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Molecularly Doped Metals

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CONSPECTUS

The many millions of organic, inorganic, and bioorganic molecules represent a very rich library of chemical, biological, and physical properties that do not show up among the approximately 100 metals. The ability to imbue metals with any of these molecular properties would open up tremendous potential for the development of new materials. In addition to their traditional features and their traditional applications, metals would have new traits, which would merge their classical virtues such as conductivity and catalytic activity with the diverse properties of these molecules.

In this Account, we describe a new materials methodology, which enables, for the first time, the incorporation and entrapment of small organic molecules, polymers, and biomolecules within metals. These new materials are denoted dopant@metal. The creation of dopant@metal yields new properties that are more than or different from the sum of the individual properties of the two components. So far we have developed methods for the doping of silver, copper, gold, iron, palladium, platinum, and some of their alloys, as well as Hg–Ag amalgams. We have successfully altered classical metal properties (such as conductivity), induced unorthodox properties (such as rendering a metal acidic or basic), used metals as heterogeneous matrices for homogeneous catalysts, and formed new metallic catalysts such as metals doped with organometallic complexes. In addition, we have created materials that straddle the border between polymers and metals, we have entrapped enzymes to form bioactive metals, we have induced chirality within metals, we have made corrosion-resistant iron, we formed efficient biocidal materials, and we demonstrated a new concept for batteries.

We have developed a variety of methods for synthesizing dopant@metals including aqueous homogeneous and heterogeneous reductions of the metal cations, reductions in DMF, electrochemical entrapments, thermal decompositions of zerovalent metal carbonyls, and dissolution during amalgam formation. The structures of these dopant@metal materials indicate that metals entrap the organic molecules within their agglomerated nanocrystals. As a result, these materials are porous, making the dopant accessible for chemical reactions, in particular for catalysis. We have prepared these materials in a variety of forms, including powder, granules, pressed discs, thin films, thick films, sub-micrometer particles, and nanometric particles decorating ceramic nanofibers.

Entrapment and adsorption are very different processes. If entrapped, water-soluble molecules cannot be extracted, but the same molecules, if adsorbed, are easily washed away. Likewise, most of the special properties that we have observed, such as major improvements or changes in catalytic activity, completely different thermal gravimetric analysis behavior, and more, are observed only in the entrapped cases.

1. Motivation

Why should one dope metals with organic molecules in the first place? To start with, hybrid materials composed of metals in their native form and of organic molecules have been by-and-large unknown. Of course, having metals and organics in the same context, such as dispersed metal nanoparticles in polymers, polymer protective coating of metals, molecules anchored to metallic surfaces, and so on have been well-known, but not as intimately intermixed hybrid materials. Immediately comes to mind also the very active field of MOFs, but again, our focus has not been metal–*cation* complexes, but the zerovalent metallic materials. So the most basic motivation is that this is an Everest that has not been climbed yet; but of course there are also practical motivations:

