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## Permanent Magnetism in Thiol Capped Nanoparticles, Gold and ZnO

P. CRESPO, M.A. GARCÍA, E. FERNÁNDEZ-PINEL,  
J. DE LA VENTA, J.M. MERINO, A. QUESADA, A. HERNANDO

Instituto de Magnetismo Aplicado (UCM-CSIC)  
P.O. Box 155, 28230 Las Rozas, Madrid, Spain  
and Dpto. Física de Materiales, UCM, 28040 Madrid, Spain

A. FERNÁNDEZ

Instituto de Ciencia de Materiales de Sevilla CSIC-UNSE  
Américo Vespucio s/n, 41092 Sevilla, Spain  
and Departamento de Química Inorgánica, Universidad de Sevilla, Spain

AND S. PENADÉS

Grupo Carbohidratos, Laboratory of Glyconanotechnology IIQ-CSIC  
Américo Vespucio s/n, 41092 Sevilla, Spain

In spite of the diamagnetic behavior exhibited by bulk ZnO and Au, a ferromagnetic-like behavior is induced in nanoparticles of both systems by appropriate surface functionalization. By capping with thiol derivatized molecules, magnetic hysteresis is observed even at room temperature, whereas the magnetization has a very little temperature dependence. Capping induces an alteration of their electronic configuration that depends on the capping molecule, as evidenced by X-ray absorption spectroscopy, that strongly affects their magnetic properties.

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### 1. Introduction

Nowadays, nanoparticles (NPs) are a subject of great interest in materials science due to the appearance of new phenomena that opens a broad field for technological applications. Electronic properties of NPs are different from that of their bulk counterparts due to the so-called size and surface effects [1].

In consequence, modifications on the magnetic behavior, among other physical properties could be expected by decreasing particle size to the nanoscale and/or by surface modification. Actually, some surprising results related to the magnetic properties of nanostructures and surfaces have been already observed, for instance

in proton irradiated graphite [2] and dielectric oxides [3]. An outstanding example of these surface effects is the appearance of magnetic anisotropy for single Co atoms deposited onto Pt surfaces reported by Gambardella et al. [4].

One strategy for modification of the electronic structure of NPs is the functionalization of the surface, i.e. the electronic structure can be tuned depending on the intensity of NP-capping molecule interaction. In this work it will be shown that those changes of the electronic structure drastically affects the magnetic behavior of Au and ZnO NPs when capped with different organic molecules. It is worth mentioning that although Au and ZnO do not exhibit magnetic ordering in bulk state, a ferromagnetic-like behavior is induced by capping, which is present even at room temperature. In both cases, the origin of the amazing magnetic behavior are related with the changes on the electronic structure of the NPs due to the charge transfer that takes place upon surface functionalization [5, 6].

## 2. Experimental details

Au nanoparticles stabilized with different capping systems have been prepared by chemical reduction of a metal salt precursor, in a liquid phase, in presence of “protective” species that, due to the formation of covalent links or by electrostatic interactions, isolate the metal cluster preventing its growth. Gold NPs stabilized by means of a surfactant (Au–NR sample) have been prepared following the two phase synthesis proposed by Brust et al. [7]. The surfactant is a tetralkylammonium salt (tetraoctyl-ammonium bromide  $\text{BrN}(\text{C}_8\text{H}_{17})_4$ ). Thiol-capped Au NPs (Au–SR sample) were prepared in aqueous solution by one step synthesis developed by Penadés et al. [8]. ZnO NPs were prepared by sol-gel [6, 9] and subsequently capped with three different organic molecules: tryoctylphosphine (named after here TOPO), dodecylamine (AMINE) and dodecanethiol (THIOL). Structural characterization was done by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM). Magnetic characterization has been carried out with a SQUID magnetometer. The magnetization of the nanoparticles was obtained after subtracting the diamagnetic contribution of the sample holder. Information concerning changes on the electronic structure is obtained from X-ray absorption near edge structure (XANES) at the Au  $L_3$  edge and Zn  $K$  edge, for Au and ZnO respectively.

## 3. Experimental results

### 3.1. Au nanoparticles

Two sets of Au NPs stabilized with different molecules have been prepared for studying the role played by the surface-protective molecule interaction on the magnetic behavior. For the Au–NR sample, the interaction between surface Au atoms and the surfactant molecules is very weak, whereas for the Au–SR sample the dodecanethiol capping molecule is strongly bonded to the Au surface atoms by means of a covalent bond.

TEM micrographs show monodispersed particles with an average particle size of around 2 nm, see Fig. 1a. Figure 1b shows the XANES spectra of the Au

$L_3$  edge for the different Au NPs. The first resonance at the edge is often known as white line and arises from  $2p_{3/2,1/2} \rightarrow 5d$  dipole transitions. Thus, the area under white line can be used to study the  $d$ -charge (hole) redistributions.

