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Chirality Induction in Bulk Gold and Silver**

By *Hanna Behar-Levy, Oara Neumann, Ron Naaman,** and *David Avnir**

In a recent series of papers we introduced a new family of materials, namely, organically doped metals.[1–5] Both small molecules[1,4,5] and polymers[2–5] were used for the preparation of these new composites, which exhibit properties that are both metallic and organic. A typical example is silver doped with the acidic polymer Nafion (Nafion@Ag), rendering this metal with an unorthodox acidic property that was indeed applied to some classical organic catalytic reactions.[3] Entrapment within the metal is a distinctly different process from adsorption. For example, water-soluble molecules, which are easily washed away from the metal surface when adsorbed on it, do not readily leach out of the composites when they are washed with water. The intimate entanglement of the organic component between the aggregated metallic nanograins was proven by various methods, of which thermogravimetric analysis–differential scanning calorimetry (TGA–DSC) was particularly informative.[2] Although most of our efforts have concentrated on doped silver, proving the generality of the developed methodology has also been proven by preparing organic composites with copper and gold.[5]

A particularly interesting challenge has been to dope metals with *chiral* molecules, in an attempt to induce chiral properties in the metal. Here we report that this goal has been achieved. Specifically, we present experimental evidence for consistent chiral asymmetry in the photoemission of electrons from gold and silver embedded with chiral biomolecules (L-glutathione, L-quinine, and D- and L-tryptophan). Thus, counter-clockwise circularly polarized light (ccw-CPL) and clockwise CPL (cw-CPL) induce different photoelectron emission yields from the doped metal sample, thus proving different diastereomeric interactions between light and the metal electrons. The experimental methodology, which has already been applied successfully to chiral monolayers on gold surfaces,[6–8] is described in detail below. While the silver composites have been explored in detail in past studies, the gold composites are new, and therefore some background experiments with achiral dopants (Congo red (CR) and thionine (Th)) in gold were also carried out.

It is relevant to mention some other studies in which metals and chirality were placed in the same context, including the chiral structure of metal nanoclusters with organic adsorbates,[9] the helicity of metal nanowires,[10] the adsorption of chiral molecules on the surface of metals,[11,12] and the formation of chiral "2D" surfaces by cutting metal crystals along high-Miller-index planes.[12,13] Many of these studies were carried out with metallic gold; the induction of chirality in metallic silver has been much less explored,[14] although there is a recent example of induction of chirality in silver nanoparticles through the adsorption of DNA.[15]

Chirality is detected, amongst other methods, by circular dichroism (CD) spectroscopy, which requires good optical transparency. However, the compressed discs of dopant@metal are devoid of this property. Therefore, the idea behind the present study was to look for possible electron circular dichroism[6] in photoelectrons emitted from the metals. Any successful detection of chirality involves different diastereomeric interactions between the enantiomers of a chiral specimen and a chiral probe, or between a chiral specimen and the enantiomers of the chiral probe. In our experiment, the chiral specimens are chiral-molecule@metal, and the chiral probe is circularly polarized UV light (ccw-CPL and cw-CPL). The details of the experiment are given below.

Entrapment of Molecules in Gold: Because one of the novel aspects of this report is the extension of the homogeneous entrapment-in-metal methodology to gold, we first performed some comparative experiments to those reported for achiral CR and Th entrapped in Ag at a ratio of 1:100.[1] X-ray diffraction (XRD) analysis (Table 1; carried out with a Philips automated powder diffractometer equipped with a PW1830

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Table 1. X-ray diffraction patterns of CR-doped and undoped gold.