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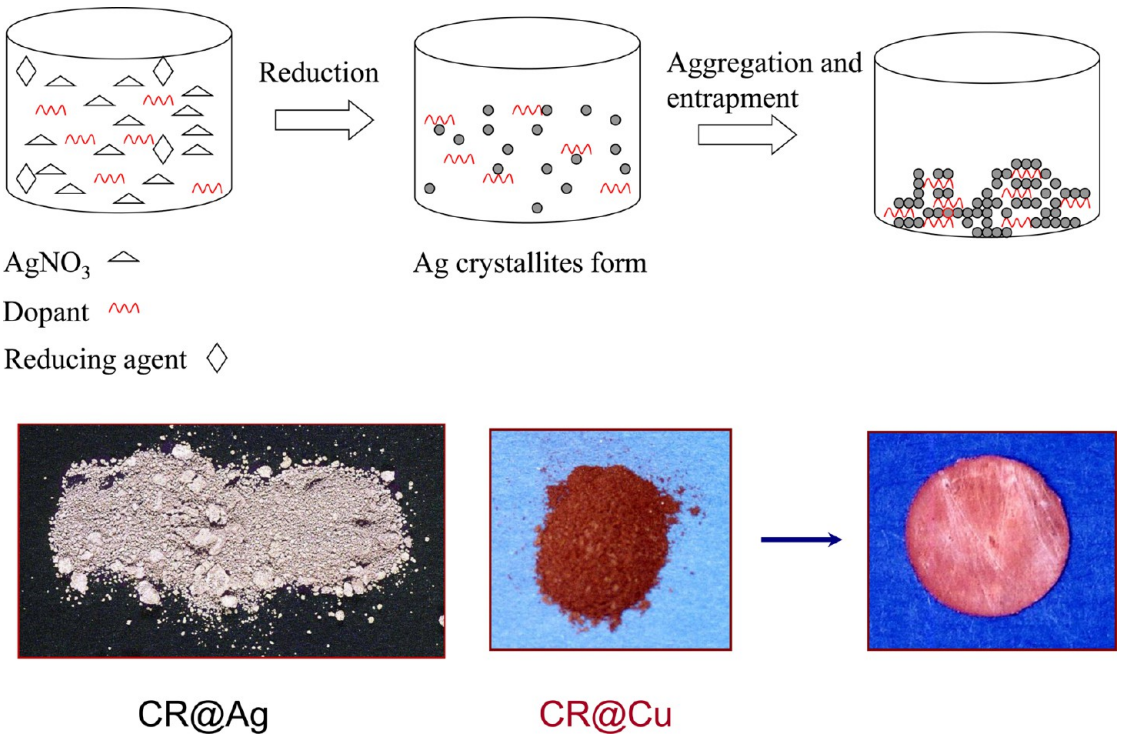

FIGURE 1. (top) Entrapment of dopant molecules within a metal, Congo-red (CR) within silver in this example, is obtained by a homogeneous reduction; a metallic granular powder of CR@Ag, is obtained (bottom left). CR@Cu is obtained heterogeneously by reducing Cu^{2+} with Zn (bottom center), which can be pressed into a metallic disc.

- Most elements are metals. When considering a potential source of new materials, focusing on this large portion of the periodic table as a group with a new concept may turn out to be fruitful.
- Metals are everywhere. Any new methodology for affecting their properties is potentially interesting. This is particularly so because of the following:
- The library of organic compounds is huge while the number of metals is small; merging both enlarges dramatically the scope of metallic materials.
- Placing a molecule in a sea of electrons should affect its properties.
- Placing foreign molecules within a metal should affect its properties as well.
- Synergetic effects between the metal and the dopant may emerge, in chemical and biochemical reactivities and in physical properties.

Within the last decade, a number of methods for preparing these materials have been developed and many of these predictions have materialized: new type of catalysts, new bioactive materials, metals with altered properties, metals with new, unorthodox properties, dopants with altered properties, and more emerged. It also became clear that entrapment (a 3D process) and adsorption (a 2D process) are distinctly very different, and in practically all of these findings, the entrapping 3D process was essential. Here are the details.

2. The Methodology

2.1. Synthesis. After some search for suitable synthetic approaches for these composite materials, the solution was found to be basically a first-year chemistry text-books solution:[1] Reduce the metal cation in the presence of the molecule to be entrapped; the metal precipitates dragging and entrapping the dopant tightly within it. Methods for entrapment of molecules within metals have been developed, based on this general approach. For instance, for the entrapment of the dye Congo-red (CR) in silver,[1] to a solution of $AgNO_3$ and CR, NaH_2PO_2 is added and dissolved; metallic Ag begins to form, and eventually precipitates with CR in it, leaving the supernatant solution colorless, despite the high solubility of the dye in water: CR@Ag (we use this notation) is obtained (Figure 1). The art in this elementary process is to find a reducing agent that will not harm the dopant, that will allow an easy wash-off of the byproducts, and that will comply with the kinetics of the mechanism described below.

