

## Electronic Supplementary Information

### **Rational Design of Plasmonic Catalysts: Matching the Surface Plasmon Resonance with the Lamp Emission Spectra for Improved Performances in AgAu Nanorings**

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## Experimental Section

### *Materials and Instrumentation*

Analytical grade silver nitrate ( $\text{AgNO}_3$ , 99%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 10,000 g/mol), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 55,000 g/mol), ethylene glycol (EG, 99.8%, Sigma-Aldrich), sodium citrate dihydrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$ ,  $\geq 99.9\%$ , Sigma-Aldrich), tetrachloroauric acid ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ,  $\geq 99.9\%$ , Sigma-Aldrich), 4-nitrophenol ( $\text{C}_6\text{O}_3\text{NH}_5$ ,  $\geq 99\%$ , Sigma-Aldrich), MB hydrate ( $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot x\text{H}_2\text{O}$ ,  $\geq 95\%$ , Sigma-Aldrich), and sodium borohydride ( $\text{NaBH}_4$ , 98%, Sigma-Aldrich) were used as received.

The scanning electron microscopy (SEM) images were obtained using a JEOL field emission gun electron microscope JSM6330F operated at 5 kV. The samples were prepared by drop-casting an aqueous suspension containing the nanostructures over a silicon wafer, followed by drying under ambient conditions. High-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL JEM2100 microscope operated at 200 kV. Energy dispersive X-ray (EDX) spectrum was obtained in this instrument with an EDX detector configuration which has a total solid angle of  $\sim 0.13$  sr. Samples for HRTEM were prepared by drop-casting an aqueous suspension of the nanostructures over a carbon-coated copper grid, followed by drying under ambient conditions. UV-VIS spectra were obtained from aqueous suspensions containing the nanostructures with a Shimadzu UV-1700 spectrophotometer. The Ag and Au atomic percentages were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Spectro Arcos equipment at the IQ-USP analytical center facilities. The X-ray diffraction (XRD) data were obtained using a Rigaku - Miniflex equipment,

CuK $\alpha$  radiation. The diffraction pattern was measured in the range of 10 – 90 ° 2 $\theta$  with a 1 ° min<sup>-1</sup> angular speed scan.

#### *Synthesis of Ag nanospheres*

Ag nanospheres were prepared by the polyol process. In a typical procedure, 5 g of polyvinylpyrrolidone (M.W. 10,000 g/mol) were dissolved in 37.5 mL of ethylene glycol (EG). Then, AgNO<sub>3</sub> (200 mg, 1.2 mmol) was added and mixed until complete dissolution. The resulting solution was heated to 125 °C for 2.5 hours, leading to the appearance of a greenish-yellow color, allowed to cool down to room temperature, and diluted to 125 mL of water. For the catalytic tests, 1 mL of Ag nanospheres suspension was washed three times with water by successive rounds of centrifugation at 15,000 rpm and removal of the supernatant. After washing, the Ag nanoparticles were suspended in 1 mL of deionized water. In this case, the concentration of Ag in the nanoparticles suspensions corresponded to 2.2 mM (measured by ICP-OES).

#### *Synthesis of Au nanospheres*

The synthesis of Au nanospheres was performed by a seeded growth approach. In the first step, Au seeds were synthesized by adding 150 mL of a 2.2 mM sodium citrate aqueous solution to a 250 mL round-bottom flask under magnetic stirring. This system was heated to 100 °C for 15 minutes. Then, 1 mL of a 25 mM AuCl<sub>4</sub><sup>-</sup><sub>(aq)</sub> solution was added, and the reaction mixture was kept at 100°C under vigorous stirring for 30 minutes. The obtained Au nanoparticles were employed as seeds for the synthesis of Au NPs having larger sizes by two

successive steps of Au deposition. For the first deposition step, 1 mL of a 60 mM sodium citrate solution was added to the same 250 mL round-bottom flask containing the Au NPs seeds under magnetic stirring at 100°C for 5 minutes. Afterwards, 1 mL of a 25 mM  $\text{AuCl}_4^-$  (aq) solution was added to the reaction mixture containing the Au NPs seeds and the reaction mixture was carried out for another 30 min. Similarly, a second deposition step could be performed by adding another 1 mL of a 60 mM sodium citrate solution and 1 mL of a 25 mM  $\text{AuCl}_4^-$  (aq) solution to the reaction mixture obtained after the first deposition step, in which the Au NPs produced after the first deposition step served as seeds for further growth. After the reaction, the resulting suspension was allowed to cool down to room temperature. For the catalytic tests, 5 mL of Au nanospheres suspension was washed three times with water by successive rounds of centrifugation at 15,000 rpm and removal of the supernatant. After washing, the Au nanoparticles were suspended in 1 mL of deionized water. Here, the concentration of Au in the nanoparticles suspensions corresponded to 2.2 mM (measured by ICP-OES).

