Electronic Supplementary Material (ESI) for Environmental Science: Nano.

**Electronic Supplementary Information for:**

# Efficient method of arsenic removal from water based on photocatalytic oxidation by a plasmonic-magnetic nanosystem

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## Homogeneous redox reaction

Pettine et al.[37] found that the kinetic is of first order in As(III) concentration:

$$-\frac{d[As(III)]}{dt} = k \cdot [As(III)] \cdot [H_2O_2] \qquad (1)$$

where the reaction rate constant $k$ depends on the $pH$, ionic force $(I)$ and temperature $(T)$ as follows:

$$log\ k = 5.29 + 1.41 \cdot pH - 0.57 \cdot I + 1.40 \cdot \sqrt{I} - \frac{4898}{T} \qquad (2)$$

The first 4 terms on the right-hand side of Eq. 2 integrate the pre-exponential factor of the Arrhenius equation:

$$k = A\ exp\left(\frac{-E_a}{RT}\right) \qquad (3)$$

From Eq. (2) and (3) the activation energy $E_a$ of the homogeneous redox reaction between As(III) and $H_2O_2$ is 94 kJ/mol.

## Gold nanoparticles characterization

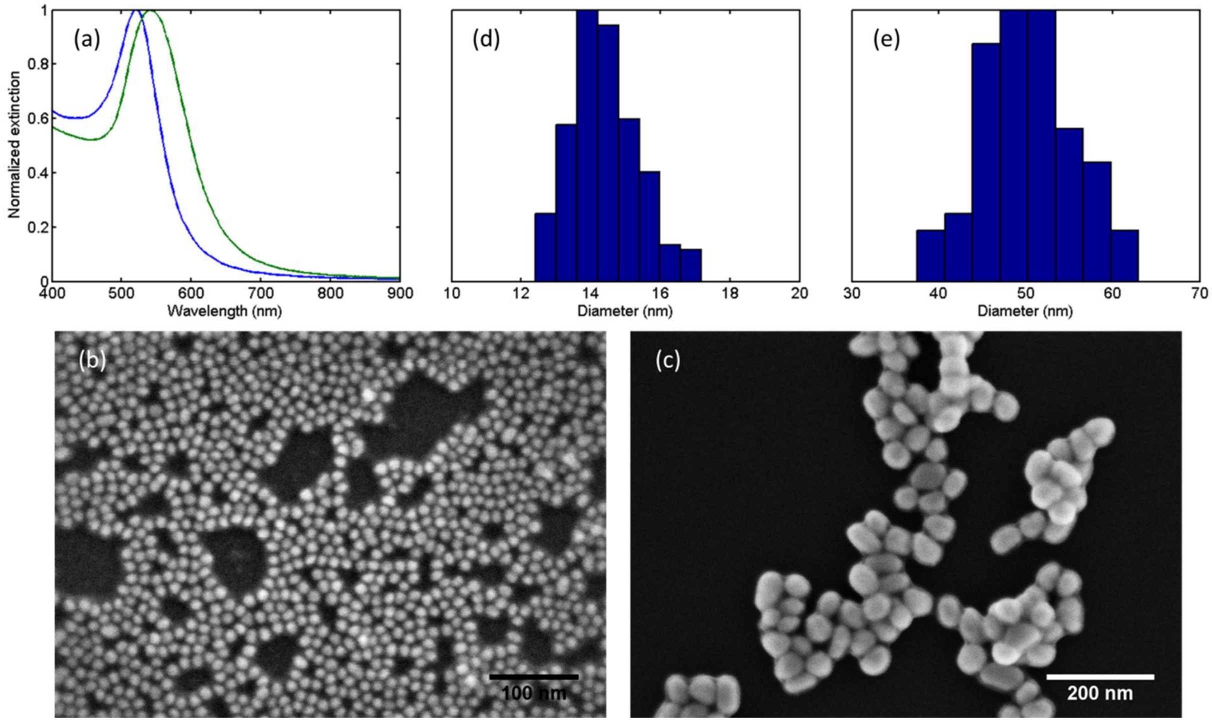

**Figure S1.** (a) Normalized extinction spectra of the synthesized gold colloids, whose average diameters are 14.4 nm (blue curve) and 50.2 nm (green curve), showing their surface plasmon resonances. (b-c) SEM images of the gold nanoparticles on graphite substrate and (d-e) histograms of measured diameters.

## Colorimetric method of Molybdenum Blue (MB)

Stock solution of As(V) was prepared by dissolving analytical grade sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) in ultrapure water. It was used for calibration of the MB method (Figure S2) based on the usual protocol.[56] Samples were prepared with known concentration [As(V)] and then a color reagent was added that gave them a blue color because of the formation of arsenic-molybdic complex. After one hour the absorbance of the samples was measured with a UV-Vis Spectrophotometer as shown in Figure S2a.