A second synthetic method that has been developed is the *heterogeneous* reduction of the metal cation with a metal

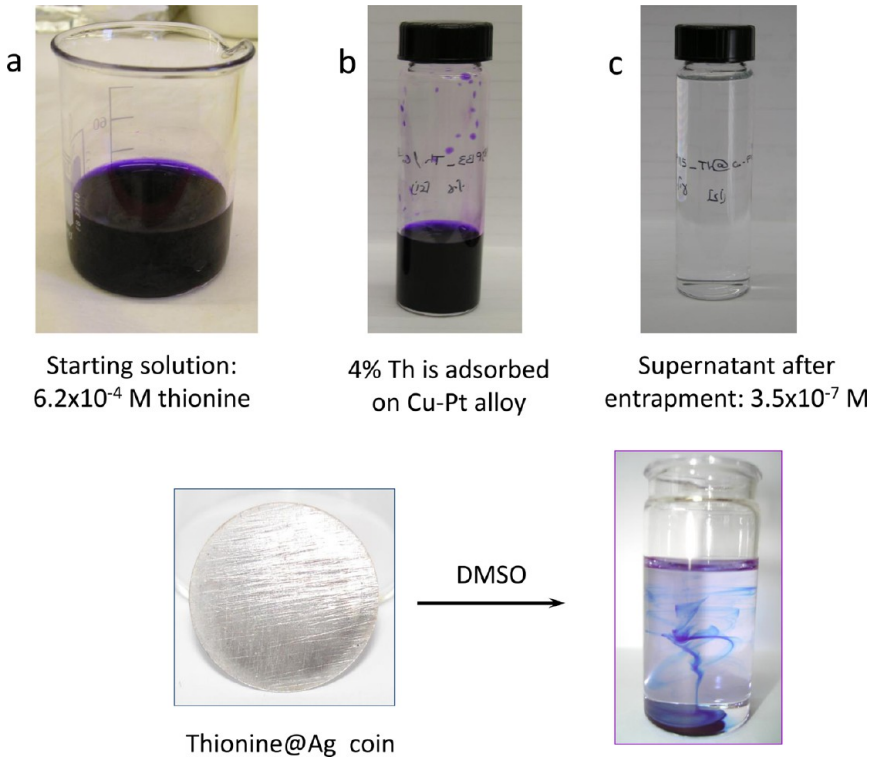

FIGURE 2. Entrapment within a metal and adsorption are very different processes. (top) When a solution of thionine (Th) (a) is exposed to powder of Cu–Pt alloy, only 4% of the Th is adsorbed (b), but practically all is entrapped while forming Th@Cu–Pt (c). (bottom) Water-soluble Th is easily washed away in adsorption, but extraction of Th from doped silver is extremely slow; only DMSO is capable of efficient extraction.

that is above it in the electrochemical series.[2] For instance, CR@Cu forms when Zn is used as the reducing agent for copper salt, in the presence of CR (Figure 1). The heterogeneous process proved particularly useful in the preparation of doped metallic alloys,[3] such as thionine@Cu–Pt; alloys extend of course the scope of the methodology, significantly (Figure 2). Next, it was necessary to develop methods for entrapment of hydrophobic dopants that cannot dissolve in water, which is the standard solvent for metal cation reduction. This has been achieved in two ways: either by solubilizing the dopant in water with a surfactant (Sudan-III@Ag was prepared in that way)[1] or by utilizing solvents such as DMF, which can dissolve both the metal salt and the hydrophobic dopant and can also act as reducing agents in the presence equimolar water.[4] This synthetic method was found to be useful for preparing metallic hybrids of polyaniline, polystyrene, and poly(acrylonitrile).[4] The classical electrochemical reduction of metal cations was harnessed as a fifth method for this goal,[5] and the generality of that approach was demonstrated by the successful entrapping of both small molecules and polymers, resulting in thionine@Cu, thionine@Ag, CR@Cu, crystal violet@Cu, safranin-O@Cu, 1,10-phenanthroline@Cu, Nafion@Cu, Nafion@Ag, and poly(allylamine)@Cu.