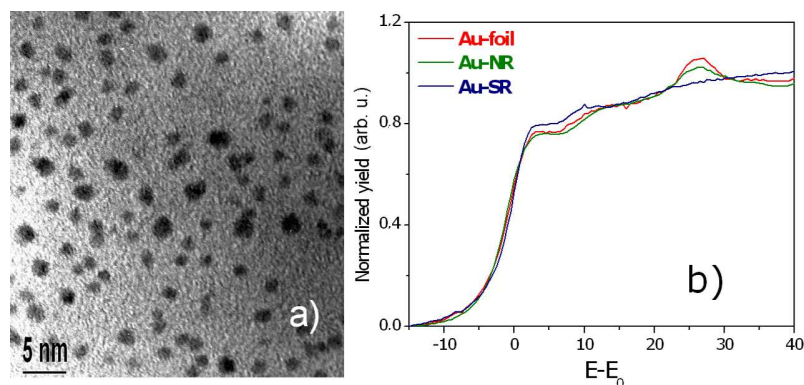


Fig. 1. (a) TEM micrograph of thiol capped Au nanoparticles, (b) Au  $L_3$  edge XANES spectra for the Au NPs compared with that of bulk gold.

It should be remarked the noticeable increase in the intensity of the Au  $L_3$  threshold resonance for the Au-SR sample when compared with Au foil and the Au-NR sample. This means that capping with thiols promotes a charge transfer from Au atoms to organic chains, that is not detected when Au NPs are stabilized with surfactant molecules. Figure 2 shows the magnetisation curves for both sets of Au NPs. Au-NR sample exhibits a diamagnetic behavior, similar to that of bulk Au. However, an unexpected behavior is found for the Au-SR sample. It is evident that gold-thiol capped NPs exhibit not only a paramagnetic behavior, as could be expected upon increasing the number of holes at  $d$  band, but ferromagnetic hysteresis even at room temperature.

It should be mentioned that the amount of Fe impurities (below 0.01 ppm) is not enough to account for the magnetization values. In addition, it has been recently shown that Fe impurities weaken the ferromagnetic-like behavior exhibited by capped Au NPs [10].

Thus, the results shown in Figs. 1 and 2 clearly point out that the electronic structure of the NPs is strongly modified upon capping with strong interacting thiols, whereas for a weak interaction between surface and protective molecule a similar behavior as that of bulk gold. These results confirm the existence of an interfacial charge transfer through the Au-S bonding, giving rise to a charge redistribution which induces a magnetic moment on the surface Au atoms.

More difficult seems to explain the ferromagnetism at 300 K. Even for the case of non-interacting Fe particles with such a small size, one cannot expect ferromagnetic ordering up to room temperature (RT). This implies that magnetic moments should be frozen due to an enormous local anisotropy field. Taking into

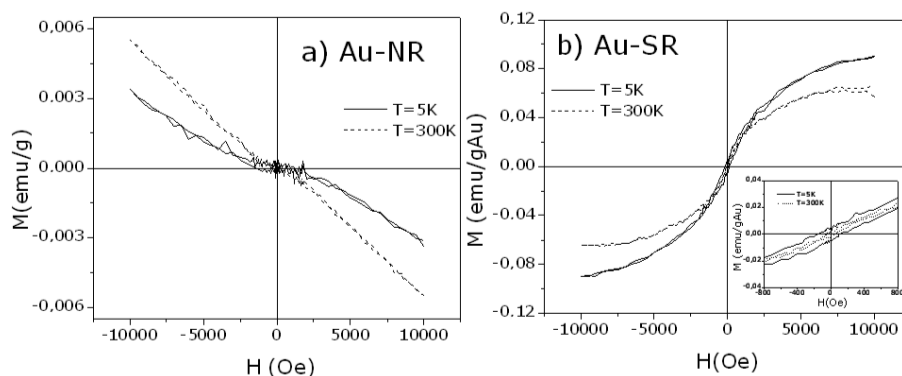


Fig. 2. Magnetization curves at 5 and 300 K for both sets of Au NPs. The inset in Fig. 2b shows that magnetic hysteresis is present even at 300 K.

account the very low density of states of Au it is very hard to invoke intra-particle exchange interaction as the origin of such large anisotropy. It seems most plausible to attribute the high anisotropy to a quenching of the magnetic moments due to the high spin-orbit coupling at gold surfaces. The localized character of the magnetic moments, inferred from surface plasmon resonance (SPR) studies [11], as well as its orbital character, have been proposed as the mechanism responsible for the ferromagnetic like behavior [12].