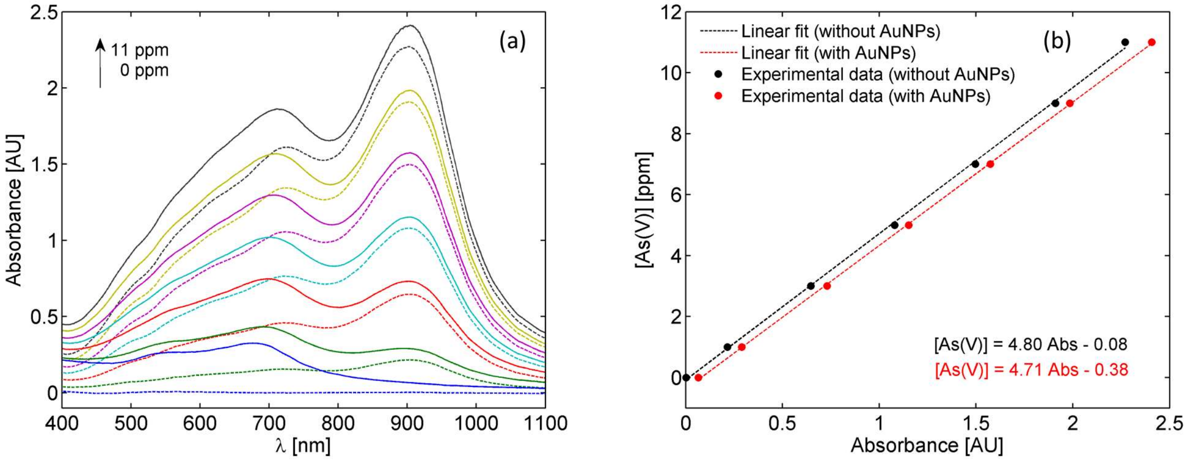

**Figure S2.** (a) Absorption spectrum of arsenic-molybdic complex in aqueous solution (in ascending order corresponds to [As(V)] = 0, 1, 3, 5, 7, 9 and 11 ppm), 1 hour after adding the color reagent (solid line with AuNPs, dotted line without AuNPs). The blue molybdenum complex concentration is measured around 900 nm. (b) Calibration of the MB colorimetric method: [As(V)] (ppm) as a function of maximum absorption of molybdenum blue complex.

The color reagent is prepared from four solutions (25 mL final volume). All the solutions were prepared with ultrapure water and were mixed in the order indicated under constant stirring.

1) Sulfuric acid ($H_2SO_4$) 2.5 M (12.5 mL)
2) 0.137 g antimony and potassium tartrate on 10 mL ultrapure water. It was kept at 4ºC and covered from light (1.25 mL)
3) 1 g ammonium molybdate on 25 mL ultrapure water. It was kept at 4ºC and covered from light (3.75 mL)
4) 0.176 g ascorbic acid in 10 mL ultrapure water. It was prepared the same day that was used (7.5 mL)

**Procedure for determination of arsenite oxidation**

The procedure established to study the conversion of As(III) to As(V) with the colorimetric method in aqueous solution was:

1) Prepare samples with $[\mathrm{As(III)}]_0$, $[H_2O_2]_0$ and [AuNPs] or [core-satellite NPs] with a 1 mL final volume.

2) Wait a certain time in which the As(III) to As(V) conversion occurs (could be minutes, hours or days).

3) In parallel prepare the color reagent to be used within a period of 4 hours.

4) Add 200 μL of color reagent and wait 1 hour until the process of formation of the arsenic-molybdic complex is completed.

5) Measure the absorption of the arsenic-molybdic complex.

6) Use the calibration curve (Figure S2b) to determinate the final [As(V)] in the sample. Knowing the [As(III)]$_0$ in the sample, calculate the percentage of As(III) to As(V) conversion (%) as a function of time.

7) The conversion time is counted from the instant that the samples are prepared until the color reagent is added, instant from which there is no As(III) oxidation due to the slow kinetics at so low pH.

## Arsenic oxidation as a function of initial arsenic concentration

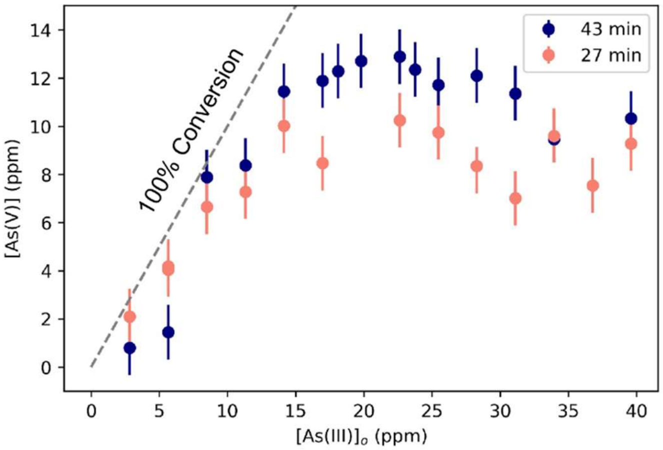

**Figure S3.** Oxidized [As(V)] as a function of [As(III)]$_0$ (ppm) for a redox time of 43 min and 27 min. All samples have [$H_2O_2$]$_0$ = 59 ppm and [AuNPs] = $7.3 \times 10^{11}$ NP/mL. The gray dotted line represents 100% conversion.