### *Synthesis of AgAu nanorings*

The synthesis of AgAu nanorings was based on the galvanic replacement reaction between Ag nanospheres and  $\text{AuCl}_4^-$  (aq). In a typical procedure, a mixture containing 5 mL of PVP aqueous solution (0.1 wt %, M.W. 55,000 g/mol) and 1 mL of the as-prepared suspension containing the Ag nanospheres (2.2 mM in terms of Ag) was stirred at 100 °C for 10 min in a 25 mL round-bottom flask. Then, 2 mL of  $\text{AuCl}_4^-$  (aq) (1.5 mM) was added dropwise and the reaction allowed to proceed at 100 °C for another 1 h. After that, the suspension was allowed to cool down to room temperature and 10 mL were washed twice with a supersaturated NaCl solution

and three times with water by successive rounds of centrifugation at 15,000 rpm and removal of the supernatant. After washing, the product was suspended in 1 mL of deionized water and then employed in the catalytic tests. After this step, the concentration of metal (Ag + Au) in the nanoparticles suspensions corresponded to 2.2 mM (measured by ICP-OES).

#### *Synthesis of AgAu alloyed nanospheres*

In a typical procedure, 0.7 mL of an aqueous 2.0 mM AgNO<sub>3</sub> solution, 95 mL of deionized water, and 1.0 mL of an aqueous 35 mM sodium citrate solution were transferred to a round bottom flask. This flask was placed on an oil bath pre-heated at 105 °C. After boiling for 1 min, 3.6 mL of a 2.4 mM AuCl<sub>4</sub><sup>-(aq)</sup> solution was added and the reaction mixture was further boiled for 40 min. After the reaction, the resulting suspension was allowed to cool down to room temperature. For the catalytic tests, 4.5 mL of AgAu alloyed nanospheres suspension was washed three times with water by successive rounds of centrifugation at 15,000 rpm and removal of the supernatant. After washing, the AgAu alloyed nanospheres were suspended in 1 mL of deionized water. After this step, the concentration of metal (Ag + Au) in the nanoparticles suspensions corresponded to 0.1 mM (measured by ICP-OES).

#### *SPR-mediated oxidation of methylene blue*

Typically, 10 mL of a 10 mg/L MB aqueous solution and 1 mL of the suspension containing the washed catalysts was added in a 25 mL round-bottom flask. The resulting mixture was stirred for 30 min in the dark to achieve the adsorption and desorption equilibrium. Subsequently, the suspensions were irradiated with a 300 W halogen tungsten

lamp (OSRAM) mounted at a 5 cm distance from the glass reactor. In all photocatalytic experiments, the temperature of the reaction mixture was carefully controlled and corresponded to 40 °C. During the experiments, 1 mL aliquots were taken and centrifuged at 15,000 rpm for 10 min to isolate the supernatant. Then, the UV–VIS spectra of the supernatant were measured as a function of time in the 500 to 750 nm range to probe the MB photodegradation. A calibration curve for absorbance as a function of the MB concentration was employed in order to monitor the transformation.

#### *Catalytic reduction of 4-nitrophenol*

Typically, 2 mL of  $4.2 \times 10^{-2}$  M sodium borohydride aqueous solution and the suspension containing the catalysts was added into a quartz cuvette. After 5 min, 1 mL of a  $1.4 \times 10^{-4}$  M 4-nitrophenol aqueous solution was added to the same cuvette. The catalytic transformation was monitored by UV–VIS spectroscopy, in which the intensity in the absorbance at 400 nm (assigned to 4-nitrophenolate ions) was monitored as a function of time (this signal decreased as the consumption of 4-nitrophenolate ions and formation of 4-aminophenol took place). In this case, the UV-VIS spectra were collected at 13 s time intervals in the 350 to 500 nm range. A calibration curve for absorbance as a function of the 4-nitrophenolate concentration was employed in order to monitor the transformation. All reactions were performed under the same amount of catalyst ( $2.2 \times 10^{-6}$  mmol of metal, which corresponds to 1, 5, and 10  $\mu$ L of Ag nanospheres, Au nanospheres, and AgAu nanorings, respectively).

