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In this experiment we investigated different hybrid magneto-plasmonic materials, in particular gold-FexOy, gold-cobalt ferrite hybrids with various geometries and sizes and gold-iron alloys nanoparticles, coupling magnetic and plasmonic materials in a single composite structure. The hybrids have been prepared by nucleation of the oxide on gold nanoparticle seeds. Different structures can be obtained by varying the preparation conditions, and the main hybrid morphologies are shown in Fig. 1.

Heterodimers

Flowers

Core@Shells

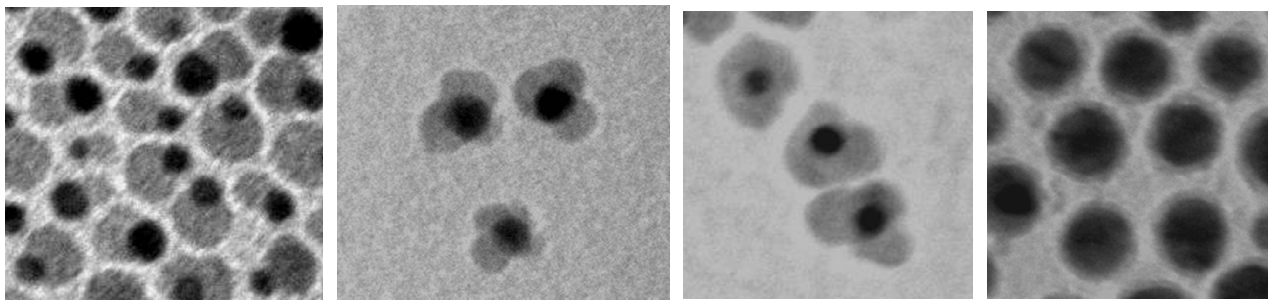


Fig. 1: TEM micrographs showing the different morphologies of the samples investigated in this experiment. The black particles are composed by gold, while the gray particles are iron oxides. The scale is such that in every picture the diameter of the Au particle is 6 nm.

