

## Dynamics of charge transfer from plasmonic nanoparticles to cerium oxide

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**Summary.** — The combination of semiconducting oxide-based materials with plasmonic nanoparticles (NPs) aims to efficiently convert solar light into chemical or electric energy, exploiting the excitation of localized surface plasmon resonance (LSPR) in the NPs that leads to a significant energy/charge transfer to the oxide. By performing UV-Visible spectrophotometry measurements on systems composed of Cu/Au NPs embedded in a matrix of CeO<sub>2</sub>, we observed a wide absorption band in the visible range, ascribed to the LSPR excitation in the NPs. Femtosecond transient absorption spectroscopy at different pump energies across the LSPR band of the NPs unveiled a persistent charge transfer from the NPs to CeO<sub>2</sub>. Efficiency up to 35% for systems with Au NPs has been estimated.

### 1. – Introduction

In recent years, the demand for systems which can act as catalysts for environmental protection has rapidly increased. CeO<sub>2</sub> is a promising material thanks to its catalytic properties [1], but CeO<sub>2</sub> alone is not efficient in solar light absorption, because of its wide bandgap [2]. To sensitize CeO<sub>2</sub> to visible radiation, it is possible to combine it with plasmonic NPs, such as Ag, Au or Cu [3-5], taking advantage of their strong absorption and scattering cross section of visible light. The interaction of light with NPs triggers the LSPRs: when the NPs are coupled with a semiconductor, the relaxation of LSPRs may lead to a charge transfer from the NPs to the surroundings. The two prevalent mechanisms are the injection of hot electrons generated in the NPs and the direct metal-to-semiconductor interfacial charge transfer [4, 6-8].

In this work, we studied systems of Au and Cu NPs coupled with CeO<sub>2</sub> (respectively Au@CeO<sub>2</sub> and Cu@CeO<sub>2</sub>), focusing in particular on the dynamics of the systems excited with visible light, to have information on the charge injection from the NPs to CeO<sub>2</sub>. The basis for this study has been set by the previous work we performed for similar system composed of Ag NPs coupled with CeO<sub>2</sub> [3, 9], where we exploited the chemical

sensitivity of free electron laser time-resolved soft X-ray absorption spectroscopy to study the charge injection from Ag NPs to CeO<sub>2</sub>. The ultrafast changes ( $\tau < 200$  fs) of the Ce N<sub>4,5</sub> absorption edge demonstrated that charges are transferred from the excited NPs to Ce atoms via highly efficient electron-based mechanisms. Here, we demonstrate that charges are injected from Au or Cu NPs to the surrounding CeO<sub>2</sub>, and that for Au@CeO<sub>2</sub> systems the efficiency of this process reaches values up to 35%.

## 2. – Methods

**2.1. Sample preparation.** – The samples were prepared in the ultra-high vacuum apparatus described in [10], and deposited onto a double side polished quartz kept at room temperature (RT). CeO<sub>2</sub> thin films of 2 nm were grown by reactive molecular beam epitaxy of Ce in an oxygen partial pressure. 2 nm nominal thicknesses of Au or Cu were evaporated by a Knudsen cell onto the CeO<sub>2</sub> substrates at RT, where they self-assemble forming NPs [11]. Finally, a second CeO<sub>2</sub> layer of 2 nm was deposited to maximize the NP-oxide interface, and (in case of Cu@CeO<sub>2</sub> system) to prevent NPs oxidation. A CeO<sub>2</sub> film of 4 nm thickness was also measured for reference.

**2.2. Sample characterization.** – After growing, the two samples were characterized by *in situ* X-Ray Photoelectron Spectroscopy (XPS) to access quantitative information on the deposited quantity of CeO<sub>2</sub> and metal and on their chemical state. Secondly, on the Au@CeO<sub>2</sub> and Cu@CeO<sub>2</sub> samples we performed steady ultraviolet-visible (UV-Vis) spectrophotometry measurements using a white light source generated by a Xe lamp. The sample surface normal was oriented at an angle of 22° with the incident photon beam, and we deduced absorption  $A$  by measuring the fraction of transmitted  $T$  and reflected  $R$  light ( $A = 1 - T - R$ ). The results were compared with a reference film of CeO<sub>2</sub>.

To characterize the charge injection from the NPs to the surrounding oxide, femtosecond transient absorbance spectroscopy (FTAS) measurements have been performed using a pump-probe femtosecond laser system described in [3]. The pump-probe delay was scanned between  $-1$  ps and 300 ps, using a white light supercontinuum pulse as a probe in the range of 360–750 nm. We also estimated the charge injection efficiency for both systems, and compared it with the efficiency calculated for the Ag@CeO<sub>2</sub> system previously studied [3].

