-Driven Photocatalysis

Mengye Wang,^{1,2} Xinchang Pang,¹ Dajiang Zheng,² Yanjie He,¹ Lan Sun,² Changjian Lin,^{2*} and Zhiqun Lin^{1*}

¹School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.

²State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

* To whom correspondence should be addressed. Email: zhiqun.lin@mse.gatech.edu and cjlin@xmu.edu.cn



Scheme S1. Schematic illustration of the synthesis of uniform PEO-capped TiO_2 nanoparticles by using star-like PAA-*b*-PEO as nanoreactor.

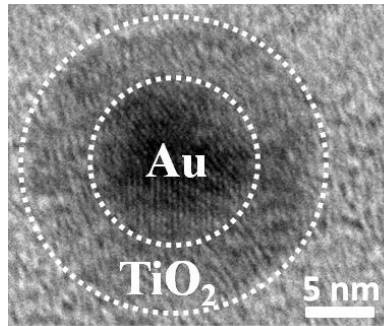


Figure S1. HRTEM image of plasmonic/semiconducting Au/TiO₂ core/shell nanoparticles capped with PEO chains on the surface. The diameter of Au core and the thickness of TiO₂ shell are 10 nm and 5 nm, respectively. White dashed circles are for guidance.

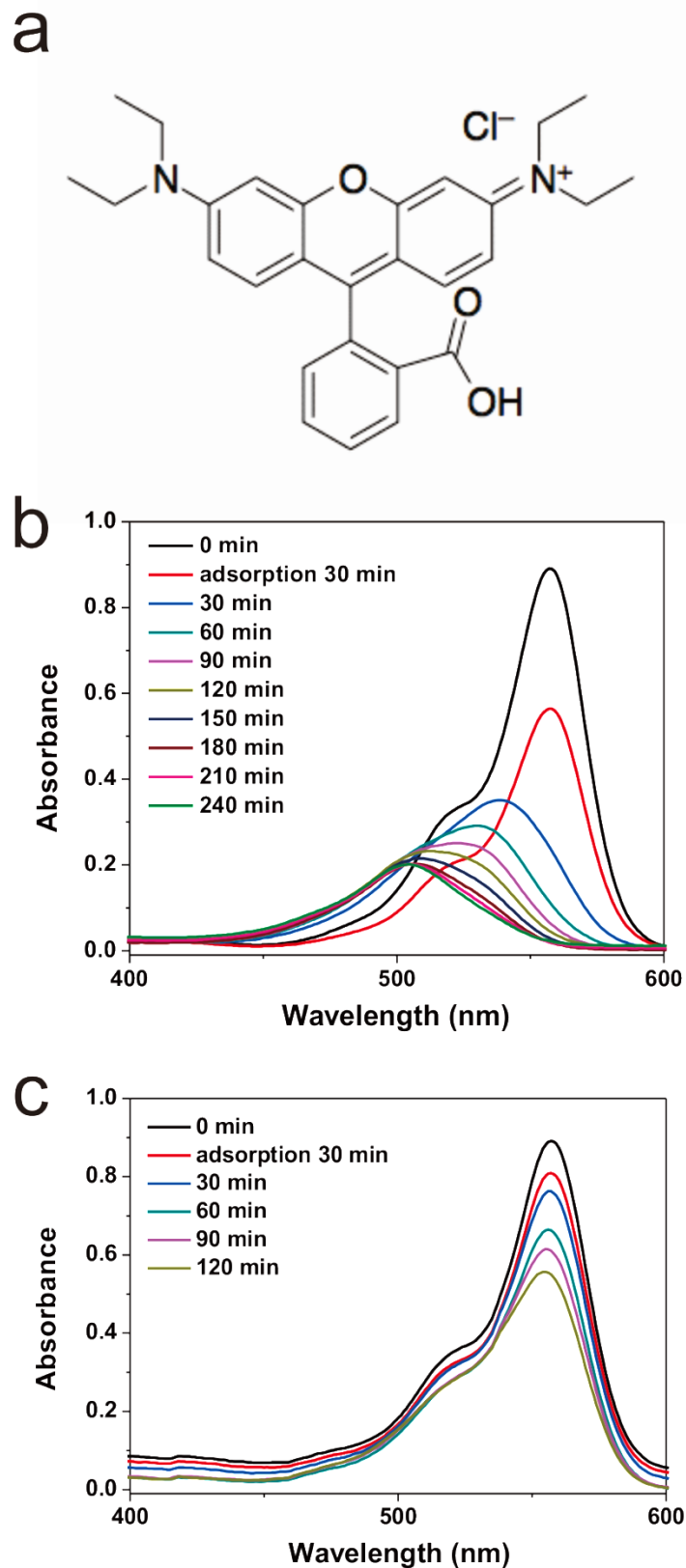


Figure S2. (a) Chemical structure of RhB. (b) UV-vis spectra of RhB at different times by employing PEO-capped Au/TiO₂ nanoparticles (15-nm Au core and 5-nm TiO₂ shell) as photocatalysts to degrade RhB under visible light irradiation. The