### *Estimation of Surface Area*

The surface areas for the nanoparticles studied were estimated using ICP and TEM analysis data. Ag and Au nanoparticles were considered perfectly spherical and AgAu nanorings were considered perfect cylinders with height corresponding to the length of the outer circumference.

$$A_{\text{sphere}} = 4\pi r^2$$

$$V_{\text{sphere}} = (4\pi r^3)/3$$

r = sphere radius

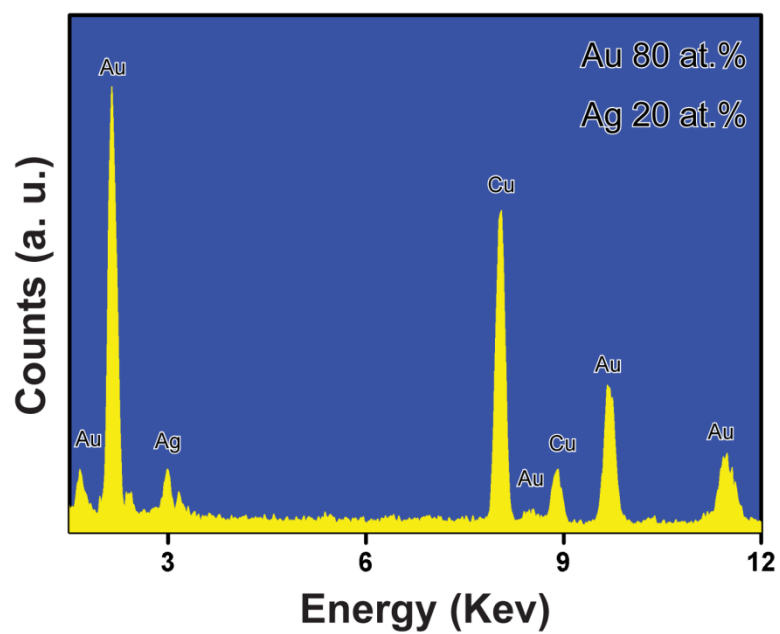
$$A_{\text{cylinder}} = 2\pi rh$$

$$V_{\text{cylinder}} = 2\pi r^2 h$$

r = cylinder radius (half of thickness of the ring)

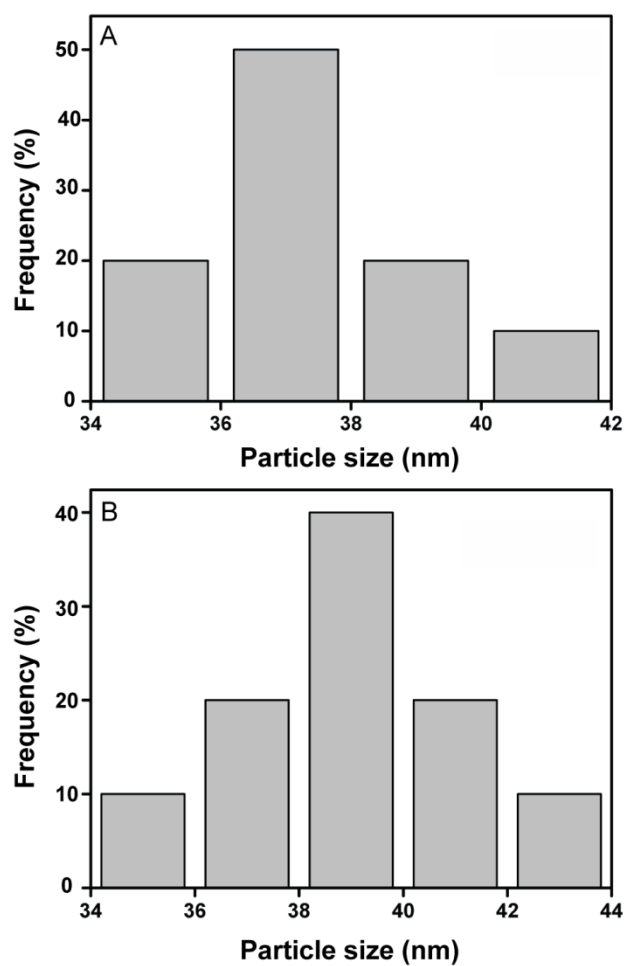
h = cylinder height (length of the outer circumference)