CR@Au		Literature data for Au [a]		Plane
2θ [°]	Intensity	2θ [°]	Intensity	(hkl)
100	38.355	100	38.184	111
33.3	44.545	52	44.392	200
15.4	64.750	32	64.576	220
13.5	77.710	36	77.547	311
4.4	81.840	12	81.721	222
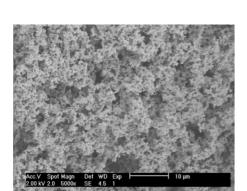
[a] Data from 2003 Joint Committee on Powder Diffraction Standards (JCPDS).

generator, a PW1710 control unit, a PW1820 vertical goniometer, at 40 KV, 35 mA, and Cu Kα (1.5405 Å)) indicates that the gold in CR@Au has a regular cubic-packed structure, practically unchanged from pure gold. The diffraction lines are quite narrow, indicating a fairly narrow crystallite size distribution, centered (by application of Scherer's equation) at ca. 3.1 nm. High-resolution scanning electron microscopy (HRSEM) images (Fig. 1; taken with a Sirion microscope) show that these elementary building blocks cluster into aggregates ca. 500 nm in size, which are further aggregated into a macroporous solid, with pores of the order of ca. 5–10 μm. This hierarchical structure resembles the structure found for organically doped silver.[3]
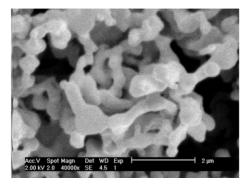
tracted by water, they are still accessible to interaction with external water-soluble reagents that can penetrate the porous matrix, reach the entrapped molecule, and interact with it. Thus, when CR@Au was subjected to $Na_2S_2O_4$, CR underwent the known bleaching reaction,[16] and DMSO extraction of the dye showed that after 24 h, 70 % of the extracted molecules had reacted with $Na_2S_2O_4$.

Chiral Gold: We begin with the result of an important blank experiment that will serve to indicate the real nature of the enantioselective observations reported later. Figure 2A shows the electron energy distribution profile obtained for photoelectrons ejected from pure gold (prepared as in the doping procedure, but without the dopant). When the photoelectrons
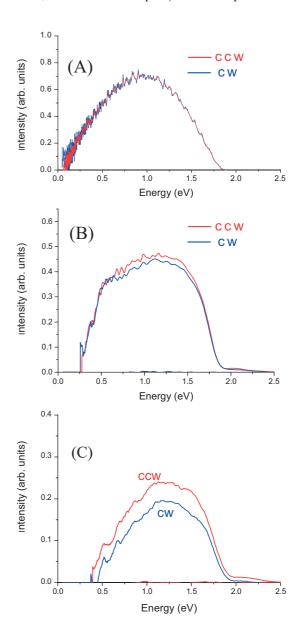

Figure 1. HRSEM images of organically doped gold at two magnifications.

The fact that entrapment is a distinctly different process compared to adsorption is evident from the observation that CR, a water soluble dye, cannot be extracted from the gold by using water; with a better solvent, dimethyl sulphoxide (DMSO), it is possible to extract 50 % of the entrapped dye (which was then spectroscopically shown to be intact after the entrapment process). These values are practically the same for CR@Ag, 0 % and 50 % for water and DMSO, respectively, indicating a similar strength of dye–metal interaction in both cases.[1] For another water soluble dye, Th, the observations were similar: water extracted 9 % of the dye from Th@Au, whereas DMSO extracted 55 %.

Also similar to the entrapment in silver was the finding that although the entrapped water-soluble molecules are not ex-

Figure 2. The electron energy distribution profiles obtained for photoelectrons ejected by either ccw-CPL or cw-CPL from: A) pure gold; B) gold doped with L-glutathione (L-Glu@Au); C) gold doped with L-quinine (L-Qui@Au).

