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Plasmon-assisted spin transition in gold nanostar@spin crossover heterostructures†

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Herein we report the design of core@shell nanoparticles formed by a metallic Au nanostar core and a spin-crossover shell based on the coordination polymer [Fe(Htrz)₂(trz)](BF₄). This procedure is general and has been extended to other metallic morphologies (nanorods, nanotriangles). Thanks to the photothermal effect arising from the plasmonic properties of the Au nanostar, 60% of iron centers undergo a thermal spin transition inside the thermal hysteresis triggered by a 808 nm laser low intensity irradiation. Compared to other Au morphologies, the great advantage of the nanostar shape arises from the hot spots created at the branches of the nanostar. These hot spots give rise to large NIR absorptions, making them ideal nanostructures for efficiently converting light into heat using low energy light, like that provided by a 808 nm laser.

1. Introduction

The use of molecular switching materials (especially organic and metal–organic) has emerged as a very appealing possibility for their application in molecular electronics.^{1,2} In this context, spin-crossover materials (SCO) are one of the most promising molecular compounds. They are a particular type of coordination compound that can switch between two possible electronic configurations, namely low spin (LS) and high spin (HS),³ upon the application of an external stimulus such as temperature, pressure, light, electric field or molecular sorption in the case of porous materials.^{4–7} Remarkably, both electronic states display entirely different physical properties, which make them highly interesting multifunctional molecular materials.^{8–12} Even more, they may exhibit a strongly cooperative spin transition with a thermal hysteresis near room temperature, endowing memory to the material.^{5,13} This hysteresis and the transition temperatures depend on the coordinated ligands, the metal, and the compound's crystallinity.¹⁴

Among the plethora of SCO compounds, the [Fe(Htrz)₂(trz)](BF₄) polymer (Htrz = 1,2,4-triazole) is one of the most promising due to its high cooperativity and transition temperatures above room temperature. Indeed, these chain coordination polymers display a broad hysteresis of 40 K, maintained even for nanoparticles (NPs) as small as 4 nm.^{15–18}

Furthermore, the controlled synthesis of these compounds has permitted the design of hybrid heterostructures.¹⁹ In this context, core@shell NPs based on [Fe(Htrz)₂(trz)](BF₄) as core and a shell of silica or even of another SCO compound, have been successfully prepared.^{18,20–22} One of the most appealing hybrids combines SCO with metallic NPs to afford electronic devices based on these multifunctional nanostructures.^{23–25} A recent example of this electronic boosting has been reported by us in a core@shell nanostructure based on an Au core surrounded by a [Fe(Htrz)₂(trz)](BF₄) SCO shell. This material displayed a significant improvement in the electrical detection of the spin state thanks to the enhancement in the conductivity provided by the metallic core.²⁶ This system was synthesized by growing the SCO shell *via* the alternative sequential addition of the precursors over 12 nm spherical Au in an aqueous solution and at room temperature.

Another possibility of this hybrid nanostructure is that of inducing the spin transition by low-intensity light irradiation, thanks to the heating of the nanostructure due to the plasmonic metal, which can convert light into heat.²⁷ In this direction, Au NPs have been anchored to [Fe(Htrz)₂(trz)](BF₄)@SiO₂ through the silica shell.^{28,29} For this hybrid, the power of a 633 nm laser irradiation required to induce the transition a few degrees before the transition temperature could be reduced by *ca.* 70%.²⁹ However, the thick SiO₂ shell and the bridging molecule may reduce the heat transfer between the metal and the SCO. At the same time, the high energy of the laser may indirectly warm the sample.

Therefore, the synthesis of hybrids with metallic NPs in closer contact with the SCO compound and plasmonic nanostructures that exhibit an efficient thermal conversion by

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2. Experimental section

All chemical reagents were purchased and used without further purification. Chloroauric acid, 1,2,4-triazole, iron tetrafluoroborate hexahydrate, sodium citrate tribasic dihydrate, sodium borohydride hexadecyltrimethylammonium bromide (CTAB), hexadecyltrimethylammonium bromide (CTAC), L-ascorbic acid, potassium iodide and polyvinylpyrrolidone-30K (PVP) were purchased from Sigma-Aldrich. Silver nitrate was purchased from Alfa Aesar. Ultra-pure water (18.2 MΩ) was used in the following synthesis.