Densities:  $d_{\text{Ag}}$ : 10.50 g/mL and  $d_{\text{Au}}$ : 19.28 g/mL

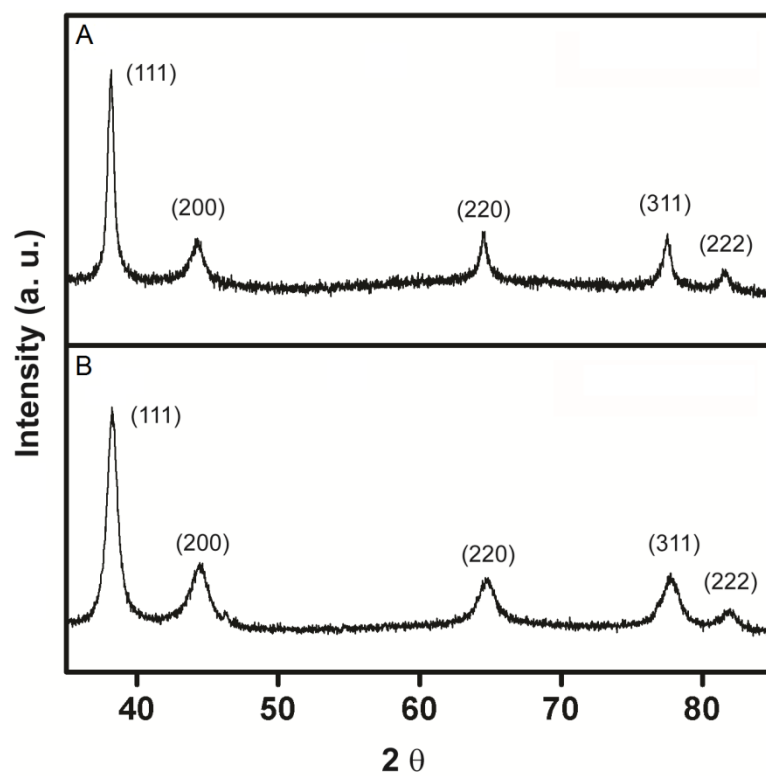


**Figure S1.** EDX spectrum obtained from an individual AgAu nanoring.

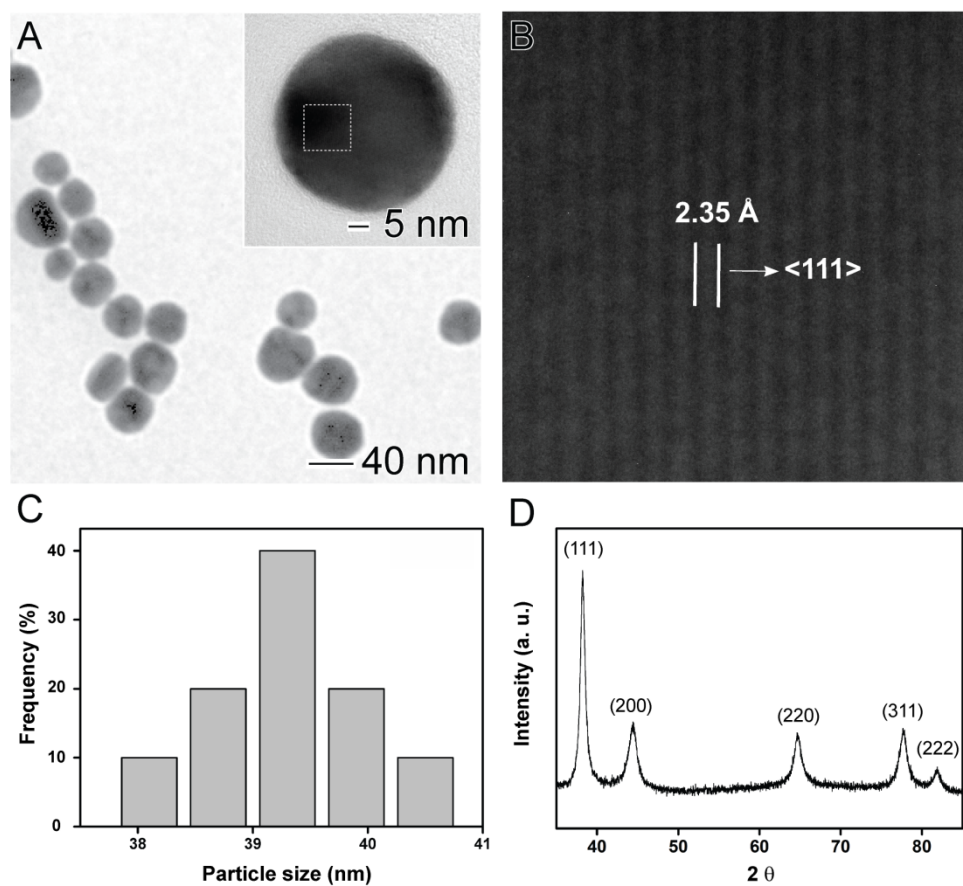




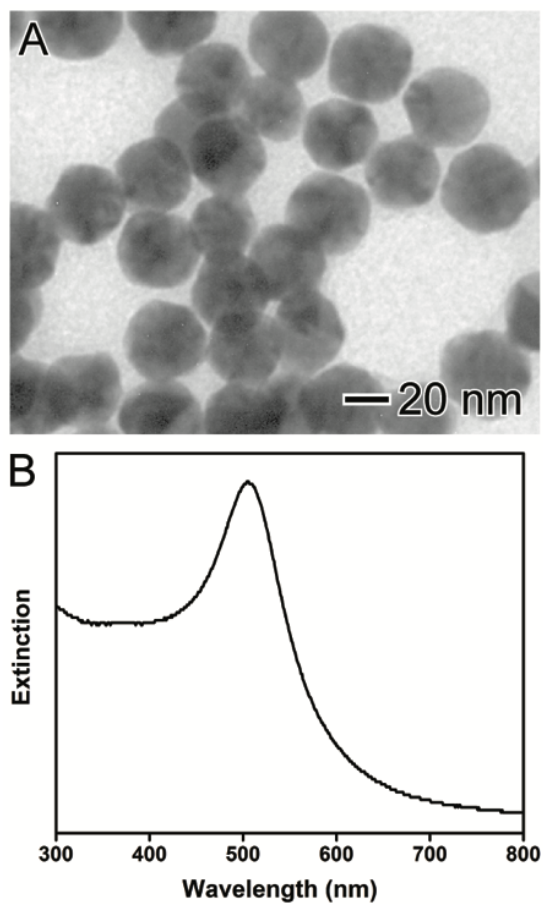
