

Supporting Information

Interface interactions and enhanced room temperature ferromagnetism of Ag@CeO₂ nanostructures

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1. Preferential crystallographic orientation at the interface and in the ceria shell.

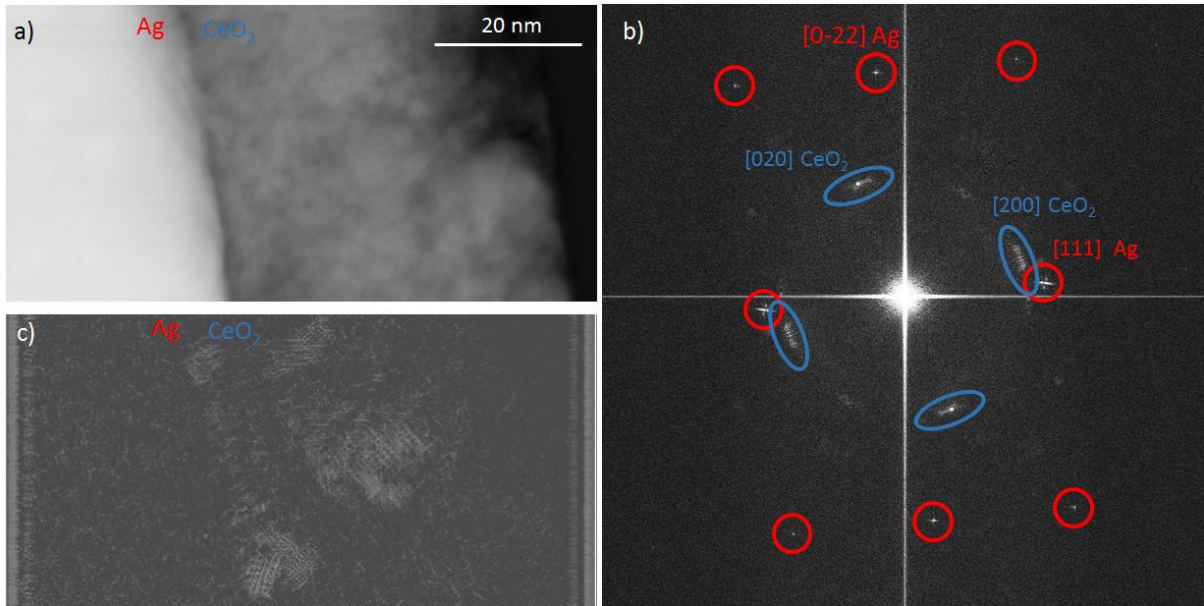


Fig S1 : Preferential crystallographic orientation at the interface and in the ceria shell.

a) STEM-HAADF of core shell Ag@CeO₂.

b) Diffractogram from the STEM-HAADF images. The Ag core has a monocrystalline structure exhibiting narrow [hkl] spots. The Ag zone axis is [-211]. The ceria shell has mostly an orientation corresponding to a zone axis [002]. The [hkl] spots show elongated features corresponding to the strain, defect and misorientation between grains.

c) Fourier filtered images obtained by selecting the [020] and [200] spots. The preferential orientation can extend from the interface to several tens of nanometers into the shell.

