Photoproduction of hydrogen with alloy plasmonic nanoparticles made with the spark-discharge particle generator

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Photoelectrochemical (PEC) water splitting is a promising technology to convert solar energy directly into H_2. When a PEC water splitting device consisting on a single semiconductor photoanode is irradiated with light, electron-hole pairs are created in the semiconductor due to interband excitations. The holes migrate to the surface of the semiconductor to drive the water oxidation reaction, while the electrons migrate to the counter electrode to drive the water reduction reaction. One of the factors that limits the efficiency of the PEC water splitting devices are the relatively large bandgaps of promising semiconductor photoanodes (for example, TiO_2). These large bandgaps restrict the light utilization of the device to the UV region of the spectrum.

To extend the light utilization to the visible region of the spectrum, the semiconductor can be functionalized with light absorbing metallic nanoparticles (NPs). Due to the surface plasmon resonance phenomenon, metallic NPs can interact with visible light, creating electron-hole pairs due to intraband excitations in the metal. This way, the holes can drive the water oxidation reaction on the NP surface and the electrons can be injected to the conduction band of the neighbouring semiconductor and migrate to the counter electrode to drive the water reduction reaction. Therefore, the semiconductor and the metallic NPs simultaneously absorb light and drive the water splitting half reactions.

The absorption spectra of the decorating NPs should be tuned to absorb light with lower energies than the neighbouring semiconductor bandgap edge. This is done to avoid screening of light to the semiconductor and to extend the visible light utilization of the device. Since the metallic NPs' absorption range highly depends on their composition, it is important to be able to synthesize NPs with control and flexibility over their composition. This work demonstrates that the spark discharge particle generation technique (Schwyn et al., 1988) is ideal to produce alloy metallic NPs with tunable absorption range for efficient solar H_2 production.

Methodology: Alloy electrodes (Ag/Au) were used as feedstock in the spark-discharge particle generator (SDG) to produce aerosol alloy (Ag/Au) NPs. The particles are sintered into spheres in a tube oven. Subsequently, they are size-selected with a differential mobility analyzer. An electrostatic precipitator is used to deposit the particles on a semiconductor (TiO_2) film.

Results: Figure 1A shows the absorption spectrum of the synthesized alloy (Ag/Au) NPs. In the same figure, the absorption spectra of pure Ag and Au NPs are shown for comparison. It can be clearly seen that the absorption range of the alloy NPs covers a distinct region of the spectrum that is not covered by the pure NP counterparts. Figure 1B shows the corresponding H_2 photoproduction of the synthesized NPs.

Conclusions: The SDG ability to synthesize NP from arbitrary conducting feedstock materials (for example, alloys), allows this technique to produce metallic NPs with a tunable absorption range. This versatility allows to study and optimize the performance of solar energy conversion devices.

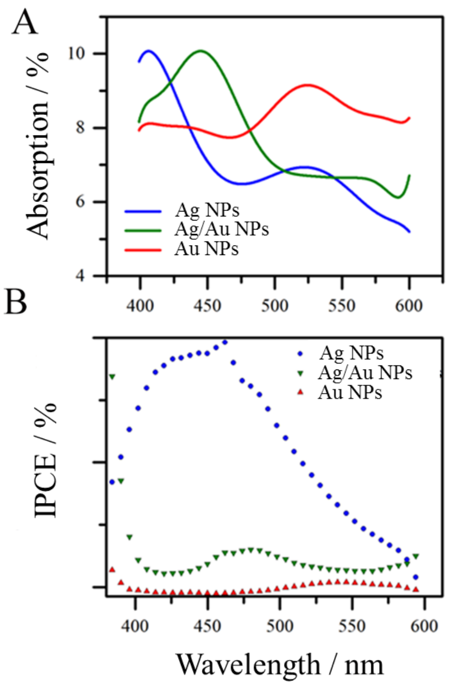

Figure 1. A) NP absorption spectra. B) IPCE enhancement of TiO2 films when decorated with 15 nm NPs at 0.6 V vs RHE.

Schwyn, S., Garwin, E. & Schmidt-Ott, A., *J. AerosolSci.*, 19(5), 639-642 (1998).