NanoMORALs — Metal nanoparticles doped with organic molecules

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Abstract: A new class of nanosized metal–organic alloys (MORALs) has been synthesized for the first time. Silver nanoparticles doped with Cu(II) and Fe(III) phthalocyanines were thus synthesized in the presence of sodium dodecyl sulfate (SDS). The resulting materials were characterized by means of XRD, SEM, TEM coupled to energy dispersive X-ray analysis, and thermogravimetric analysis. No leaching of the photoactive dopant species was observed in water or in common organic solvents.

Key words: hybrid, alloy, nanoparticle, metal–organic.

Résumé : On a synthétisé pour la première fois une nouvelle classe d'alliages métallo-organiques « MORALs » à l'échelle nano. On a ainsi synthétisé des nanoparticules d'argent dopées avec des phtalocyanines de Cu(II) et de Fe(III) en présence de sulfate de dodécyle et de sodium. Les produits obtenus ont été caractérisés par les techniques de diffraction des rayons X (DRX), de microscopie électronique à balayage (MEB) et de microscopie électronique à transmission (MET) couplées à des analyses de rayons X à dispersion d'énergie et d'analyse thermogravimétrique. On n'a observé aucune lixiviation des espèces dopantes photoréactives, que ce soit dans l'eau ou dans les solvants organiques communs.

Mots-clés : hybride, alliage, nanoparticule, métallo-organique.

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Introduction

Metal–organic alloys (MORALs) are new materials with a variety of potential applications in different fields. Organic molecules as diverse as dyes[1] and polymers,[2] both water-soluble and not, have been efficiently incorporated within Ag, Au, and Cu either by simple homogeneous reduction of the corresponding metal cations in the presence of the desired organic species, or by heterogeneous reduction by a sacrificial reducing metal in solution.[3] In general, the encapsulated organic dopant is not affected by the mild encapsulation process, and once entrapped, it remains accessible to reactants in solution. As expected, however, the physicochemical properties of the doped metal species are largely altered. For example, various functional applications were readily proved, such as the use of Nafion@Ag as acid catalyst,[4] and the improvement of Ag catalytic performance upon encapsulation of Congo Red for oxidation of methanol to formaldehyde.[5] Clearly, considering the immense variety of organic molecules and the abundance of metals in the periodic table, these findings have opened the route to a new, and large, chemistry of doped metals.[1–5]

Entrapment is markedly distinct from adsorption and confers interesting new properties to the resulting hybrid composites. For example, although a water-soluble species such as Congo Red readily leaches out in water when adsorbed at the surface of Ag,[1] no leaching is observed from the corresponding MORAL (with DMSO being the only solvent capable to extract the organic dopant molecules).[3] Moreover, a one-to-two orders of magnitude larger amount of organics can be entrapped in metal compared with simple surface adsorption. Such first-generation MORALs consist of macro-mesoporous materials.

Herein, we report the first preparation of Ag-based MORAL nanoparticles made of silver doped with Cu(II) and Fe(III) phthalocyanines (CuPc and FePc, respectively). We demonstrate that carrying out the reductive encapsulation in the presence of micellar sodium dodecyl sulfate (SDS) makes it possible to obtain particles with diameters as small as the nanometer fraction. The method is general and opens the way to the practically viable synthesis of a new class of nanostructured hybrid metals of large applicative potential.

Experimental

Silver nanoparticles doped with metal phthalocyanines (MPc) were prepared by reducing Ag(I) ions with NaH_2PO_2 in the presence of SDS micelles (Scheme 1).

A solution of SDS (6.92 mmol) and NaH_2PO_2 (34.1 mmol) in H_2O (0.5 L) was left under agitation at
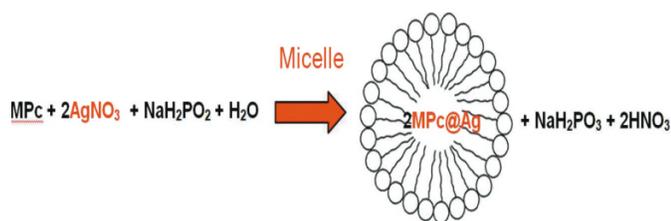
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Scheme 1. Reaction scheme describing the synthesis of MORALs nanoparticles.

$$MPc + 2AgNO_3 + NaH_2PO_2 + H_2O \longrightarrow 2MPc@Ag + NaH_2PO_3 + 2HNO_3$$

