

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Hollow Au-Ag Bimetallic Nanoparticles with High Photothermal Stability

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1. General EDS spectrum of the sample prepared at pH 8.0 and final Au concentration of 0.20 mM.

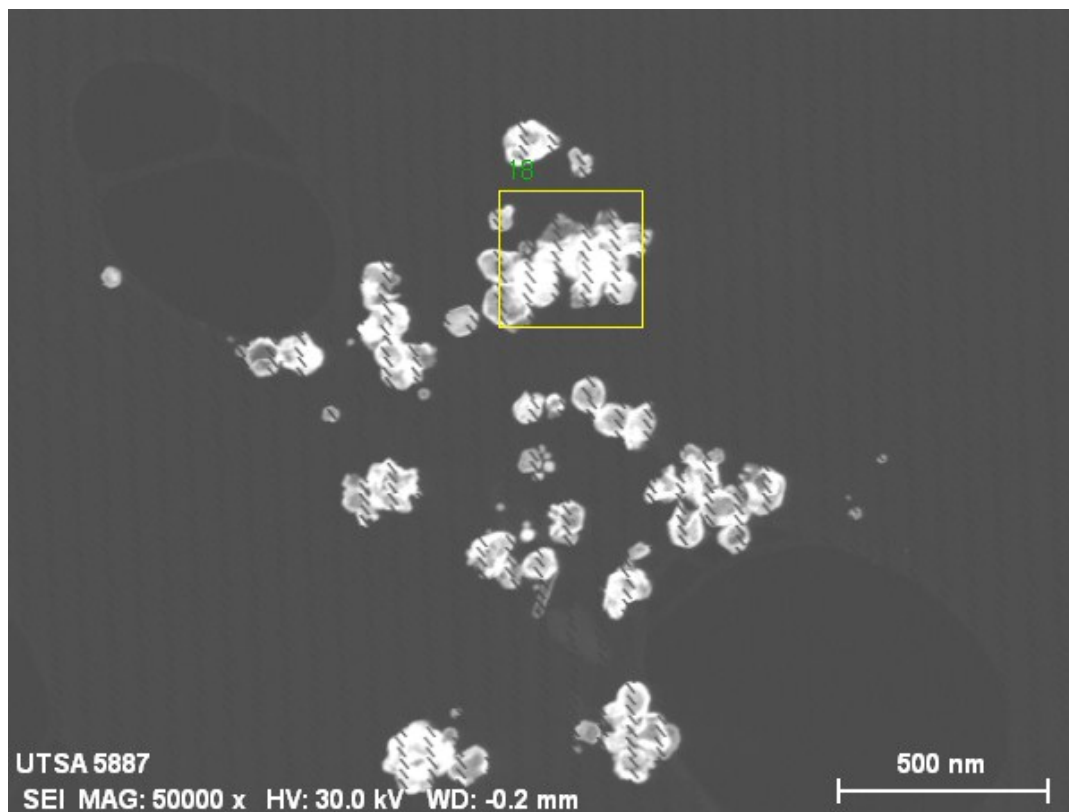


Figure ESI 1. STEM image of the sample analyzed to obtain the general EDS spectrum.