nanoparticles were added to the RhB aqueous solution (black solid squares: *0 min*) and stirred for 30 min in dark to reach the adsorption/desorption equilibrium (red open squares: *Adsorption for 30 min*). The changes in RhB concentration were explored by monitoring the absorption maximum. After the adsorption for 30 min, the peak decreased dramatically (red open squares: *Adsorption for 30 min*) as the PEO chains on the surface the Au/TiO₂ nanoparticles contributed to the physisorption of RhB. Subsequently, the photocatalytic degradation by Au/TiO₂ nanoparticles occurred (*30 min - 240 min*). Thus, the adsorption of RhB by PEO and the degradation by Au/TiO₂ nanoparticles coexisted at the same time. The absorption maximum decreased with the degradation time increased. A hypsochromic shift of the absorption maximum was observed due to the formation of a series of stepwise N-de-ethylated intermediates of RhB.¹ Notably, the absorption maximum remained unchanged and the adsorption rate is proposed to be faster than the degradation rate after 180 min. The degradation of RhB stopped as the RhB adsorbed on the surface of PEO-capped Au/TiO₂ nanoparticles formed a thick layer prior to being degraded and prevented the nanoparticles from reacting with O₂. (c) UV-vis spectra of RhB at different times by employing Au/TiO₂ nanoparticles (15-nm Au core and 5-nm TiO₂ shell) as photocatalysts to degrade RhB under visible light irradiation. After calcination at 500 °C in air for 2 h, PEO chains were totally removed. A regular degradation of RhB was observed, suggesting RhB was mineralized into small molecules as expected.

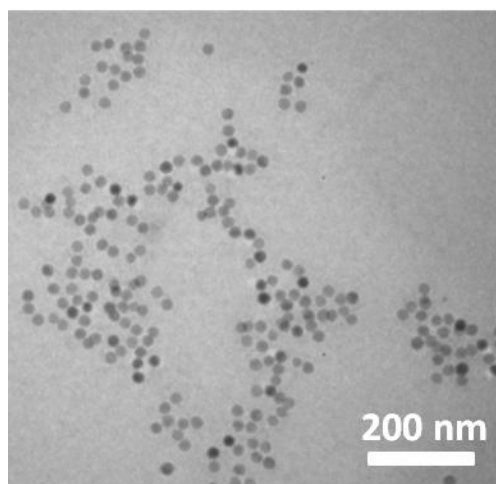


Figure S3. TEM image of homemade PEO-capped TiO₂ nanoparticles prepared using star-like PAA-*b*-PEO as nanoreactor.

Table S1. Summary of molecular weights of amphiphilic star-like P4VP-*b*-PtBA-*b*-PEO triblock copolymers and the corresponding dimensions of Au/TiO₂ core/shell nanoparticles.

Dimensions of Au/TiO ₂ core/shell nanoparticles	$M_n, P4VP$	$M_n, PtBA$	M_n, PEO	PDI
5 nm/5 nm	6,200	11,600	5,000	1.15
10 nm/5 nm	10,200	11,400	5,000	1.09
15 nm/1 nm	13,000	2,800	5,000	1.14
15 nm/5 nm	13,000	11,300	5,000	1.16
15 nm/10 nm	13,000	23,800	5,000	1.19

M_n of each arm was calculated from ¹H-NMR data. The polydispersity index, PDI was determined by GPC.

Table S2. Summary of the sizes of Au core and different Au/TiO₂ core/shell nanoparticles in Figure 1.

Nanoparticles	Average diameter (nm) ± diameter distribution (nm)
15-nm Au core	15.06 ± 0.44
Au/TiO ₂ core/shell nanoparticles with 15-nm Au and 1-nm TiO ₂	17.04 ± 0.30
Au/TiO ₂ core/shell nanoparticles with 15-nm Au and 5-nm TiO ₂	24.60 ± 0.38
Au/TiO ₂ core/shell nanoparticles with 15-nm Au and 10-nm TiO ₂	35.02 ± 2.86

Table S3. Summary of the sizes of Au core and different Au/TiO₂ core/shell nanoparticles in Figure 2.

Nanoparticles	Average diameter (nm) ± diameter distribution (nm)
5-nm Au core	4.98 ± 0.10
10-nm Au core	10.03 ± 0.09
Au/TiO ₂ core/shell nanoparticles with 5-nm Au and 5-nm TiO ₂	14.84 ± 0.39
Au/TiO ₂ core/shell nanoparticles with 10-nm Au and 5-nm TiO ₂	19.91 ± 0.71

Reference

- (1) Yang, J.; Chen, C. C.; Ji, H. W.; Ma, W. H.; Zhao, J. C. Mechanism of TiO₂-assisted photocatalytic degradation of dyes under visible irradiation: Photoelectrocatalytic study by TiO₂-film electrodes. *J. Phys. Chem. B* **2005**, *109*, 21900-21907.