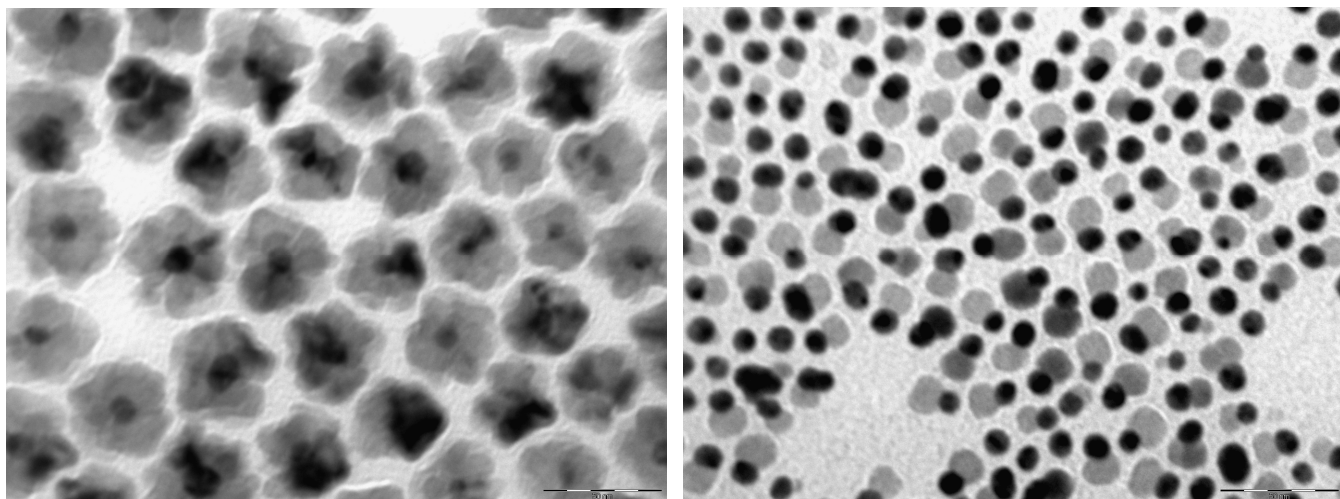


Fig. 2. Morphologies of the two samples discussed in this report. Left: **sample VV130** (Au@Fe_xO_y core@shell heterostructures made of 8-10 nm Au cores and a compact flower-like 12-14 nm thick Fe_xO_y shell); right: **Sample VV129** (Au-Fe_xO_y heterodimers individually made of one 7-10 nm Au domain and one 12-15 nm Fe_xO_y domain).

The XMCD results on VV130 at 9 K and 6 T, Au-L_{2,3} edges are shown in Fig. 3.

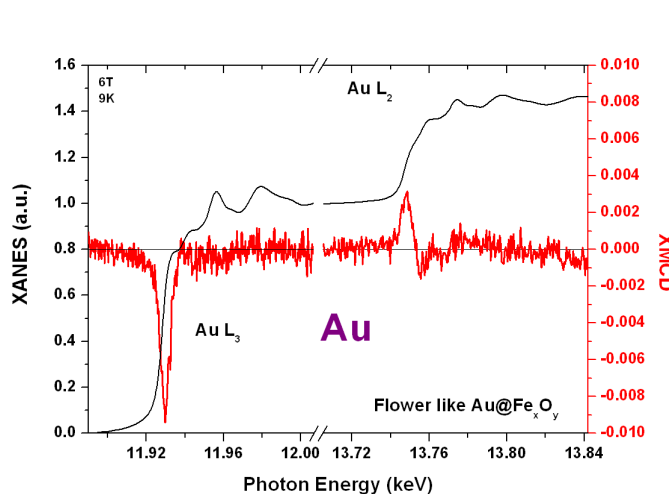


Fig. 3. XAS and XMCD at the Au-L_{2,3} edges for sample VV-130, at $T=9$ K and in field of 9 T.

A clear dichroic signal is present, with a magnitude equal to *ca.* 1 % of the edge step. This is smaller, but comparable, with respect to what is found in Au-Fe alloys. Sitting in energy on the minimum of the dichroism at the L₃ edge, and scanning the field at fixed T , we could prove that the magnetisation on gold is largely saturated at 6 T.

This is contrary to what we have found on sample VV129. The XMCD results for this sample are illustrated in Fig. 4.

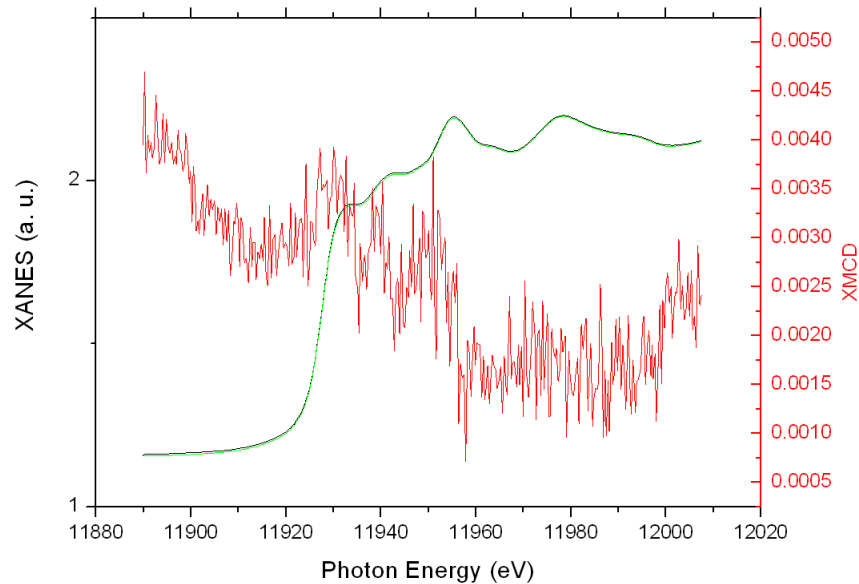


Fig. 4. XAS and XMCD at the Au- $L_{2,3}$ edges for sample VV-129, at $T=9$ K and in field of 9 T.