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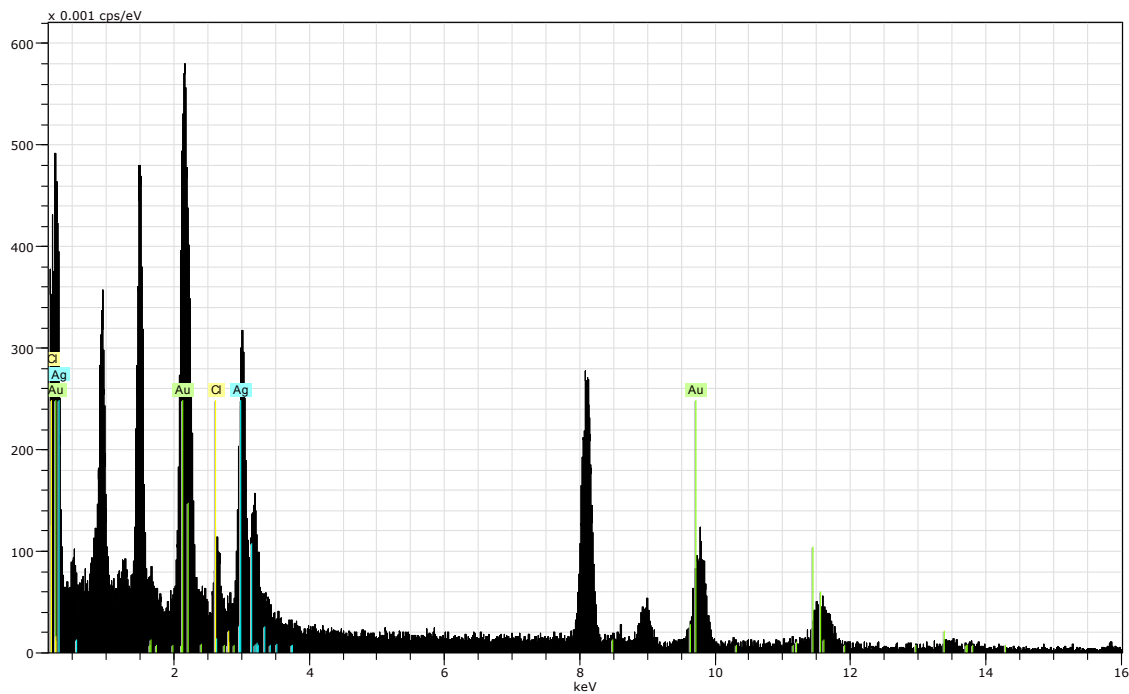


Figure ESI 2. General EDS spectrum of the sample synthesized at pH 8.0 and final Au concentration of 0.20 mM.

Spectrum: 18

El	AN	Series	unn. C	norm. C	Atom. C	Error (1 Sigma)
			[wt.%]	[wt.%]	[at.%]	[wt.%]
Au	79	L-series	51.49	58.50	39.17	1.53
Ag	47	L-series	32.97	37.46	45.80	1.15
Cl	17	K-series	3.56	4.04	15.03	0.20
Total:			88.02	100.00	100.00	

2. Calculation of the photothermal transduction efficiency

The photothermal transduction efficiency of the hollow Au-Ag bimetallic nanoparticles was calculated according to the model proposed by Roper.¹

The energy balance of the system is:

$$\sum_i m_i C_{p,i} \frac{dT}{dt} = Q_I + Q_O - Q_{ext}$$

(1)

where m_i and $C_{p,i}$ are the mass and heat capacity of every element in the system (cuvette, cuvette cap, water), T is the temperature of the solution.

Q_I is the energy input induced by the laser, and represents the heat dissipated by electron-phonon relaxation of plasmons on the surface of the nanoparticles and can be evaluated using the next equation:

$$Q_I = I(1 - 10^{-A_\lambda})\eta_T$$

(2)

where I is the incident laser power (1 W), η_T represents the transduction efficiency and A_λ is the absorbance of the solution at the excitation wavelength (808 nm).

Q_O is the heat dissipated from light absorbed by the cuvette and the solvent. It was measured in an independent experiment using a quartz cell containing 1.5 mL of deionized water, in our system it takes a value of 65.42 mW.

The term Q_{ext} represents the external heat flux in the system and is proportional to the linear thermal driving force, with a heat-transfer coefficient, h :

$$Q_{ext} = hS(T - T_{amb})$$

(3)

If a dimensionless driving force temperature, θ , is introduced, scaled using the maximum temperature of the system, T_{max} ; and a simple system time constant τ_s :

$$\theta = \frac{T_{amb} - T}{T_{amb} - T_{max}}$$

(4)

$$\tau_s = \frac{\sum_i m_i C_{p,i}}{hA}$$

(5)

Which are substituted into equation 1 and rearranged to yield:

$$\frac{d\theta}{dt} = \frac{1}{\tau_s} \left[\frac{Q_I + Q_O}{hA(T_{max} - T_{amb})} - \theta \right]$$

(6)

At the cooling stage, when the laser is turned off, $Q_I + Q_O = 0$, and equation 6 can be simplified to equation 7:

$$dt = -\tau_s \frac{d\theta}{\theta}$$

(7)

Integrating equation 7:

$$t = -\tau_s \ln \theta$$

(12)

In this way, we can obtain the value of τ_s through a linear fit of the t vs $-\ln\theta$ curve from the cooling stage of the temperature vs time curve data. From the value of τ_s , we can

deduce the value of h , and calculate the photothermal conversion efficiency (η) using equation 13:

$$\eta = \frac{hA(T_{max} - T_{amb}) - Q_0}{I(1 - 10^{-A\lambda})}$$

(13)

Figure ESI3 show the linear fit of the experimental data obtained from the cooling stage of the temperatura vs time curve of figure 6. The experimental data corresponds to 600 seconds after the laser was turned off. The calculated photothermal transduction efficiency of our system was 74.68%, according to equation 13.