**Figure S2.** Histograms showing the particle size distribution for the obtained Ag nanospheres (A) and AgAu nanorings (B).



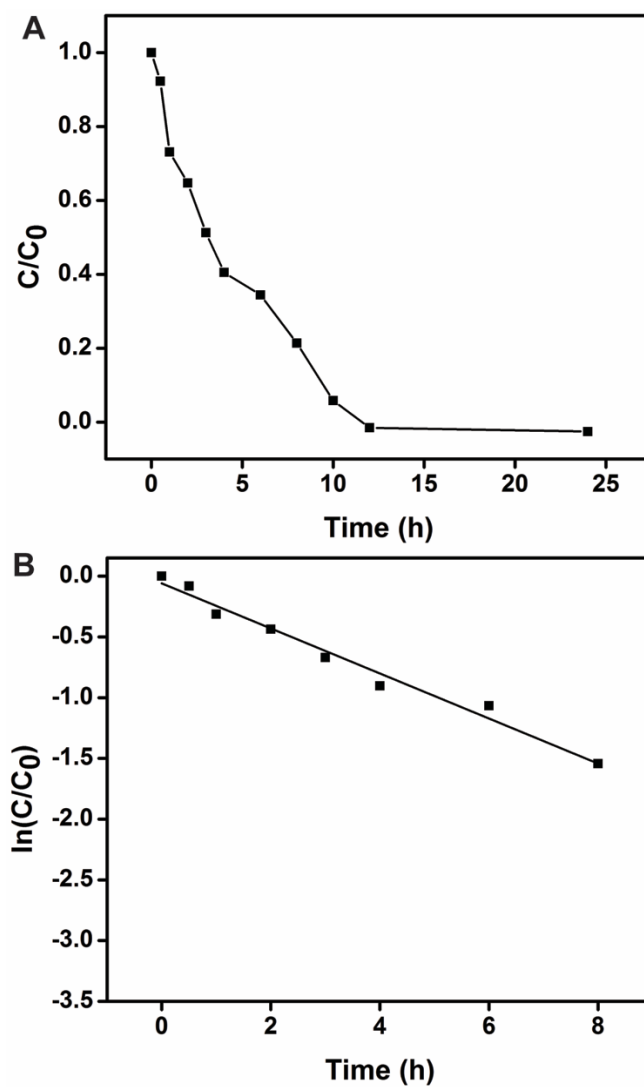
**Figure S3.** X-ray diffraction patterns recorded from the obtained Ag nanospheres (A) and AgAu nanorings (B).