2. Oxygen vacancy at the surface and the interface.

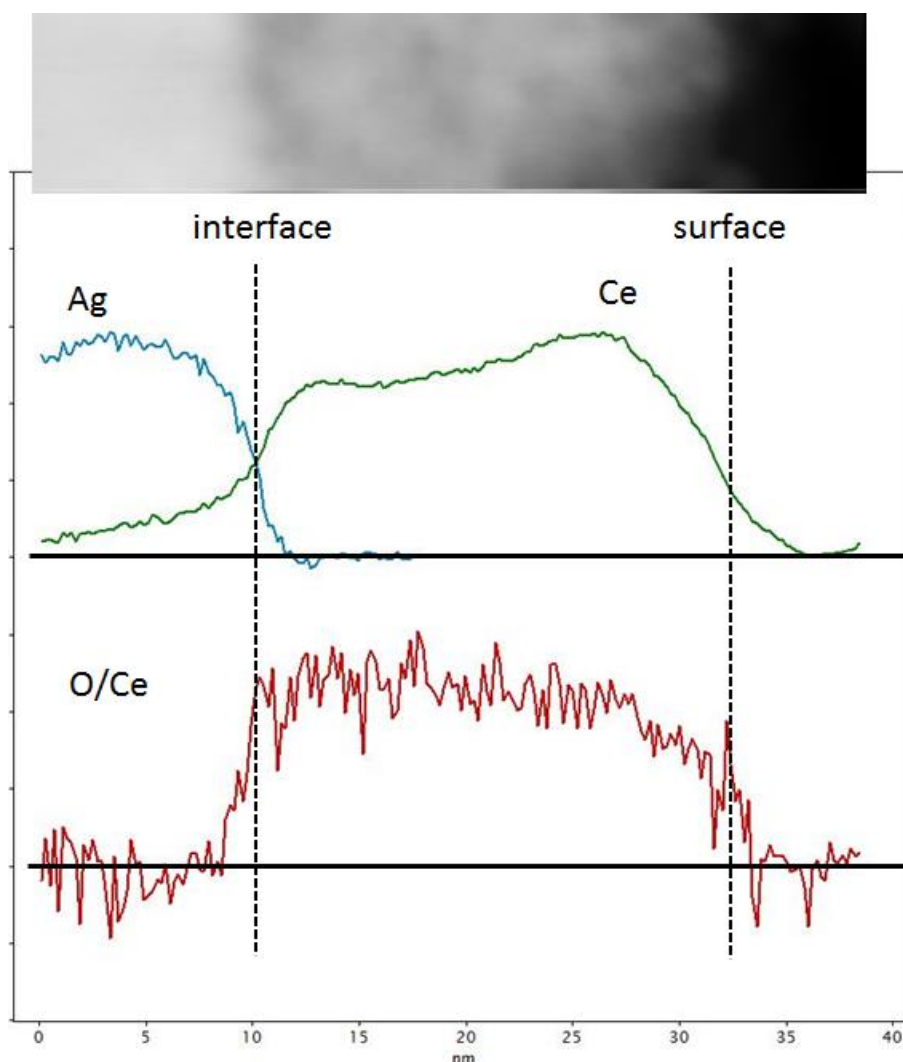


Fig. S2 : **STEM-EELS investigation of the elemental concentration.**

At the upper part is the STEM-HAADF image collected during the spectro-microscopy measurements.

At the lower part, the profiles obtained with the EELS intensity of the Ag-M and Ce-M edges confirm the position of the interface and surface. The O/Ce ratio, obtained with the quantification of the O-K/Ce-M edges intensity ratios, evidences the presence of oxygen vacancies at the surface that extended over several nanometer. At the interface, the O/Ce ratio does not show significant alteration.

The elemental EELS quantification has also confirmed that a small amount of Ti atoms were present at the surface of the Ag core before and after core-shelling as it was reported previously for a similar system [Tsai 2015].

3. Ag $M_{4,5}$ EELS spectra.

The Ag $M_{4,5}$ edges are located at around 360 eV and can be measured with atomic resolution. The Fig. S3 show the overall shape of the Ag $M_{4,5}$ measured at the central part of the Ag core and at the interface with the ceria. The spectra exhibit a small pre-edges at around 360-380 eV and a very intense delayed edges at higher energies. As reported previously [Paolucci 1991] the pre-edge is mostly occurring from transition from $3d$ state to p final states while the intense edges is related to f final states. Due to selection rules ($\Delta l = -1$ contributions are weaker than $\Delta l = +1$) the p states have weak cross section and appears as a weak pre-edge. The signal to noise ratio of the EELS spectra is then limited, despite the use of a Cs corrected STEM microscope and of a home-design efficient EELS detection. A faint difference at around 380 eV can be observed at the interface edge with respect to the bulk edge (Fig. S3-a). Due to the very weak intensity, it was not possible to quantify the ratio between the pre-edge and the main edges.

The Ag $M_{4,5}$ edges are scarcely reported in the literature and no other references than for metallic Ag were found with high energy resolution. The EELS spectra have thus been simulated by calculating dipole allowed transitions from $3d$ core state to unoccupied density of states [Gao 2008]. The density of states have been calculated for the ground state within a DFT-LDA approach implemented within a plane wave basis and pseudo-potential approximations [Clark 2005]. These rather crude approximations result in a good agreement of the calculated EELS with the experimental EELS for pure Ag (Fig. S3-b). Calculations have also been done for (001) and (111) surfaces of Ag. As expected electronic reconstructions occur at these interfaces. Mulliken population [Segall 1996] analysis indicates that at the (001) Ag surface, p orbitals lose 0.12 electrons while s and d orbitals gains respectively 0.04 and 0.08 electrons. At the (111) Ag surface, p orbitals lose 0.14 electrons while s and d orbitals gains respectively 0.14 and 0.06 electrons. Such charge redistribution between orbitals as obtained for computed surface (Ag- $p \rightarrow$ Ag- s,d) are compatible with the observed charge redistribution measured by XAS for the core-shell. Surface and interface charge redistribution in silver share common figures.