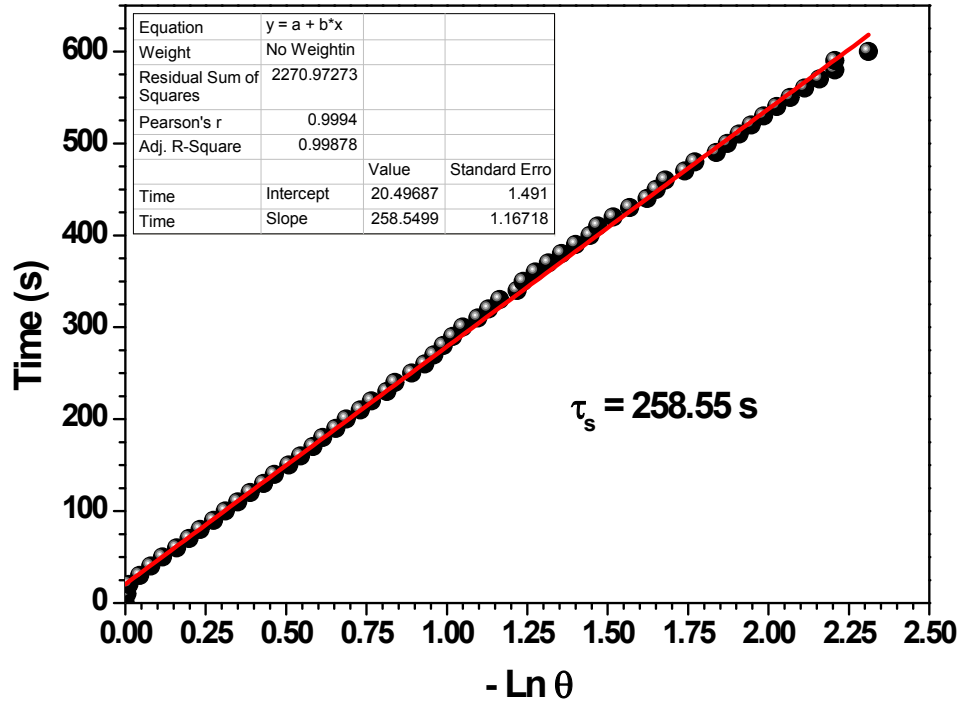


Figure ESI 3. Linear fit of the time vs $-\ln\theta$ obtained from the cooling stage of the heating experiments (Figure 6).

Figure ESI4 presents the fitting of the heating and cooling stages of the experimental data obtained from the heating experiment of a nanoparticle solution with an absorbance of 1.0 (figure 6). Given the exponential dependence of both stages, they can be fitted using the next pair of equation for the cooling and heating regions, respectively:

$$\theta = \exp\left(\frac{-t}{\tau_s}\right)$$

(14)

$$\theta = 1 - \exp\left(\frac{-t}{\tau_s}\right)$$

(15)

and then resolving equation 4 for T .