## 3. – Results and discussion

Figure 1 shows the steady UV-Vis absorbance of the Au@CeO<sub>2</sub> and Cu@CeO<sub>2</sub> samples, compared with a film of CeO<sub>2</sub>. The peak at  $\simeq 300$  nm present for all samples can be ascribed to the interband transitions in CeO<sub>2</sub> [3]. When metal NPs are introduced, the broad peak between 400 and 500 nm (550 for Cu) corresponds to interband excitations in the metal, while the broad band at higher wavelengths is due to LSPR excitation [5, 12].

Figure 2 reports the false-color map of transient absorbance (TA) spectra of Au@CeO<sub>2</sub> and Cu@CeO<sub>2</sub> pumped above the CeO<sub>2</sub> optical band gap (275 nm) and below it (550 nm for Au, 650 nm for Cu). The maps report the TA intensity as a function of the pump-probe delay time ( $x$ -axis) and of the probe wavelength ( $y$ -axis). The Au TA map is dominated by three main features: a positive and a negative broad bands between 400 nm and 700 nm, which can be ascribed to the LSPR excitation of NPs and a sharp positive band at 350 nm. In the Cu@CeO<sub>2</sub> map, the negative wing is not visible because

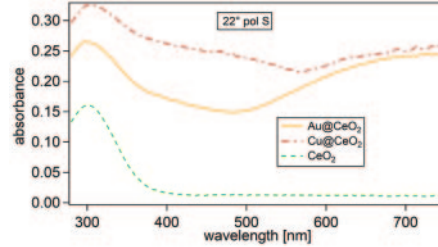


Fig. 1. – UV-Vis spectra of Au@CeO<sub>2</sub> (solid line), Cu@CeO<sub>2</sub> (dash-dotted line) and CeO<sub>2</sub> layer (dashed line).

it is located at higher wavelength, while we can clearly distinguish the two positive features. The peak at 350 nm is associated with the photoinduced absorption (PIA) signal in CeO<sub>2</sub>, since the position of this peak corresponds to the energy separation between the Ce 4f and the Ce 5d levels, and its long duration ( $t > 300$ ) ps is compatible with the stability of the photoexcited electrons in CeO<sub>2</sub> with respect to recombination [3]. The presence of the PIA signal in the samples pumped at the LSPR peak, well below the CeO<sub>2</sub> band gap, clearly demonstrates the transfer of charges from the NPs to the oxide. To calculate the charge injection efficiency, we compared the TA signals at 350 nm of the Au@CeO<sub>2</sub> sample pumped at 550 nm with the signal of CeO<sub>2</sub> pumped at 275 nm, in the time range following the LSPR-related transient signals, *i.e.*, between 50 ps and 300 ps (see [3] for details). For Cu@CeO<sub>2</sub> system we derived a charge injection efficiency around 10%, while for Au@CeO<sub>2</sub> the efficiency is up to 35%. Comparing this result with the one we previously found for Ag@CeO<sub>2</sub> systems, around 15%, we can conclude that the Au@CeO<sub>2</sub> system is very efficient in terms of charge transfer into CeO<sub>2</sub>.

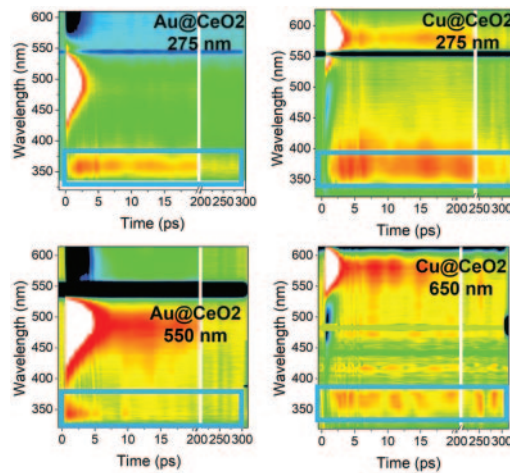


Fig. 2. – TA maps of Au@CeO<sub>2</sub> system pumped at (a) 275 nm and (b) 550 nm and of Cu@CeO<sub>2</sub> system pumped at (c) 275 nm and (d) 650 nm. The box at 350 nm highlights the PIA signal.

#### 4. – Conclusions

We reported that systems composed of Au or Cu NPs coupled with CeO<sub>2</sub> exhibit a broad optical absorbance band in the visible range that can be ascribed to the LSPR excitation in the NP. We demonstrated the charge transfer from the metal NPs into the surrounding oxide, facilitated by the LSPR excitation. Au@CeO<sub>2</sub> system showed a really high injection efficiency.

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