All of these methods involve the reduction of the cation of the desired metal. This is a limitation for the doping of metals with low or negative reduction potentials, and there are many important metals in this category. The problem is that reduction procedures for such cations maybe too harsh for the dopant. The approach for this case was therefore different: to start with metallic precursors that are already at zero oxidation level.[6] This nonreductive method was used for the entrapment of several polymers in iron by the solution thermolysis of $Fe(CO)_5$, leading to highly corrosion resistant iron (section 4). Finally, specific cases may require the development of specific methods. An example is a method developed for entrapment in Hg–Ag amalgams. Here we used the fact that Hg is a very good solvent of metals (e.g., Au, Ag, Cu), and prepared the triple amalgam hybrids, organics@Ag–Hg, by dissolving organics@Ag in Hg, obtaining, for instance, the potentially antibacterial amalgam chlorhexidine@Ag–Hg.[7]

2.2. Scope. 2.2.1. The Metals. So far we have developed this new class of materials with the following metals (in order of increasing atomic number): iron,[6] cobalt,[8] copper,[2,5]

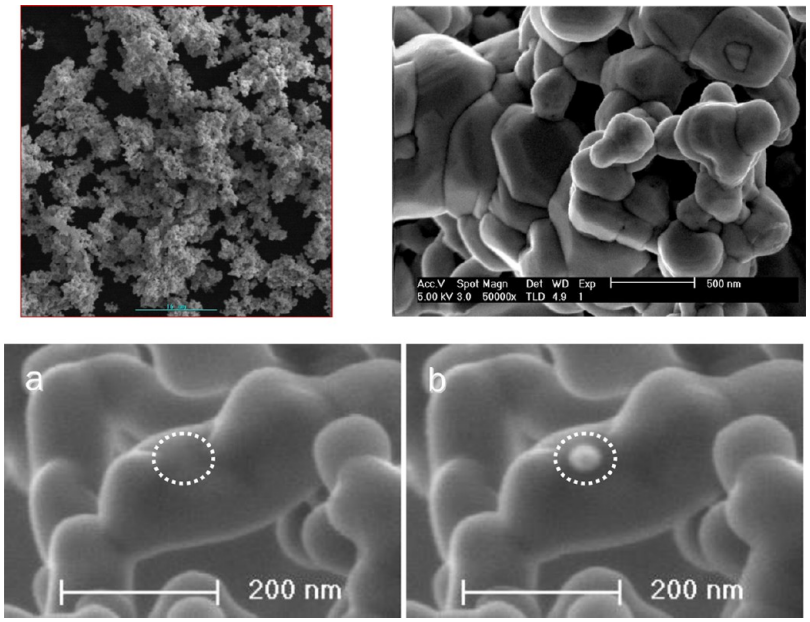

FIGURE 3. (top) Poly(styrene sulfonic acid)@Ag at two resolutions (bars are 16 μm and 500 nm), revealing the porous hierarchical nature of the material. (bottom) The existence of the dopant in RhCl(COD)($Ph_2P(C_6H_4SO_3Na)$)@Ag (a) is revealed by its oozing out (b) upon exposure to the heat of the probing electrons.