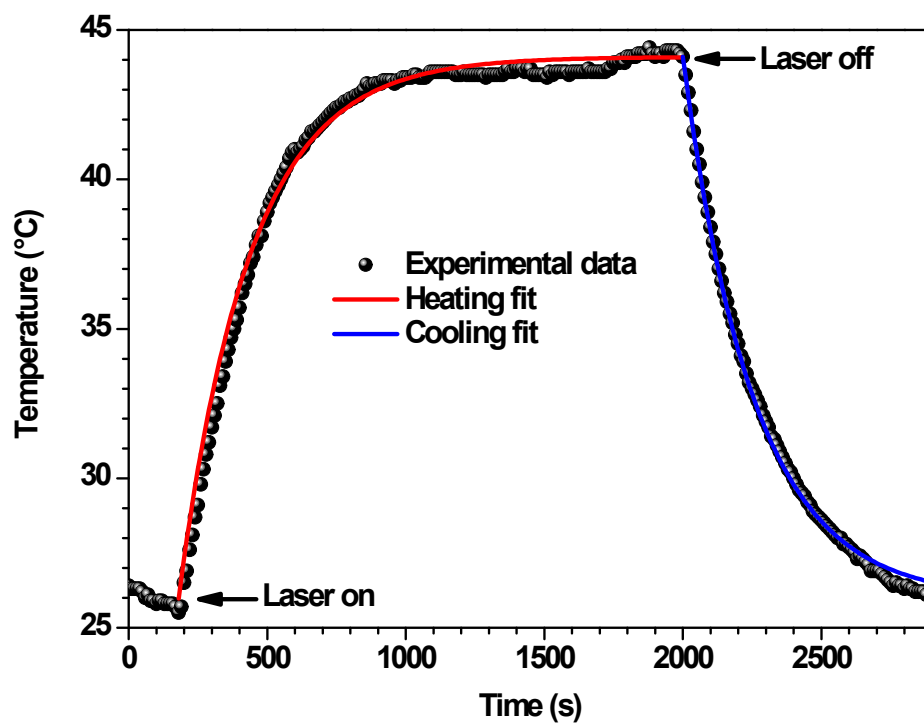


Figure ESI 4. Fitting of the experimental data for both heating (red line) and cooling (blue line) stages of the temperature vs time curve.

3. Colloidal stability of the nanoparticles at different pH values

Aqueous solutions of the nanoparticles were prepared at different pH values in the interval 2-11; hydrochloric acid and sodium hydroxide were utilized to adjust pH values. The extinction spectra of the solutions were obtained after an incubation period of 15 minutes at the desired pH and is presented in figure ESI5.

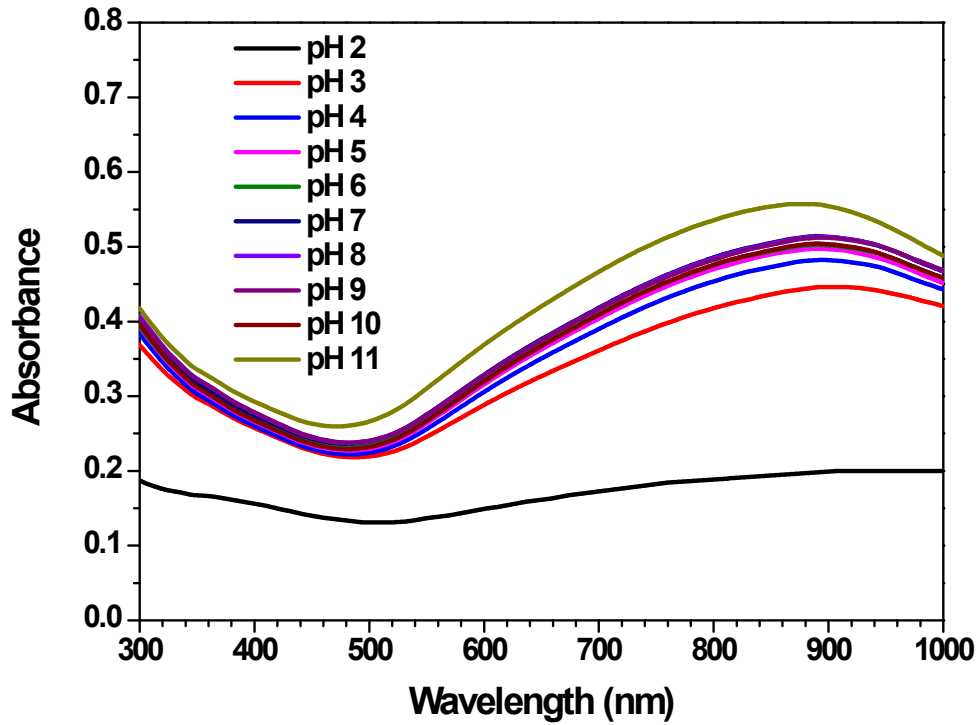


Figure ESI 5. Extinction spectra from nanoparticle solutions at different pH values.

4. References

- 1 D. K. Roper, *J. Phys. Chem. C*, 2007, **111**, 3636.
- 2 Z. Liu, L. Cheng, L. Zhang, Z. Yang, Z. Liu, J. Fang, *Biomaterials*, 2014, **35**, 4099.