The corresponding Ag $M_{4,5}$ spectra of these surfaces have been calculated but do not evidence significant changes associated with these electronic reconstructions (see Fig. S4). We have also computed Ag₂O compounds where a stronger electronic reconstruction is achieved by the ligand association. In this oxide compound, the Ag orbitals loses respectively 0.06, 0.24 and 0.02 electron for s , p , d orbitals with respect to metallic Ag. The corresponding Ag $M_{4,5}$ spectrum is displayed in Fig. S3(b) and show some difference at around 20 eV from the edge onset where many p type states are present in the unoccupied density of states. None of these calculated spectra can match with the interfacial EELS Ag $M_{4,5}$ signal but they indicate that the observed faint change at the interface might involve primary change in p orbital populations that is stronger than in pure surface case.

It is noteworthy that the formation of a pure Ag₂O layer will result in a diminution of the Ag d orbital populations that is not experimentally observed by XAS. This confirms that Ag cores do not form an oxidize layer at the interface and that the observed charge transfer might occur from the formation of Ag-O bonds across the Ag/CeO₂ interface.

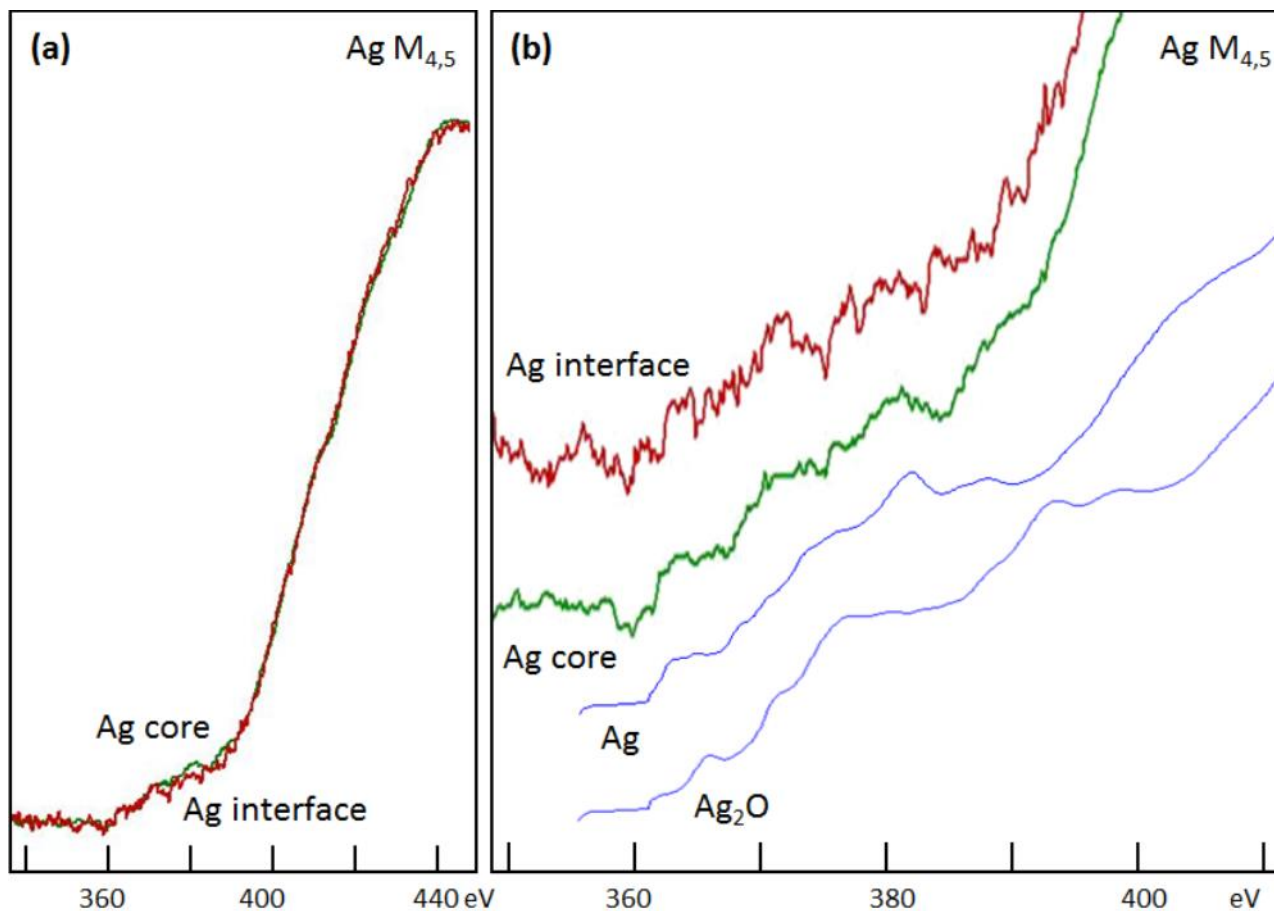


Fig. S3. Experimental STEM-EELS measurement of Ag $M_{4,5}$ edges.

(a) EELS Ag $M_{4,5}$ from the Ag core and from the Ag/ CeO_2 interface position (b) EELS Ag $M_{4,5}$ pre-edge from the Ag core and from the Ag/ CeO_2 interface position and simulated Ag $M_{4,5}$ for Ag and Ag_2O .

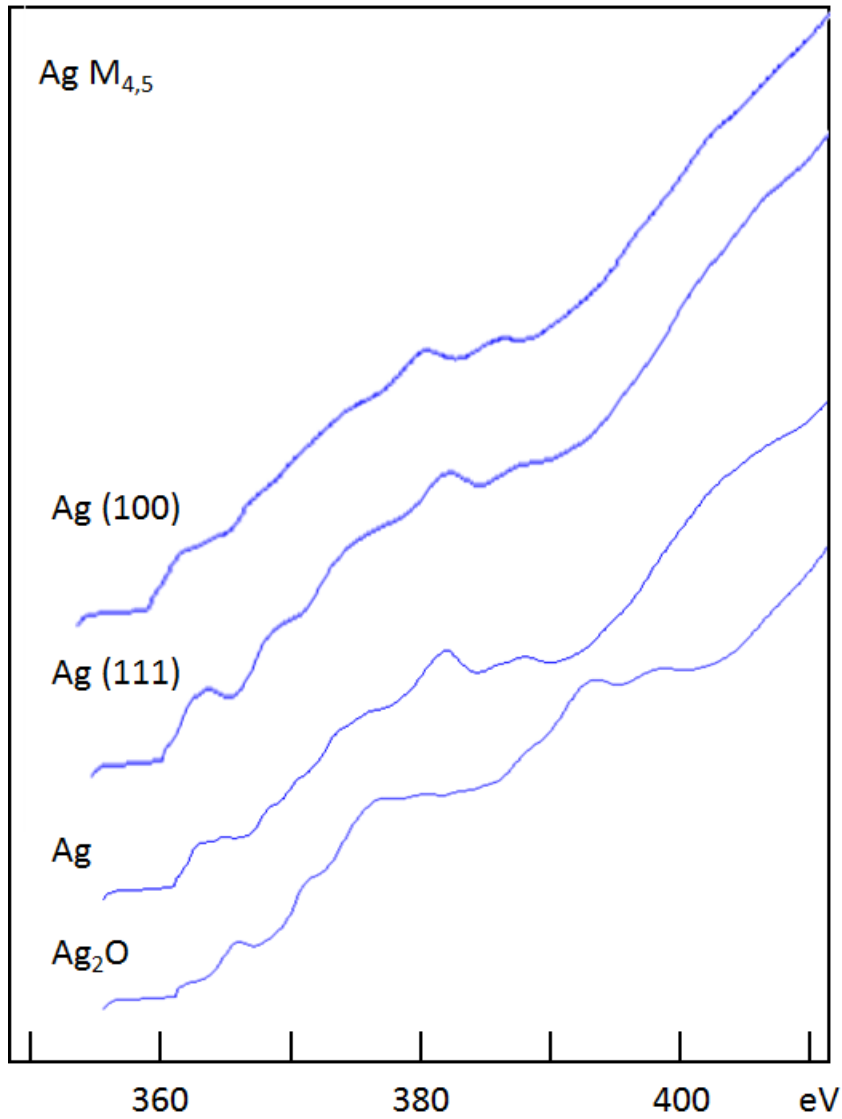


Fig S4 : Comparison of calculated Ag $M_{4,5}$ EELS spectra. Calculated EELS Ag $M_{4,5}$ pre-edge for the Ag core and for the surface atoms of Ag(100) and Ag(111) surfaces. The spectrum obtained for bulk Ag₂O is also shown.

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