Micelle

**Fig. 1.** XRD spectrum of undoped silver.

room temperature for 5 min, after which $AgNO_3$ (712 µmol) was added. Both doped and pure Ag samples were prepared. In the case of doped silver, 6.46 µmol CuPc or FePc were added to the starting solution, sonicating the reaction mixture (Bandelin Sonorex Digitec instrument) for 1 h to ensure complete solubility of the phthalocyanines. The solution thereby obtained was kept under slow agitation (300 rpm) for 4 days, after which it was centrifuged at 5 °C to separate the doped nanoparticles, which segregate from the micelles. The resulting silver MORAL particles were characterized by X-ray diffraction on Bruker D8 Advance instrument (40 kV, 35 mA, Cu Kα 1.542 Å). A Zeiss DSM-950 instrument operating at 80 kV was used for scanning electron microscopy images. Tablets of MORALs and pure silver powders were prepared applying uniaxial pressure (2.26 t/cm²) and metallizing with gold before the analysis. Transmission electron microscopes JEOL mod. JEM-2000 FX and LEO 910 were employed for TEM analyses at 200 kV. Samples for TEM were prepared by sonicating a diluted suspension of MORAL in water (~10 mg MORAL in 1 L H_2O) for 10 min . A drop of this suspension was deposited on the Cu grid support used for analysis. Eventually, water was evaporated at 50 °C for 2 days. EDAX analyses were carried out with an energy dispersive X-ray analysis system connected to TEM. Thermogravimetric analysis (TGA) was performed on a SEIKO TG/ATD 320U, SSC 5200 (Seiko Instruments) from 25 to 900 °C at a heating rate of 10 °C/min in flowing dry air (100 mL/min). UV spectra were recorded on a UV–vis Shimadzu UV2401 spectrometer.

Results and discussion

Phosphite is a mild reducing agent, which does not react with the MPc (as shown in blank experiments). The SDS surfactant, in its turn, does not interfere with the efficiency of the molecular entrapment in the metal particles. The resulting nanoparticles of doped silver in the aqueous phase, in which the inorganic salts are dissolved, are thus readily sequestered in the hydrophobic core of the micelle as their formation takes place. Silver nanoparticles, indeed, are highly hydrophobic, and this property has been exploited, for example, in the synthesis of elegant nanostructures.[6]

The by-products together with SDS were easily washed off with EtOH and after a mild thermal treatment powders with the classical shine of silver (in the case of the undoped metal) or coloured in green (FePc@Ag) and blue (for the CuPc@Ag) were eventually isolated. No leaching was observed by keeping the metal–organic composite particles in contact with water or with common organic solvents, such
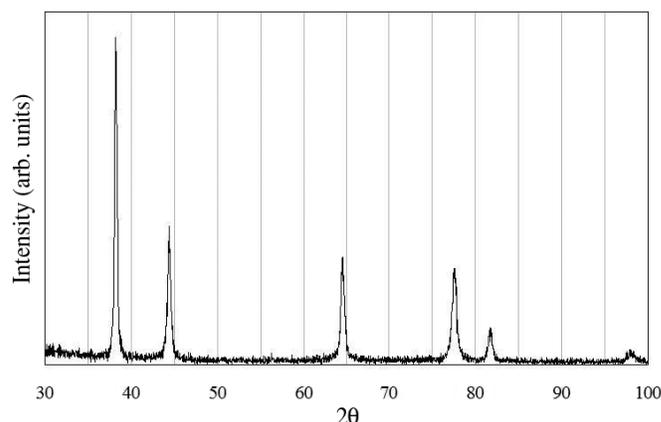
as ethanol, acetone, and toluene, for prolonged time (as shown by the UV spectra of the filtered suspension, which showed no presence of organics even after 4 weeks). Ag nanocrystals slowly form and agglomerate within the structure of the SDS micelles. The crystallinity of silver is revealed by XRD diffractogram (Fig. 1) that showed the absence of silver oxides or salts.
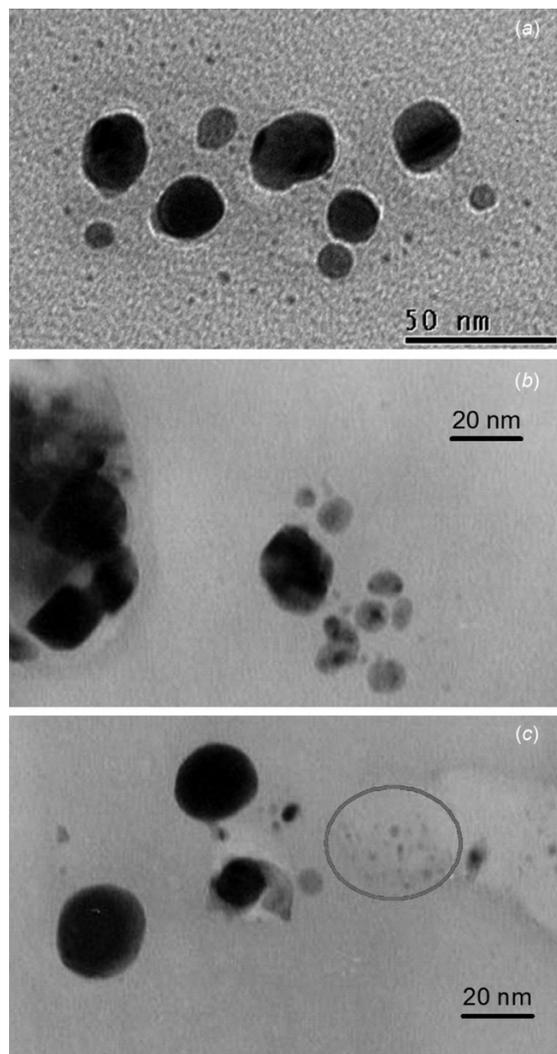
It may be noted that all the peaks are attributable to the metal. The presence of entrapped phthalocyanines does not influence the position and shape of typical lines in the diffractogram ($2\theta = 38.2°, 44.4°, 64.6°, 77.6°, 81.8°, 97.9°$). Thus, similar patterns were obtained for both the doped and undoped metal. The primary particle size by the Scherrer's equation[7] applied to all the six peaks gave results ranging from 9 to 13 nm, with an average value of 11 nm, both for doped and undoped silver. The presence of smaller particle sizes, however, is evident from TEM images (Fig. 2), coupled with EDAX (Fig. 3), that show how MORALs nanoparticles ranging from ~30 nm down to fraction of nanometers are actually obtained by carrying out the synthesis in the presence of the micelle (the particles are not mono-disperse, as the synthesis protocol was not optimized for that purpose).