Gold nanostar (NS). Au NPs with star-like shapes were obtained by a seeded-growth process,³⁴ using citrate-stabilized Au NPs as seeds, obtained following the Turkevich method.³⁵ For the preparation of growth solution, hydrochloric acid (10 μ L, 1 M) was added to a HAuCl₄ solution (10 mL, 0.25 mM). Afterward, aqueous solutions of ascorbic acid (50 μ L, 0.1 M) and AgNO₃ (100 μ L, 0.003 M) were added, followed by the addition of 100 μ L of seed solution. Finally, PVP was added as capping agent (0.5 mL, 10 g L⁻¹). After 30 minutes of

NS@SCO. SCO system was grown onto PVP-stabilized NSs following a two-step approach. In a first step, a triazole aqueous solution (250 μL , 0.5 mM) was added into the previously prepared NSs aqueous solution (5 mL, 0.16 mM) under continuous stirring at N_2 atmosphere for 30 min. In a second step, iron tetrafluoroborate hexahydrate (5 mL, 0.5 mM) and triazole (5 mL, 1.5 mM) aqueous solutions were simultaneously added (4 mL h^{-1}) under stirring at N_2 atmosphere and room temperature. All aqueous solutions were previously purged with Ar before starting the synthesis. The obtained core@shell NS@SCO NPs were then collected by centrifugation (3500 rpm, 20 min) and easily re-dispersed in different solvents (water, ethanol, acetone, and chloroform).

Au nanotriangles (NTs). These NPs were prepared *via* a seed-mediated growth method (Fig. S3, ESI†).³⁷

NRs@SCO, NTs@SCO and Ag@SCO. To overgrow the SCO shell a triazole aqueous solution (200 μL , 0.5 mM) was added to the plasmonic NP aqueous solution (3 mL, 0.16 mM) and the mixture was stirred for 30 min. Then, aqueous solutions of the precursors, iron tetrafluoroborate hexahydrate (3 mL, 0.16 mM) and triazole (3 mL, 0.5 mM), were simultaneously added at a continuous rate (4 mL h^{-1}) under stirring at room temperature. After completion of the addition, the colloidal suspension was centrifuged and washed with water.

UV-vis absorption spectra were recorded on a Jasco V-670 spectrophotometer in baseline mode from 400 to 800 nm range, using 1.000 cm-optical-path plastic cuvettes. Transmission electron microscopy was carried out on a Technai G2 F20 microscope operating at 200 kV and a JEOL-1010 operating at 100 kV. Samples were prepared by dropping suspensions on lacey formvar/carbon copper grids (300 mesh).

Dynamic Light Scattering (DLS) measurements were performed at room temperature with a Zetasizer Nano ZS instrument (Malvern Instruments Ltd) of the as-synthesized suspension. X-Ray Photoelectron Spectroscopy (XPS) samples were analyzed at the X-ray Spectroscopy Service at the Universidad of Valencia using a K-ALPHA Thermo Scientific spectrometer. All spectra were collected using Al K α radiation (1486.6 eV), monochromatized by a twin crystal monochromator, yielding a focused X-ray spot (elliptical in shape with a major axis length of 200 μ m) at 30 mA and 2 kV. The alpha hemispherical analyzer was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band and 50 eV in a narrow scan to selectively measure the particular elements. XPS data were analyzed with Avantage software. A smart background function was used to approximate the experimental backgrounds. Charge compensation was achieved with the system flood gun that provides low energy electrons and low energy argon ions from

The morphology of the hybrid NS@SCO NPs was investigated through TEM, Fig. 2a. We observe that, once the addition was complete, a well-defined shell of 15 ± 8 nm surrounding the metallic core is obtained, Fig. 2b and Fig. S5 (ESI[†]). Besides, the metallic composition of the core and shell,

3.1 NS@SCO preparation and characterization

In a second step, iron tetrafluoroborate hexahydrate (5 mL, 0.5 mM) and triazole (5 mL, 1.5 mM) aqueous solutions are dropwise added (4 mL h⁻¹) under a N₂ atmosphere and at room temperature, Fig. 1(ii). This slow addition allows the successful Fe coordination, forming the SCO compound around the Au surface, while the SCO self-nucleation is minimized. The final