## Increment of temperature induced by light

Under uniform and continuous illumination of irradiance *I*, the temperature increment of the NP in the steady-state regime can be approximate by:[40]

$$\Delta T = \frac{\sigma I}{4\pi \kappa_w R} \qquad (4)$$

where σ is the optical absorption cross section of the NP at resonance, *R* its radius, and $\kappa_w$ the thermal conductivity of water. For the nanoparticles used in this work and the irradiance values of the experiments, this temperature increase is in the order of $10^{-3}$ °C, which is negligible considering the measured temperatures in the illuminated colloidal solutions and the appreciable thermal contribution observed in the arsenic oxidation. For this reason, as stated in the Results and Discussion section, we argue that light undergoes multiple scattering in concentrated NPs, increasing their effective absorption cross section.

## Experiments with lower initial arsenic concentrations

Experiments described in Results and Discussion with AuNPs and core-satellite NPs, with initial As(III) concentration of 11 ppm, were also carried out with lower initial arsenic concentrations ($[As(III)]_0$ = 2 and 4 ppm), as can be seen in Figure S4. In the AuNPs case, the conversion percentages are approximately the same as with 11 ppm, and the thermal and hot carriers' contributions to heterogeneous catalysis are still observed (the As oxidation is close to saturation). With core-satellite NPs, the conversion values by heterogeneous catalysis (blue bars) and thermal contribution (red) do not vary significantly for 2, 4 and 11 ppm of initial [As(III)]. In contrast, the plasmonic contribution (green) is clearly larger with 11 ppm because of the higher efficiency in the use of hot carriers in the oxidation process for larger amounts of arsenic in solution.

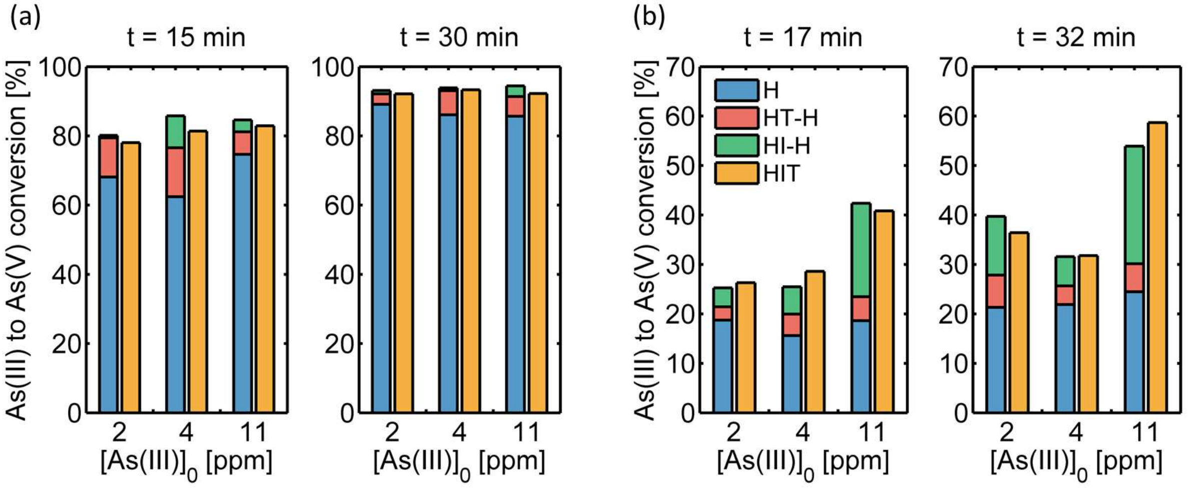

**Figure S4.** (a) Comparison of the sum of heterogeneous (H, blue), thermal (HT-H, red), and plasmonic (HI-H, green) contributions to arsenic conversion with AuNPs after (left panel) 15 and (right panel) 30 minutes, with all contributions together in measurements under plasmon-resonant light (HIT, orange), with initial As(III) concentrations of 2, 4 and 11 ppm. (b) The same comparison of the different catalytic contributions to arsenic conversion with core-satellite NPs after (left panel) 17 and (right panel) 32 minutes.