are ejected by either ccw-CPL or cw-CPL, the two curves practically coincide. On the contrary, the kinetic energy distribution profiles of the photoelectrons ejected from gold doped with L-glutathione (L-Glu@Au) show a clear difference between the two curves (Fig. 2B); this is even more evident with another chiral molecule, L-quinine (Fig. 2C). In both cases, ccw-CPL interacted diastereomerically differently (better) with the chiral L-dopant@Au, compared with the interaction with cw-CPL. Needless to say, an important test for the authenticity of the phenomenon is to see if L-dopant@Au and D-dopant@Au produce reversed effects when interacting with either ccw-CPL or cw-CPL. This is indeed what we found. Figure 3 shows the results for L-Trp@Au and D-Trp@Au: while for the former, the curve corresponding to electrons emitted by the ccw-CPL is *above* the cw-CPL curve, for the latter it is *below*!
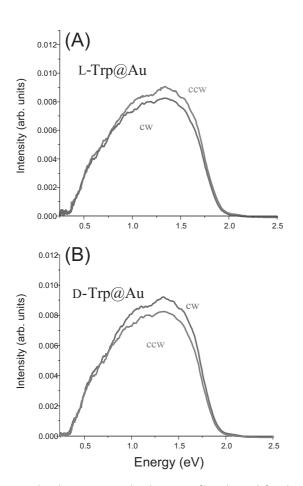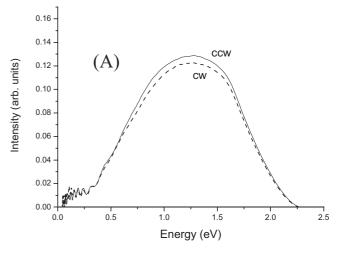

Figure 3. The electron energy distribution profiles obtained for photoelectrons ejected by either ccw-CPL or cw-CPL from A) L-Trp@Au or B) D-Trp@Au; note the reversal in the order of the lines.

Chiral Silver: The possibility of inducing chirality in a metal has the potential to be general. The observations with doped Au were also obtained with doped Ag. Ccw-CPL and cw-CPL interacted differently with L-Glu@Ag (Fig. 4A) and again dif-
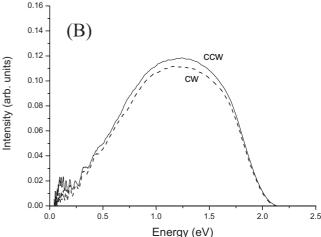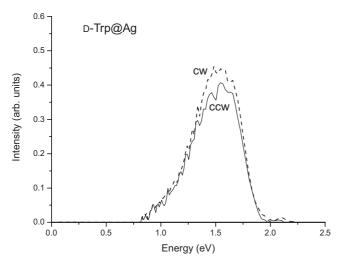

Figure 4. The electron energy distribution profiles showing the different interaction of ccw-CPL and cw-CPL with A) L-Glu@Ag, and B) Qui@Ag.

ferently with Qui@Ag (Fig. 4B). As in the case of chiral gold, all four possible diastereomeric interactions were observed for Trp (Fig. 5): ccw-CPL/L-Trp@Ag, cw-CPL/D-Trp@Ag, cw-CPL/L-Trp@Ag, and ccw-CPL/D-Trp@Ag. Note that the first and second pairs of diastereomers are actually pairs of enantiomers, and therefore these two pairs should behave similarly within each of them; this is indeed what is seen in Figure 5: the first pair of enantiomers are the top lines in the two figures, while the second pair comprise the lower lines. The same analysis and observations also hold for Trp@Au (Fig. 3).

In conclusion, we have described experiments demonstrating that doping of gold or silver with a chiral organic molecule induces chirality in the metal. Because the observed diastereomeric phenomena is associated with the metal-emitted electrons, it is the metal which exhibits the chirality. The fact that we observed all possible diastereomeric interactions between ccw-CPL and cw-CPL and dopants supports the conclusion that the dopant-induced chirality effect is real and signifi-
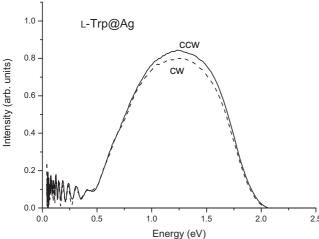
Figure 5. The electron energy distribution profile obtained for photoelectrons ejected by either ccw-CPL or cw-CPL from (top) D-Trp@Ag or from (bottom) L-Trp@Ag; note again the reversal in the line order, and the complete set of all four diastereomeric interactions: ccw-CPL/L-Trp@Ag, cw-CPL/D-Trp@Ag, cw-CPL/L-Trp@Ag and ccw-CPL/D-Trp@Ag.

cant. At this stage we can propose two possible mechanisms for the effect, but cannot distinguish between them. The two possibilities are:[17] 1) The surface of the metallic cage entrapping the chiral molecule is chirally imprinted, and therefore the actual morphology of the metal surface is chiral, leading to chiral electronic orbitals; 2) No chiral morphology is formed in the metal, however the interaction of the metal electrons with the electrons of an adsorbed/entrapped chiral molecule is enough to produce the chirality observed. A comment is also required for the observation that ccw-CPL interacts better with L-doped metals compared with cw-CPL. Elsewhere we have discussed in detail the known tentativeness of handedness labeling of chiral objects.[18] It is indeed just a label, and so the ccw/L preference is coincidental.