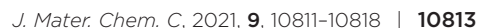




Fig. 2 (a) TEM images of the NS@SCO heterostructure and (b) histograms of the size distributions for the gold core (black) and the overall core@shell nanoparticle diameter (red). These sizes have been calculated from manual counting of more than 100 NPs. (c) UV-vis spectra of the NS@SCO and the NS NPs.

examined by EDX (Fig. 3), evidences a well-defined distribution of Au in the core and Fe in the shell with a Fe/Au ratio of 1.4.

Notice that this synthetic protocol is very versatile and reproducible and can be extended to other metallic nanostructures, as evidenced in Fig. S8–S11 (ESI[†]) where the same approach was employed using Au nanorods, Au nanotriangles, or Ag nanospheres as the core. Nonetheless, the difficulty in obtaining some of these nanostructures and their poor colloidal stability at high concentrations have prevented us from obtaining enough core@shell NPs to characterize them properly. In contrast, thanks to the high colloidal stability of the Au NSs provided by the PVP, large amounts of these heterostructures have been obtained, thus permitting a complete study and characterization.

Focusing on the NS@SCO heterostructure, one observes that the UV-vis spectrum is dominated by the localized plasmon band resonance (LSPR) arising from the Au (Fig. 2c). This LSPR band shifts from 697 to 738 nm after the SCO growth due to the change of the dielectric constant in the surrounding of the NS core during the shell formation.^{40,41} This indicates that, despite the PVP resilience, the SCO shell and the NS core are in intimate contact. Noticeably, this plasmon shift is considerably more pronounced than the one reported for the Au nanospheres covered with the same SCO compound (41 vs. 12 nm). This is a consequence of the higher sensibility of the LSPR in the NSs, accounted by the Au branches.⁴²

Further proof of the presence of the SCO compound in the NS@SCO heterostructure can be obtained from XPS. In this sense, the presence of iron (from the metal), nitrogen (from the ligand), and fluorine (from the counterion BF_4) are evidenced, Fig. S2 and S6 (ESI[†]). Taking a closer look at the Fe 2p region, a mixture of Fe^{3+} and Fe^{2+} species at the surface of the heterostructure can be discerned. On the one hand the Fe^{2+} bands at 708.7 eV (Fe 2p_{3/2}) and 721.1 eV (Fe 2p_{1/2}) are clearly visible, while the other bands are attributed to Fe^{3+} . A quantification of Fe oxidation state content reveals ca. 43% of Fe^{2+} . The high percentage of Fe^{3+} results from the fact that the shell is exposed and free from any surfactant moiety, being the Fe^{2+} susceptible to oxidize. This has been further proved by studying the XPS of the samples after 24 h in the air. Thus, as the Fe 2p region shows (Fig. S6, ESI[†]), the SCO shell fully oxidizes in contact with ambient O_2 , vanishing the Fe^{2+} signal. It is worth mentioning that the core@shell can also be synthesized in air instead of under an inert atmosphere. However, even if the resulting NPs display spin transition, the SCO shell only contains 20% of Fe^{2+} (Fig. S6, ESI[†]).

Finally, the crystallinity of the NS@SCO has been checked by PXRD. As it was previously reported for the Au@SCO system, no diffraction peak related to the SCO component is observed. This may come from the screening of the signal produced by the crystalline Au, owing to its large electron density, Fig. S13 (ESI[†]),²⁸ or to the poor crystallinity of the SCO shell due to the high mismatch between the $[\text{Fe}(\text{HTrz})_2(\text{trz})](\text{BF}_4)$ and the Au crystal structures.