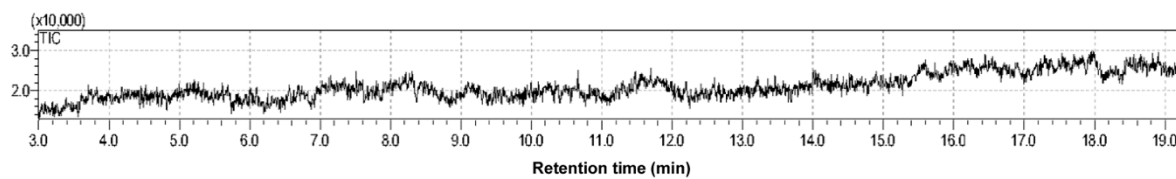
**Figure S4.** TEM and HRTEM (A and B) images for Au nanospheres employed in our photocatalytic and catalytic experiments. The image in (B) corresponds to a zoom-in image of the area highlighted by the white square in inset of (A). (C) Histogram showing the particle size distribution and (D) X-ray diffraction pattern from the Au nanospheres.



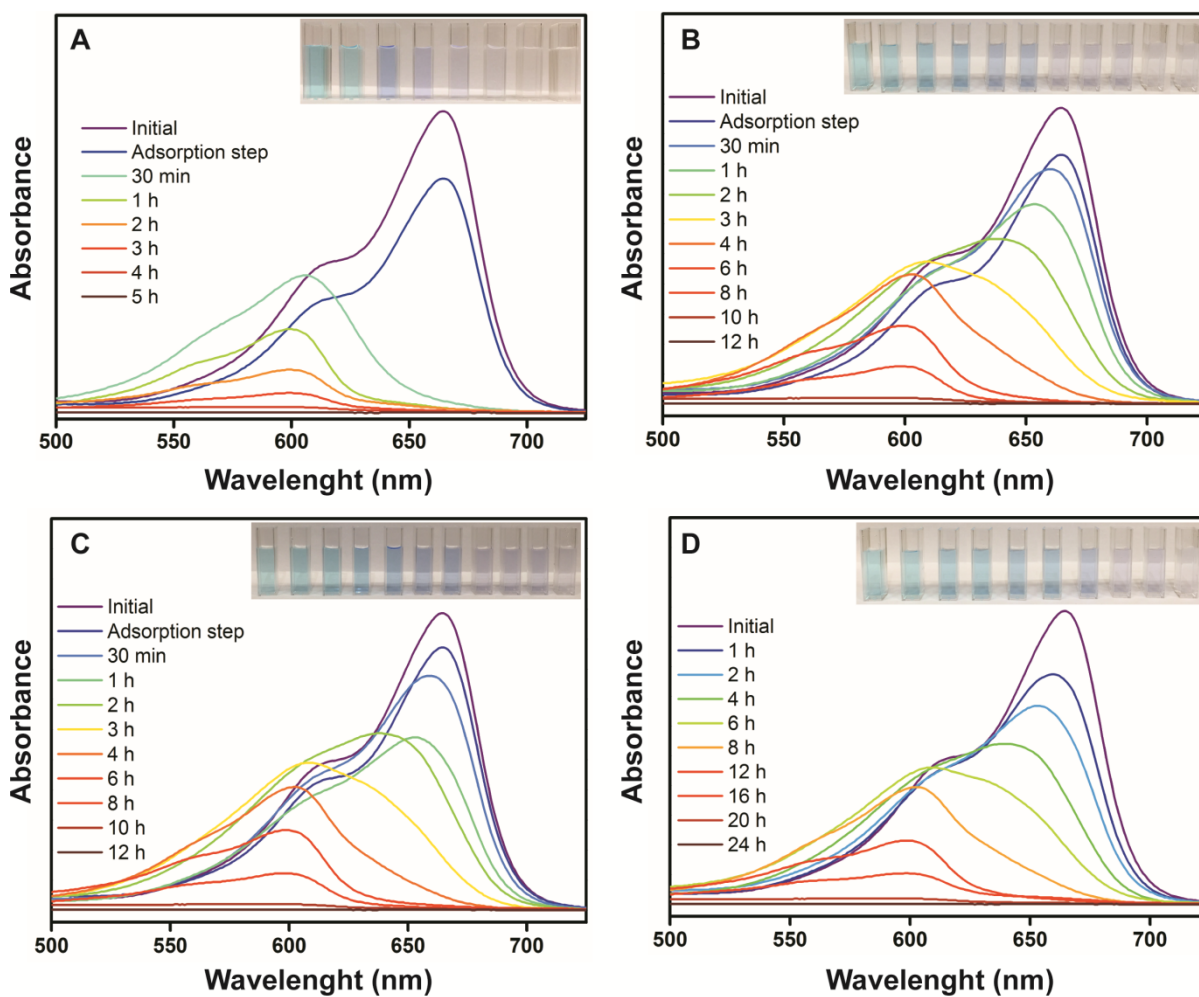
**Figure S5.** (A) TEM image and (B) UV-Vis extinction spectra for AgAu alloyed nanospheres employed in our photocatalytic and catalytic experiments.