Work is in progress to further explore the generality of the induction of chirality in metals and to distinguish between the two possible chiral induction mechanisms.

Experimental

$AuCl_3$, $AgNO_3$, Congo red (CR), thionine (Th), the tripeptide reduced L-glutathione (γ-L-glu-L-cys-gly) (Glu), D- and L-tryptophan (Trp), L-quinine (Qui), $Na_2S_2O_4$, and $NaH_2PO_2\cdot \sim 0.2\,H_2O$ were purchased from Aldrich.

Entrapment in Gold: In a typical experiment 0.26 g of $AuCl_3$ (0.86 mmol) was dissolved in 10.0 mL of a water solution of 6.0 mg of CR (0.0086 mmol). While stirring, 0.22 g of sodium hypophosphite (2.0 mmol) was added, and stirring continued at room temperature for 48 h. Gold is formed according to the following reaction, while entrapping the organic molecule: $2\,AuCl_3 + 3\,NaH_2PO_2 + 3\,H_2O \rightarrow 2\,Au + 3\,NaH_2PO_3 + 6\,HCl$.

The precipitate, dopant@Au, was washed with five 20 mL portions of water, dried, and kept under nitrogen. The reduction of the gold cation then proceeds to completion. Either all of the dopant molecules (CR) or at least 90 % (Qui and Glu) were entrapped. For the photoelectron emission experiments, the powder was compressed into a disk.

Blank Experiments: All dopants were checked for their stability towards the reducing agent hypophosphite and found to be stable. Typically, 6.0 mg CR was dissolved in 10.0 mL water, to which 0.22 g of the hypophosphite was added and the solution stirred for 24 h. Spectra before and after the exposure to the reducing agent were compared, and found, in all cases, to be identical.

Stability to the Gold Cation: Similarly, all dopants were found to be stable to the oxidative nature of Au^{3+}. Typically, 6.0 mg of CR was dissolved in 10.0 mL water, to which 0.26 g of $AuCl_3$ was added. The solution was stirred for 2 h in the dark. The solutions were checked spectroscopically or by CD (with a JASCO J810 instrument).

Stability Checked by Extraction: 0.01 g of dopant@Au was treated with 3.0 mL of DMSO for 24 h, and the partially extracted dye solution was checked spectroscopically. In all cases, it was found that the dopant was unaffected.

Entrapment in Silver: These experiments were carried out using a procedure similar to that reported earlier [1]. Likewise, similar blank experiments were carried out to assure stability of the dopant to the reaction conditions.

Accessibility of the Dopant to Reaction with an External Reagent: 0.09 g of CR@Au (1:100) was stirred in a 5.0 mL solution of $Na_2S_2O_4$, in order to affect the reductive cleavage of CR to benzidine and diaminonaphthalene sulfonic acid [16]. After 24 h the solid was washed with 10.0 mL water, the residual CR that had not reacted was extracted with DMSO, and its quantity determined spectroscopically. A blank reaction carried out in solution is described in the literature [1].

Enantioselective Photoelectron Emission Experiment: The samples (at a 1:1000 ratio of dopant to metal) were inserted into an ultrahigh vacuum chamber at $< 10^{-8}$ mbar (1 bar = 100 kPa). The photoelectrons are ejected from the substrate by applying a laser beam at 193 nm (6.4 eV) using a $\lambda/4$ plate to create either ccw or cw circularly polarized light. The ejected electron energy distribution is analyzed by using a time-of-flight spectrometer [19,20]. The laser energy is maintained very low (20 pJ per pulse, energy density ca. 2 nJ cm^{-2}) to avoid any nonlinear processes.

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