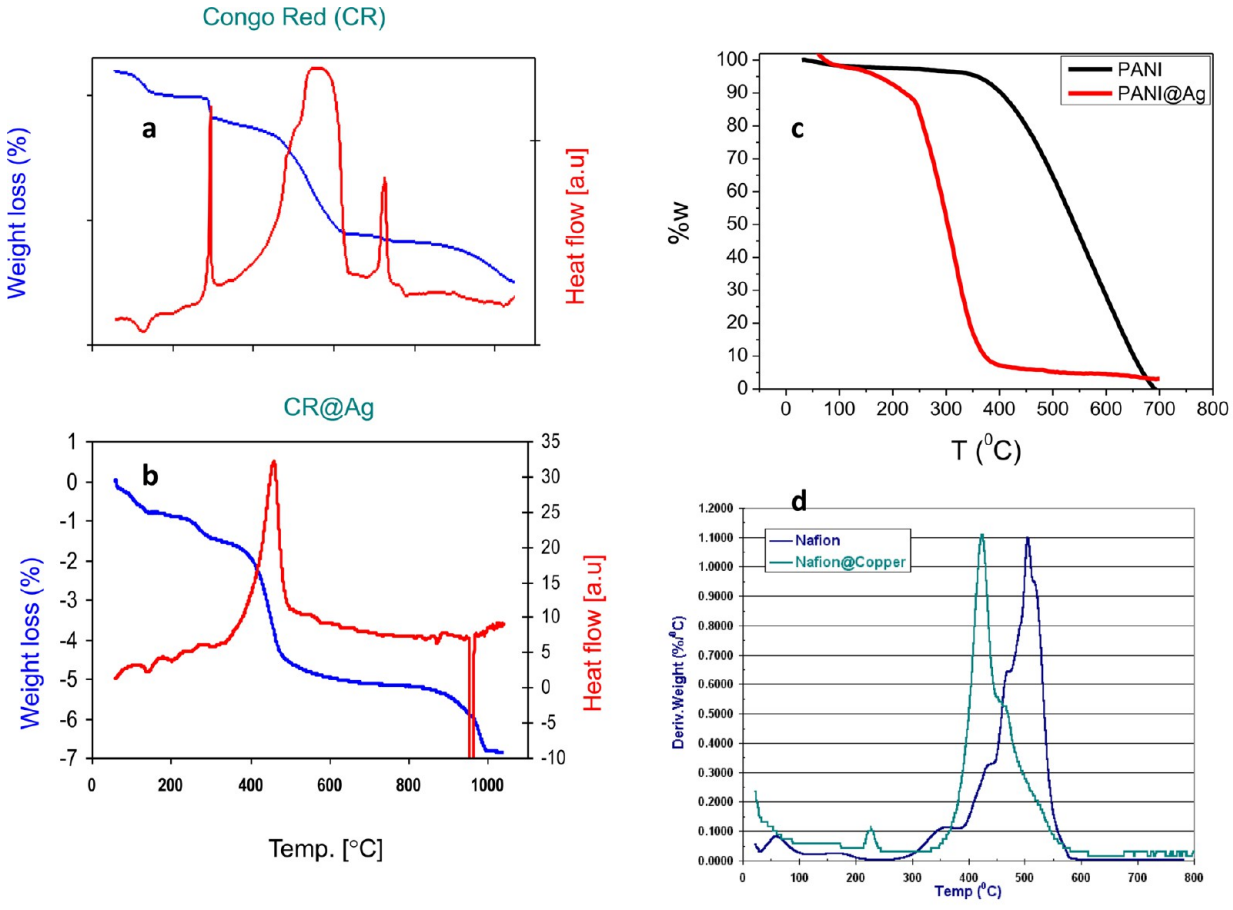

FIGURE 4. (a) The TGA (blue; DTA in red) of free Congo-red. (b) Upon entrapment in silver, there is a significant lowering of the oxidative temperature, a cleaner decomposition, and narrowing of peaks. This is also observed for other dopants, (c) polyaniline@Ag and (d) Nafion@Cu.