### 3.2. ZnO nanoparticles

Let us now analyze the experimental results obtained for ZnO NPs capped with three different organic molecules TOPO, AMINE, and THIOL, which bond to the particle surface through an O, N, and S atom, respectively. Structural characterization, by XRD and TEM evidences, for the three cases, the formation of hexagonal ZnO nanoparticles (wurtzite structural type) with average size around 10 nm. Figure 3 shows the XANES spectra at the Zn  $K$  edge measured at RT. It is evident that the spectra are clearly different for the three capping molecules. The Zn  $K$  edge, corresponding to the transition Zn  $1s \rightarrow 4p$ , has been shown to be more sensible to the Zn chemical bonding than  $L$  edges.

Although  $4p$  level of Zn isolated atoms is empty, chemical bonding with different chemical species leads to hybridization. In particular, a larger intensity at the first maximum is associated with a larger charge transfer between the Zn atoms and the surrounding atoms, that can be due to an increase in the coordination number [13] or changes in the electronegativity of these surrounding atoms. Hence, variations in intensity at the first maximum are related to a different degree of occupation for the outer orbital of Zn atoms for the three samples.

Figure 4 shows the magnetization curves of the samples.

Besides the diamagnetic contribution similar to that of bulk ZnO it is observed an additional contribution that depends on the capping molecule. For the AMINE and THIOL capped NPs there is a ferromagnetic-like contribution that

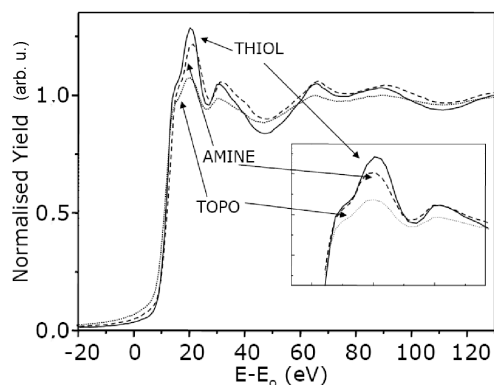


Fig. 3. XANES spectra at the Zn  $K$  edge for the ZnO NPs capped with different molecules. Inset shows a detail of the white line region.

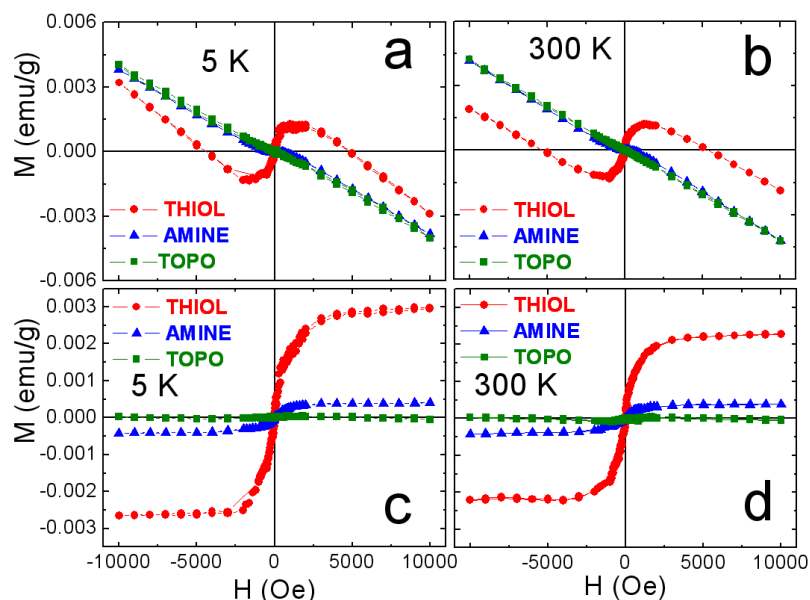


Fig. 4. (a), (b) Magnetization curves loops for ZnO NPs capped with different molecules. (c), (d) The curves after subtracting the diamagnetic/paramagnetic background.

can be clearly observed after subtracting the diamagnetic background (Figs. 4c and d). Identical results were found at 5 K.

It should be remarked the perfect correlation between the evolution of magnetization with the capping molecule: THIOL sample shows the highest XANES absorption, the absence of PL emission (totally quenched by appearance the new surface states, [6]) and the largest magnetic moments (despite the diamagnetic character of ZnO). On the contrary, the TOPO sample presents the electronic

configuration more similar to bulk ZnO as confirms the smallest XANES absorption (less charge transfer).

#### 4. Conclusions

Electronic structure of Au and ZnO NPs, both diamagnetic in bulk, has been modified by appropriate capping that promotes a ferromagnetic like behavior even at room temperature and in absence of ferromagnetic elements. Charge transfer between surface atoms and capping molecule is in the origin of the observed behavior. However, identification of the particular electronic configuration that originates this magnetism is an amazing challenge that would open a world of possibilities for the use of these materials.

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