Electronic Supplementary Material (ESI) for Faraday Discussions.

Supplemental Information – Unearthing the factors governing site specific rates of electronic excitations in multicomponent plasmonic systems and catalysts

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1. Ag nanocube synthesis

Ag nanocubes were synthesized utilizing a standard colloidal synthesis method.[1] Ethylene glycol (VWR International, semigrade), $AgNO_3$ (Acros Organics, ultrapure grade 99.5%) and polyvinylpyrrolidone (PVP, MW=55,000 Sigma-Aldrich) were purchased and used as received. First, 10 mL of ethylene glycol were placed in a 20 mL glass vial and allowed to heat to 140°C in an oil bath. Next, 80 µL of a 36 mM aqueous HCl solution was added to the vial after 1h. After 10 min, 5 mL of a 10 mg/mL solution of PVP in ethylene glycol was added to the reaction. Subsequently, 2 mL of a 25 mg/mL solution of $AgNO_3$ in ethylene glycol was added and a ventilated cap was placed on the vial. The vial and its contents were then heated for ~24 h. next, the ventilated caps were replaced with non-ventilated caps to prevent O_2 from entering the system. After ~8-10h, the nanoparticle solution transmits a vibrate pink/purple, corresponding to ~75 nm cubes. The vial was then quenched and the nanoparticles were washed with a 1:10 water:acetone mixture via centrifugation and redispersed in DI water to 10 mL. The washing process was repeated twice.

2. Coating of Cu_2O onto Ag nanocube seeds

Thin shells of Cu_2O were coated onto the Ag nanocube seeds modifying a recently reported synthesis method.[2] Briefly, 5 mL of a 2500 mg/25 mL stock solution of PVP in water was added to a centrifuge tube. Next, 2 mL of the Ag cube seed solution (after washing) was added to the PVP solution under constant stirring, followed by 20 µL of an aqueous 0.1 M $Cu(NO_3)_2$ solution. Next, 11.2 µL of a 5 M NaOH solution was added. Finally, 5 µL of a hydrazine solution (30 wt% hydrazine) in water was added as a reducing agent. After 10 min, the particles were centrifuged, washed twice in ethanol and redispersed in 10 mL of water.

3. Extinction, absorption and scattering measurements

For the optical measurements, all Ag-Cu_2O nanoparticles were synthesized from the same sample of Ag nanoparticle seeds. To prepare the samples for the optical measurements, Ag and Ag-Cu_2O nanoparticles solutions were placed into 3 mL cuvettes and diluted with DI water. The samples were prepared so they gave the same amount of fractional extinction with a total solution volume of 3 mL. A UV-vis spectrometer in transmission mode was used to generate extinction spectra of the samples using the following equation:

$Extinction = 1 - Transmission\ Fraction.$

And an integrating sphere set up described previously[3] was used to measure the sum of the transmission and scattering fractions. This allowed the fractional absorption to be calculated via the equation:

$$Absorption\ fraction = 1 - (transmission + scattering\ fraction).$$

The scattering fraction can then be calculated from the extinction and absorption fractions. It is important to note that the extinction and absorption of pure water was also measured and subtracted out of all of the measurements.

4. Finite element method simulations

Model set-up

The optical characteristics of the studied plasmonic particles were simulated using COMSOL Multiphysics finite-element based software. The '*Wave optics*' module was used to calculate the radiative field resulting from a plane wave impinging on a 3-dimensional nanoparticle. The plane wave was defined as: $E = E_0 e^{-ikx}$ and was polarized in the z-direction for the nanocubes.
Each core-shell material was created in the model and the wavelength range from 300 nm to 900 nm was simulated. The corners of the nanocubes in the simulations were smoothed to reflect the particle geometry observed in TEM characterization. Dielectric data for Ag was taken from COMSOL's Optical Materials database (Rakic et. al)[4], and from the handbook of optical properties for Cu_2O[5]. A region of air (water for the Ag-MB case) was defined around the particle by setting the real part of the dielectric function equal to 1 (or 1.33 for water). The width of the region of air (water) around the particle was equal to half the wavelength of the incident plane wave and a perfectly matched layer (PML) was constructed to act as an absorber of the scattered field. The calculations are discussed in the following sections.

Extinction, absorption and scattering calculations

The absorption cross section as a function of wavelength was calculated by integrating the resistive heating losses over the volume of the nanoparticles. Absorption for a particular region of the nanoparticles (i.e. the core or the shell) were calculated by integrating the heating losses over the core and shell volumes explicitly defined in the model. To calculate the scattering cross section, the dot product of the normal vector pointing outwards from the particle surface area and the scattered intensity vector was integrated across the entire particle surface for each wavelength. The extinction was determined by summing the absorption and scattering cross sections. Fractions were obtained by defining the maximum value of the extinction (or absorption for the absorption fraction graphs) as 1 and scaling all values relative to that particular value.

Electric field calculation

The electric field at the core-shell interface was calculated by integrating the field intensity over the surface of the particle. The field intensity was normalized by the background field intensity (i.e. by the field intensity from the simulation with no particle included).

Normalized shell absorption ratio calculation

The simulated shell absorption ratio (corrected for the fields) in Fig. 5d and Fig. 6f was calculated using the following equation (using Cu_2O as an example):

$$Ratio = \frac{A_{Shell,\ AgCu2O}}{A_{Shell,\ Ag}} * \frac{E_{Ag}}{E_{AgCu2O}}$$

where $A_{\text{Shell AgCu2O}}$ (E_{AgCu2O}) and $A_{\text{Shell Ag}}$ (E_{Ag}) are the calculated absorption (field enhancements) in the Cu_2O shell of the Ag-Cu_2O particle and the absorption in the Ag shell of the Ag-Ag particle respectively. The fields were calculated at the interface between the core and the shell. For the Ag-MB case (Fig. 6f), the Cu_2O shell absorption/fields was replaced by the MB shell absorption/fields.

5. AgMB Absorption Measurements

To measure the extinction, absorption and scattering contribution for Ag nanoparticles and Ag-MB system we used diluted solutions of Ag nanoparticles (extinction ~ 1.1) and we used low MB concentration (340 nm) to avoid any dye-dye interaction.[6] We removed any contribution from the solvent by using a sample of just DI water and subtracting it from all the measurements. Extinction measurements were performed using a UV-vis spectrophotometer.

The extinction fraction is the sum of the absorption fraction and scattering fraction. To decouple absorption from scattering contribution, we performed an optical integrating sphere measurement (as described above). Similarly, to measure the enhanced optical absorption of MB in the proximity of Ag, we used integrating sphere measurement and we observed noticeable change in the absorption spectrum of MB in the vicinity of Ag nanoparticle.[6]

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