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Abstract

Plasmonic materials are intensively used to extend the photoactivity of large bandgap semiconductors within the visible light region. In the present study, we investigate and discuss the role played by core-shell Au@Ag nanorods as photosensitizing elements of TiO₂ in terms of a hot electron injection mechanism. In this framework, we observe that the use of bimetallic architectures leads to a 3-fold increase in the catalytic efficiency of the semiconductor TiO₂ compared to that found for pure Au photosensitizers. The mechanism has then been computed theoretically in order to ascertain the physical reasons behind this observation. Interestingly, the high enhancement of the electromagnetic field created inside and at the surface of the Au@Ag nanorods leads to very efficient quantum plasmon-assisted generation of high-energy electrons near the outermost layer of the Ag surface. Moreover, the blue-shifted interband transitions of silver allow for the formation of transverse plasmonic modes with very low damping, thus leading to strong and sharp peaks with high rates of hot electron generation. Such behavior is hindered in the case of pure Au nanorods, in which the transverse plasmons are strongly damped. The great potential of these architectures is confirmed by their remarkable performance toward photocatalytic hydrogen generation, rendering this approach an appealing strategy in the search for efficient solar-driven energy systems.

Synthesis and Characterization

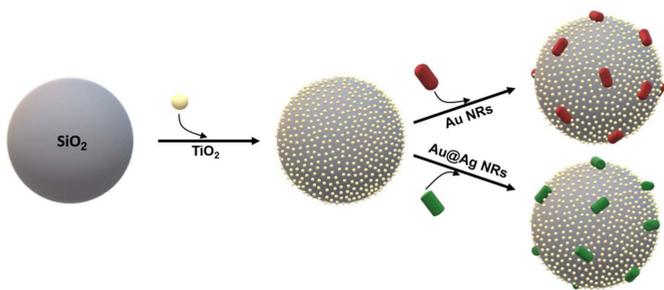


Figure 1. Scheme depicting the layer-by-layer assembly of the hybrid photocatalysts. In a first stage, TiO₂NPs are adsorbed onto 500 nm SiO₂spheres. Subsequently, the chosen plasmonic component is added

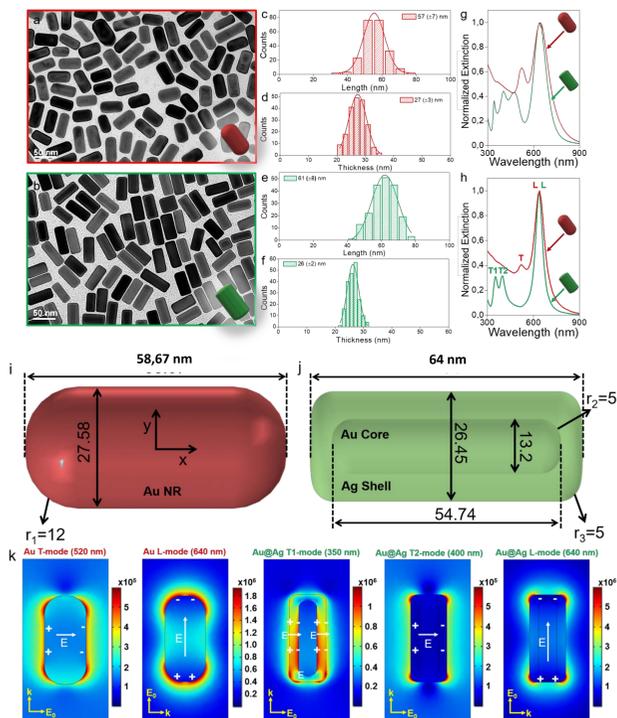


Figure 2. (a and b) TEM images, (c–f) size histograms, and (g) experimental and (h) theoretical extinction spectra of the Au NRs (red) and the Au@Ag NRs (green). Morphological features for the simulation of (i) Au NRs and (j) Au@Ag NRs (with r_1 , r_2 , and r_3 being the radius of curvature for rounding edges). (k) Near-field enhancement maps of the plasmonic modes of the Au and Au@Ag NRs.

