**Plasmonic photocurrent transients reveal charge carrier dynamics in plasmon driven catalysis**

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**Introduction**

Localized surface plasmons (LSPs) are collective electron cloud oscillations and are a key feature in noble metal nanoparticles. Non-radiative decay of this energetically excited state can generate hot charge carriers, which carry energy that may be harvested for photoelectrocatalysis before further thermalization. The mechanisms of plasmon driven catalysis is still under debate and insights into charge carrier dynamics help to understand the underlying processes.

**Aims**

Creating a well-defined photoanode system that combines the photocatalytic properties of the semiconductor WO3 with the plasmonic hot carriers generated in Au noble metal nanoparticle arrays. WO3 is an n-type semiconductor suitable for water oxidation. Plasmon excitation is introduced into this system by decorating a WO3 thin-film with an Au nanoparticle array and its effect on the photoelectrocatalytic oxidation on WO3 is investigated with focus on the charge carrier dynamics.

**Methods**

WO3 thin-films are prepared by reactive magnetron sputtering and post-annealing. The Au nanoparticle arrays are obtained by means of nanosphere lithography. Photoelectrochemical measurements are used to characterize the system performance and quantum efficiency.

**Results**

Photocurrent measurements with chopped AM1.5 light illumination reveal plasmon induced photocurrent transients. The intensity of the photocurrent transients follows the absorption intensity of the LSP resonance. This suggests a clear correlation and hence a plasmon signature in the observed photocurrents.

**Discussion**

The photocurrent transients are a result of cathodic currents. These can be described as recombination processes via surface states. In the present study, we use the concept of photogenerated surface states, i.e. hot holes generated from non-radiative plasmon decay. Photogenerated electrons can recombine with those surface states below the Fermi energy which results in a cathodic back-current.

**Conclusion**

WO3 thin-films decorated with an Au nanoparticle arrays were prepared as a composite photoanode for photoelectrochemical water oxidation. The Au nanoparticles cause an overall decrease in the photocurrent but cause the emergence of pronounced photocurrent transients. Spectral analysis shows that the photocurrent transients closely follow the spectral absorption profile of the plasmon excitation and gives insights into the charge carrier dynamics at the gold nanoparticle-WO3 thin-film interface.

**For further information:**

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