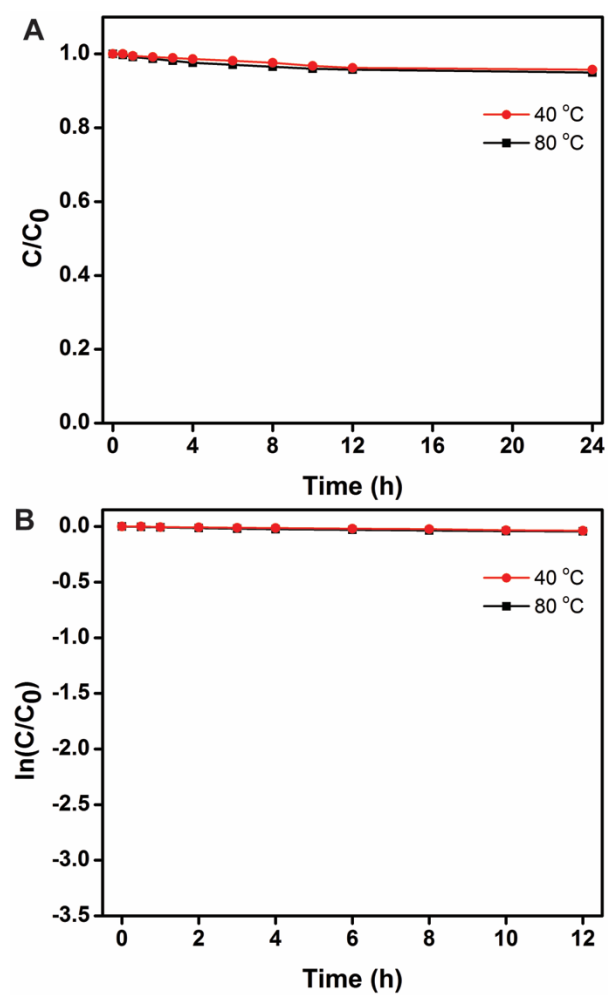
**Figure S6.** SPR-mediated oxidation of methylene blue.  $C/C_0$  (A) and  $\ln(C/C_0)$  (B) profiles as a function of time employing AgAu alloyed nanospheres as catalysts.



**Figure S7.** GC-MS chromatogram from the reaction mixture obtained after the SPR-mediated oxidation of methylene blue catalyzed by AgAu nanorings.