Catalytic Activity

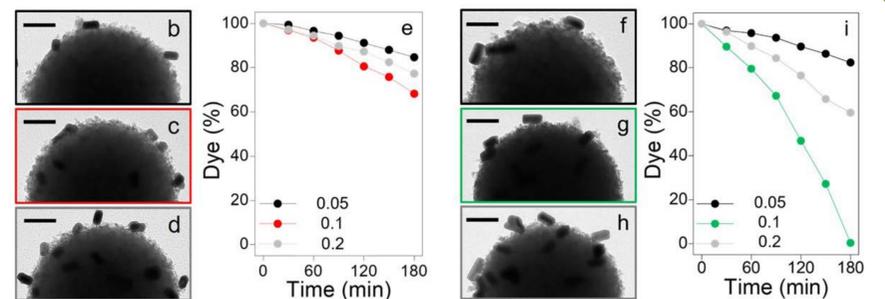


Figure 3. (b–d) TEM images and (e) photocatalytic activity profiles of the hybrid photocatalysts formed with different amounts of Au NRs, leading to metal/TiO₂ molar ratios of 0.05 (black), 0.1 (red), and 0.2 (gray). (f–h) TEM images and (i) photocatalytic activity profiles of the hybrid photocatalysts formed with different amounts of Au@Ag NRs, leading to metal/TiO₂ molar ratios of 0.05 (black), 0.1 (green), and 0.2 (gray). Scale bars in the TEM images are 100 nm.

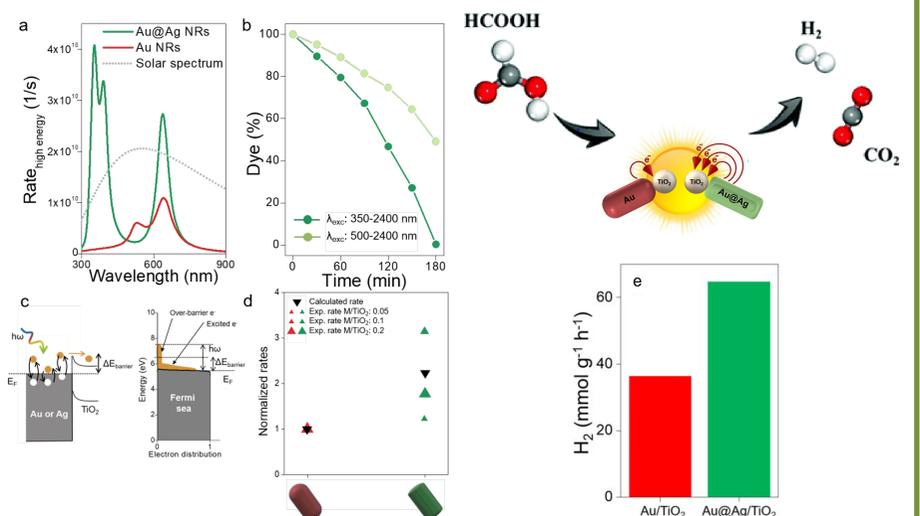


Figure 4. (a) Calculated rates for hot electrons generation of the Au and Au@Ag NRs. (b) Photocatalytic activity profiles of the hybrid photocatalyst formed with Au@Ag NRs (metal/TiO₂ molar ratio of 0.1) using the entire spectrum of the solar simulator (dark green) and only the 500–2400 nm range (light green). (c) Schematic representation of the mechanism of hot-electron injection and the distribution of excited electrons in the optically driven Fermi sea of electrons in a metal nanocrystal. (d) Comparison of the calculated hot-electron rates and the measured photocatalytic rates for the degradation of RhB. (e) Photocatalytic hydrogen generation assisted by formic acid in the presence of SiO₂@TiO₂ (gray) and SiO₂@TiO₂ nanocomposites photosensitized by Au NRs (red) and Au@Ag NRs (green). Irradiation, 350–2400 nm; T=35°C; P= 1.0 atm; metal/TiO₂= 0.1.

Conclusions

- We demonstrate that the use of bimetallic Au@AgNRs ensures an improved photocatalytic activity with respect to monometallic Au NRs with similar geometries and the role played by the nature of the plasmonic component in the photosensitization of TiO₂.
- Calculations show that the stronger plasmonic resonances and the limited interband damping effect in Ag ensure elevated hot-electron injection rates and hence improved photosensitization of the semiconductor material.
- Accordingly, the present study demonstrates how the careful selection of the type and geometry of the plasmonic component can be used to engineer hybrid systems with enhanced photochemical capabilities, thus opening the door to their implementation in different areas of photocatalysis and photovoltaics such as environmental remediation, water splitting, CO₂ conversion, and organic solar cells.