It is also worth noting that the principal Ag peak in the EDAX spectrum was present (at ~3 keV) even in the case of particles with dimensions less than 1 nm (Fig. 3b). Peaks of Cu, Si, and O atoms in the same spectra were all due to the support used for the analysis, whereas the signal of C can be ascribed to the organic moiety of Pc and partly to the support.

Moving observation at a larger scale, the morphology of the powders appeared to be the same for both doped MORALs and undoped silver (Fig. 4) with aggregates of hundreds of nanometers up to few micrometers being clearly visible in SEM images.

Successful encapsulation of phthalocyanines was verified by means of thermogravimetric analysis. Figure 5 indeed shows that, although the very close peaks for the free and encapsulated phthalocyanine point to the presence of the organic dopant inside the metal bulk, quite different thermal degradations occurred for CuPc@Ag and FePc@Ag.
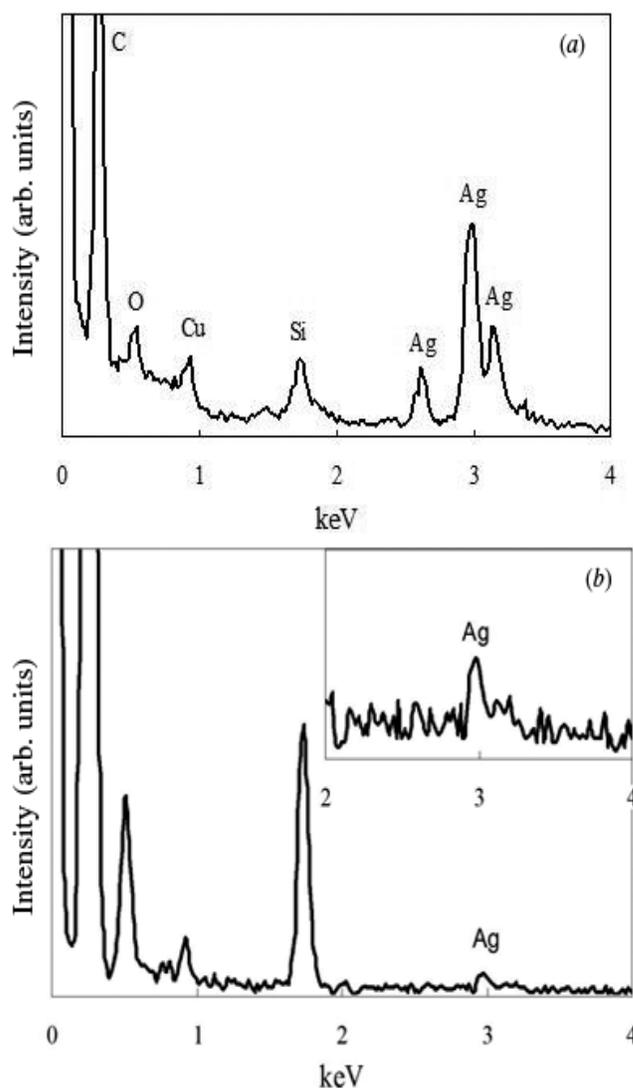
Fig. 2. TEM images of CuPc@Ag (*a*) and FePc@Ag (*b*, *c*). Magnifications: (*a*) × 400 000, (*b*) and (*c*) × 300 000.