At the L_3 edge, the dichroism is null within the noise level. Thus, we did not perform further measurements at the L_2 edge. This result indicates that, while in sample VV130 some magnetic moment is transferred to Au, in sample VV129 is not. With the remarkable exception of the Au-Fe alloy nanoparticles, we found that all the other samples investigated in this experiment, irrespective of the morphology, behave exactly in the same way of sample VV129: there is no transfer of spin polarisation between the two component of the hybrid heterostructure.

A possible rationalisation of this behaviour could be found by looking at the XAS spectra at the Fe-K edge, that are shown in Fig. 4.

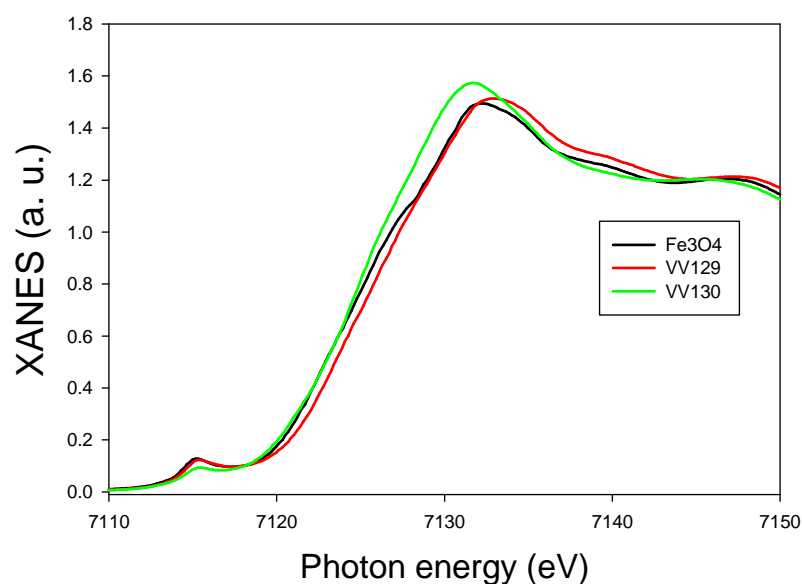


Fig. 4. XAS at the Fe-K edge for sample VV-129, VV-130 and a reference sample of Fe₃O₄ at $T=9$ K.

Here we compare the XANES at the Fe-K edge of both samples and of bulk Fe₃O₄, used as a reference. We note that the edge position is related to the oxidation state of the photoabsorber, the edge shifting towards lower energies with decreasing oxidation state. It is readily apparent that in the two samples the oxidation state of Fe is different, with the mixed valence oxide Fe₃O₄ somewhat in between. Similar results have been obtained also for all the other samples, showing no magnetic moment on Au, and an Fe edge energy position almost equal to that of sample VV129.

In conclusion, in this experiment several samples have been tested, with several different morphologies (flowers, dimers, core-shell, core-hollow shell, etc.). We found a sizeable magnetic moment on Au just in two cases: sample VV130 and nanoparticles of Fe-Au alloy. When a magnetic moment on Au is present, Fe is always in a reduced oxidation state (closer to Fe(II) than to Fe(III) in VV130, metallic in the alloy). On the contrary, the presence of magnetism on Au is independent of morphology. Thus, it appears that magnetism is transferred to Au via an electronic mechanism, that implies an electron transfer from Au to Fe, and the creation of holes in the Au *5d*

states. A possible speculation is that the contact between the Au and Fe_xO_y nanocrystals is via an Fe layer, rather than via an oxide layer.