3.2 Plasmon-assisted spin transition

The spin transition of the NS@SCO was explored by calorimetric measurements (DSC), due to the high sensitivity of the technique to characterize the SCO phenomenon in such hybrids, as only the metallic centers able to switch their spin state contribute to the endo and exothermic peaks. In this technique, the typical endothermic and exothermic signals coming from the spin transition are monitored as a function of the temperature. During the first heating, a clear endothermic peak can be seen at 103 °C, corresponding to the transition from LS to HS ($T_{1/2}^{\text{LS} \rightarrow \text{HS}}$). Then, during the cooling process, the LS recovery ($T_{1/2}^{\text{HS} \rightarrow \text{LS}}$) is

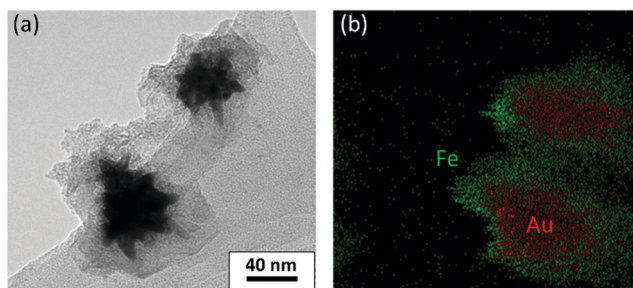
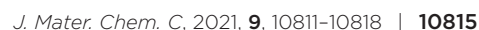


Fig. 3 (a) TEM images of the NS@SCO heterostructure and (b) EDX mapping of the same area. Green and red dots correspond to Fe and Au, respectively. The scale bar of (b) is the same as (a).



In an attempt to detect the spin transition through electrical measurements, as was previously done in spherical Au NPs surrounded by a SCO shell,²⁶ we drop cast a NS@SCO suspension on commercial fingerprint electrodes with a gap of 2.5 μm . Then, temperature dependent I - V curves were collected, leaving 5 minutes of thermal stabilization at each temperature. In Fig. S17 (ESI[†]) we



plot the electrical behaviour as a function of the temperature. We observe that in the range RT–120 °C, the current increases when the temperature is increased. This is the common electrical behaviour of a semiconductor or an insulator, proving that the metallic cores are not creating short-circuits thanks to the SCO insulating shell. Nevertheless, these short-circuits cannot be avoided when a complete hysteresis was attempted since, at some point, an abrupt increase in the conductance occurred in all the tested electrodes. For instance, in Fig. S17 (ESI[†]) an example of I - V curves at different temperatures are presented, showing that during the cooling, the recorded current is decreasing progressively until 30 °C, where a short-circuit occurs. This suggests that the SCO shell is being progressively damaged due to the high current density in the branches of the nanostars, heating them locally due to the Joule effect and making them collapse. In this line, we can conclude that isotropic Au NPs are more suitable in order to detect the spin transition electrically.

4. Conclusions

In this work, we have extended the synthetic protocol developed for Au nanospheres to wrap Au nanostars, Au nanorods, Au nanotriangles and Ag nanospheres with the SCO compound $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$. Here, we took advantage of the Au nanostars capabilities to efficiently convert light into heat (photothermal effect) in order to induce the spin transition of the shell by irradiating with a laser of 808 nm and low intensity, 0.15 mW cm^{-2} , inside the hysteresis of the SCO (at 70°C). In this context, we achieved a spin switching of the 60% of SCO Fe^{2+} centers located in the shell. The low power guaranteed that the spin transition was induced by the photothermal effect of the metallic core. Remarkably, compared with previous works, the intensity used in this work is several orders of magnitude lower. For instance, with a 633 nm laser an irradiation intensity of 3000 W cm^{-2} was required to induce the complete spin transition of the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)@\text{SiO}_2$ system decorated with Au,²⁹ whereas for Au nanorods embedded in SCO this intensity could be reduced to 15 mW cm^{-2} with a 830 nm laser.³¹ We attributed the large improvement achieved in this work mainly to two reasons: the reduced thickness of the shell, improving the heat distribution to the SCO shell, and the superior photothermal effect provided by the Au NSs, enhancing the light-temperature conversion. Nevertheless, other parameters related to the sample or the technique used to study the spin state may also play a role.

Author contributions

Both authors were responsible for the design, synthesis, characterization of the heterostructure, and the preparation of the manuscript. M. G.-M. and M.C.-P. were involved in the development and coordination of all experimental parts, discussion of results, and preparation of the manuscript. E. C. supervised all the work and the preparation of the manuscript. All authors revised and contributed to the presented manuscript.

Conflicts of interest

There are no conflicts to declare.

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