Fig. 3. EDAX spectra corresponding to images of (*a*) Fig. 2*a* and (*b*) circle in Fig. 2*c*.

In fact, a clear degradation peak was obtained at 438 °C for the free phthalocyanine (Fig. 5*a*), whereas in the CuPc@Ag MORAL, concomitant narrowing of the decomposition temperature range and enhancement in thermal stability are noticed upon entrapment (ΔT = 24 °C between the degradation temperature of the free and encapsulated CuPc, Fig. 5*b*). The first effect may be due to the known catalytic action of Ag in thermal oxidative degradation processes,[5] as well as to being a clue to material's homogeneity; whereas the second effect is in accord with the behaviour previously observed for the polyacid Nafion entrapped in silver.[4]

Free FePc degrades between 320 °C and 410 °C (Fig. 5*c*) in a two-step process resulting in a main peak at 376 °C and a lower signal at 349 °C. On the other hand, in the case of FePc entrapped in silver, a broad peak is observed at 359 °C with degradation of the organic species occurring over a rather large temperature range in which the material apparently reacts with oxygen. Indeed, the increase in mass shown by the TGA profile of FePc@Ag after the decompo-
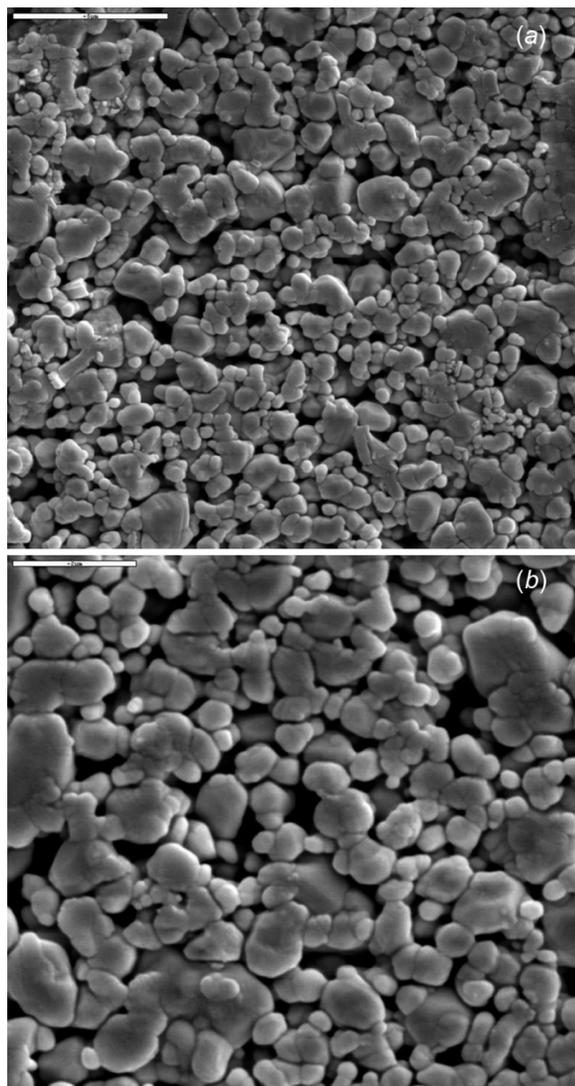
sition points to oxygen fixation and shows how markedly the reactivity of the metal is changed upon its doping with the iron phthalocyanine.

The shown TGA analyses are in some ways similar to those previously reported of similar materials, and the lack of organics' stability with temperature can be ascribed to the catalytic effect of silver.[4]

Finally, the TGA data, along with observation of (*i*) complete segregation of the metallocomplexes from the starting solution and (*ii*) lack of leaching in most common solvents, indirectly prove that MPc are located into the metallic particle, namely incorporated into the regular periodic structure of Ag nanoparticle as MPc and not as metal ions (Cu and Fe) left after washing or loose adsorbed complexes at the surface. In the latter case, in fact, water easily washes away the adsorbed molecules, while the TGA spectra should point to inhomogeneous materials when, to the opposite, data in Fig. 5 clearly point to materials' homogeneity.