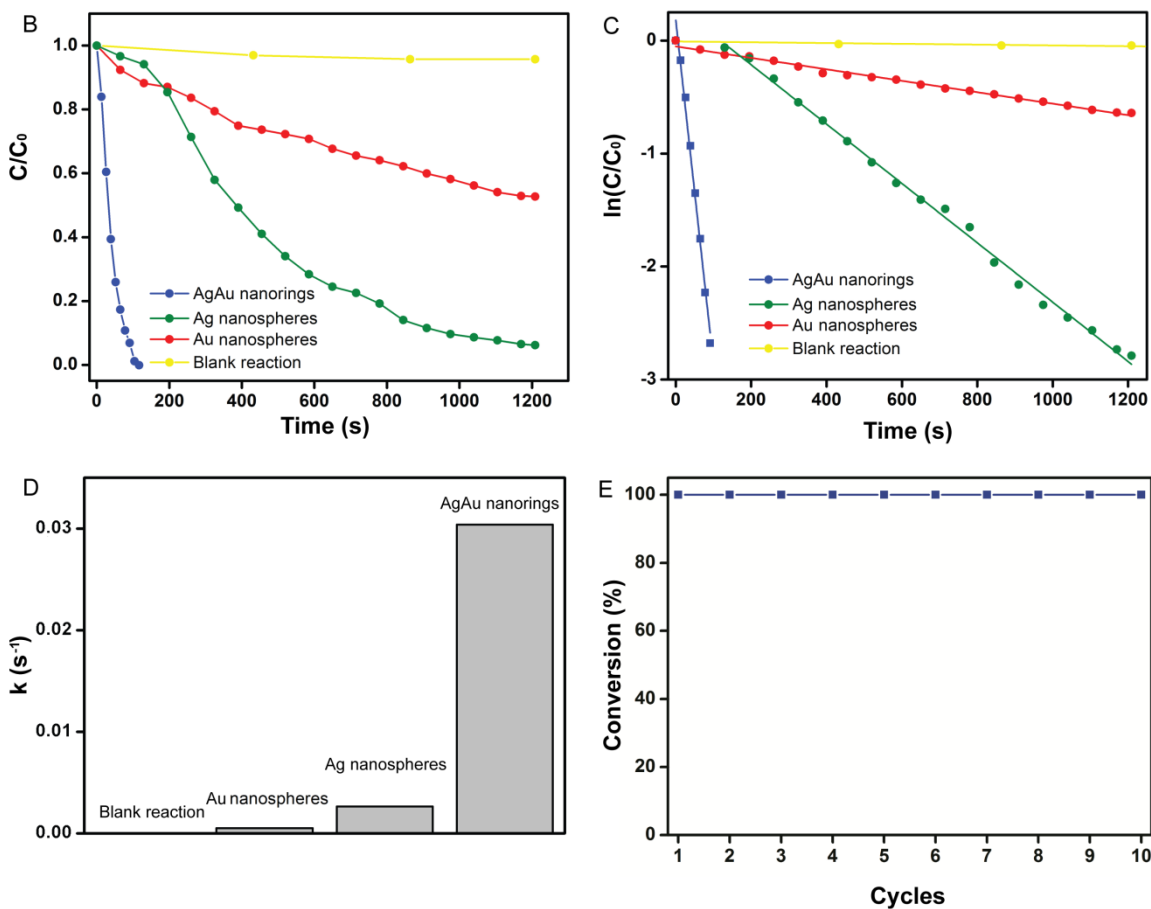
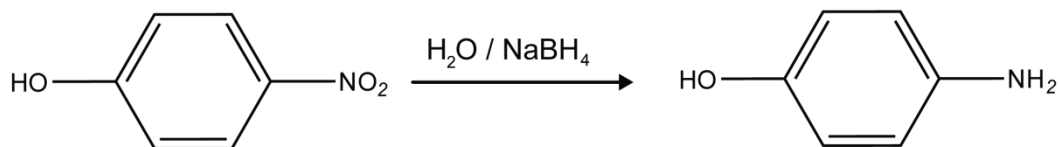
**Figure S8.** UV-VIS spectra collected as function of time during the methylene blue oxidation experiments in presence of AgAu nanorings (A), Ag nanospheres (B), Au nanospheres (C), and in the absence of any catalyst (D).



**Figure S9.**  $C/C_0$  (A) and  $\ln(C/C_0)$  (B) profiles as a function of time for the methylene blue oxidation experiments in the dark employing AgAu nanorings as catalysts at 40 (red trace) and 80 °C (black trace).



A



**Figure S10.** (A) Scheme for the 4-nitrophenol reduction by NaBH<sub>4</sub> in the presence catalyzed by the AgAu nanorings. C/C<sub>0</sub> (B) and ln(C/C<sub>0</sub>) (C) profiles as a function of time employing of AgAu nanorings (blue trace), Ag nanospheres (green trace), and Au nanospheres (red trace) as catalysts. A blank reaction without any catalyst was also performed (yellow trace). (D) Bar graph showing the pseudo-first order rate constants calculated from (C). Stability tests (E) employing AgAu nanorings as catalysts.