It is still an open question whether, in the case of Nano-MORALs, entrapment takes place inside or outside the

Fig. 4. SEM images of tablets made of CuPc@Ag (*a*) and undoped Ag (*b*). Magnifications and bars: (*a*) × 5000, 5 μm; (*b*) × 10 000, 2 μm.

Fig. 5. TGA and DTA (in dry air) of CuPc (*a*), CuPc@Ag (*b*), FePc (*c*), and FePc@Ag (*d*).
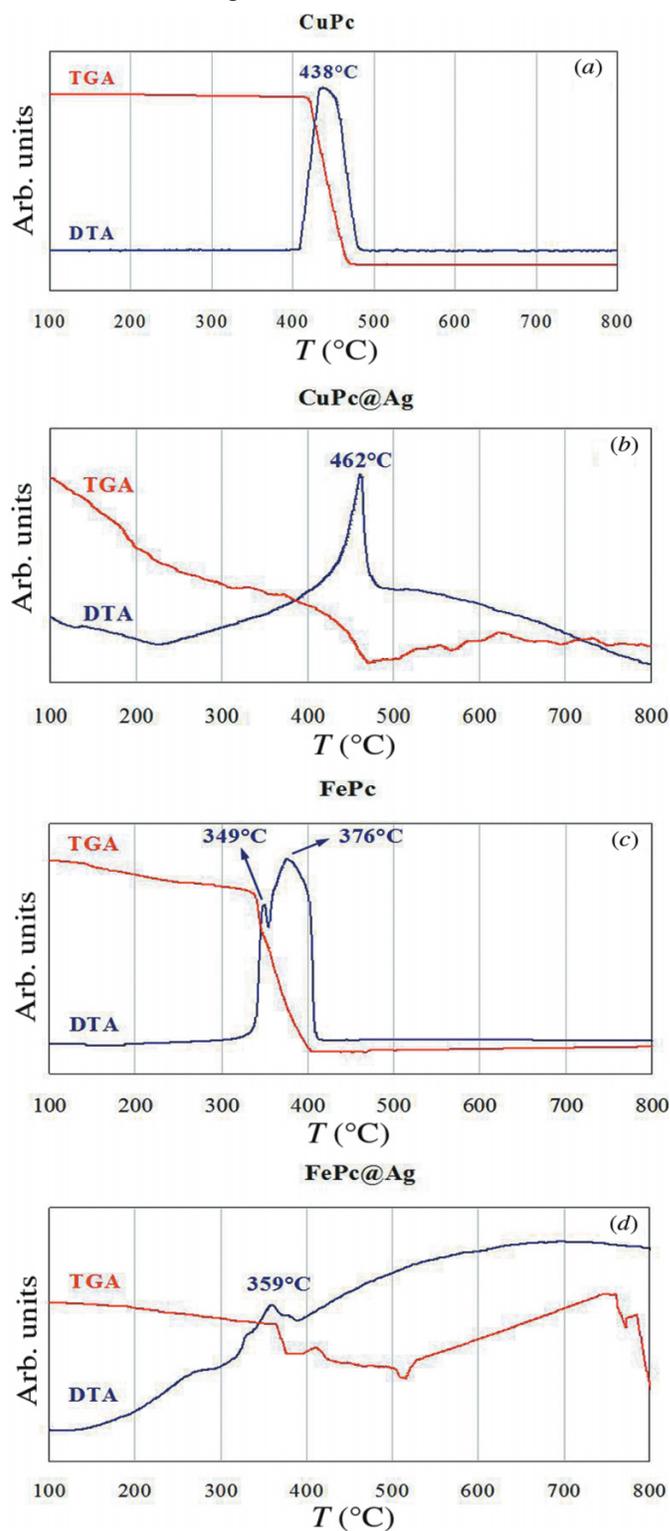

metal particle, making shells. Further structural studies on related materials are in course. In conclusion, we have developed the synthesis of nanosized metal–organic composites by employing a straightforward micelle-assisted synthesis. Silver nanoparticles[8] and metal phthalocyanines[9] have many functional applications, and soon these new nanomaterials might find practical use. From a fundamental viewpoint, however, the method described in this report is general and opens the route to the synthesis of a new class of metal–organic nanocomposites, termed NanoMORALs, whose forthcoming applications may indeed go beyond those, remarkable, being discovered in the case of the corresponding MORAL materials.

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