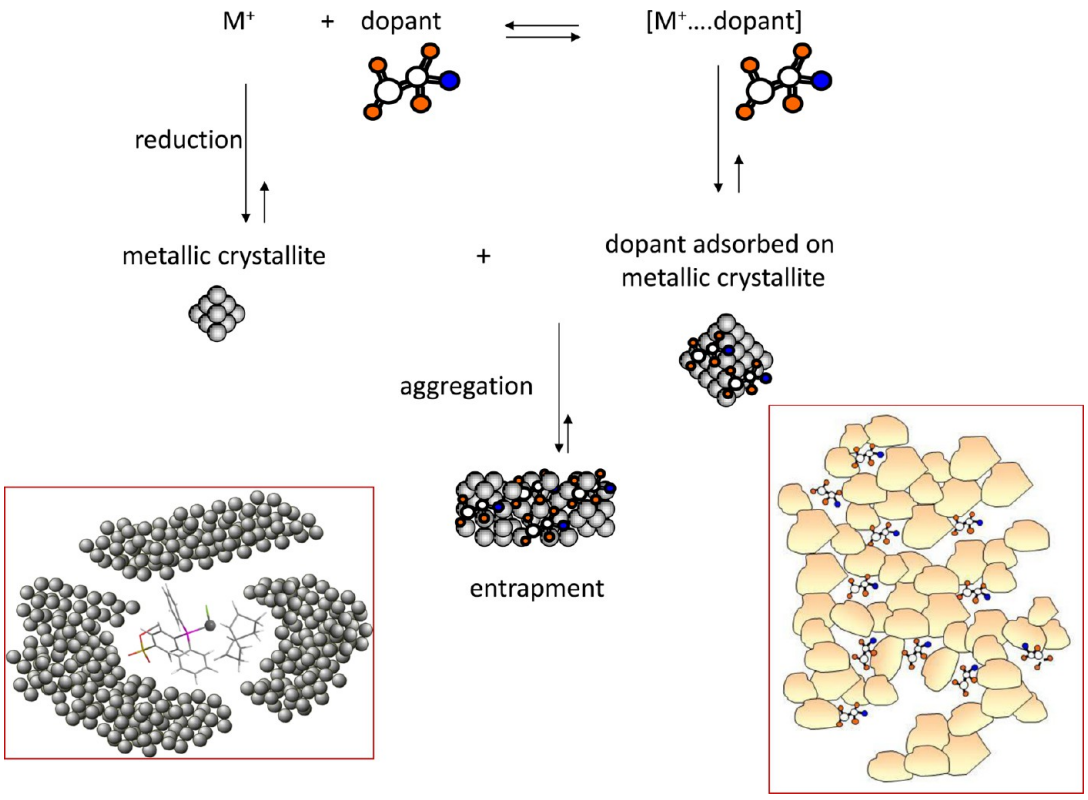

FIGURE 5. The mechanism of entrapment, see text for explanation. (left frame) An organometallic complex (RhCl(COD)($Ph_2P(C_6H_4SO_3Na)$) within a metallic cage. (right frame) The suggested picture of the entrapment.

palladium,[9,10] silver (most of the references), gold,[11,12] and mercury–silver alloy,[7] as well as alloys of copper–palladium, silver–gold, and copper–platinum.[3]

2.2.2. The Dopants. We developed procedures for the entrapment of practically all of the important classes of chemical entities: small molecules, hydrophilic such as chlorhexidine[13,14] or hydrophobic such as Sudan-III;[1] biological, such as D-tryptophan[11] and chiconidine;[9] organometallic complexes such as RhCl(COD)($Ph_2P(C_6H_4SO_3Na)$);[15] polymers, hydrophilic[16,17] such as poly(styrenesulfonic acid) (Figure 3) or hydrophobic[4,6] such polyacrylonitrile; enzymes such as acid phosphatase;[12] and inorganic dopants,[18] such as the polyoxometalate $H_3[P(Mo_3O_{10})_4]$; more examples are mentioned below.

2.2.3. The Doping Range. The doping range is from fraction of a percent, say 0.2% by weight, resulting in what we term "doped metals", up to 10% by weight, mainly polymers, which we term "hybrid materials". The fact that 10% is already a hybrid material becomes clear when one recalls the much higher atomic weight of the metal: in terms of the ratio between the number of nonmetallic atoms and metals atoms, 10% may mean a 1:1 molar ratio composite.

2.2.4. The Formats. These metallic materials were usually made as granulated powders (Figure 1), but they were also prepared as pressed coins (Figures 1 and 2),[2,6] as a thick electrochemically derived deposits,[5] as nanometric and sub-micrometer particles[19–21] (Figure 7, bottom), or as thin films.[19] Our latest addition is the development of several doping-electroless procedures, which result in doped thin films; doped gold and silver films were prepared by this new methodology and SERS and fluorescence of molecules from within gold, were observed.[22]

2.3. Structure. The materials are porous, with a hierarchical structure. As seen in Figure 3, top (poly(styrene sulfonic acid)@silver),[16] the powder is of large porous clusters, 10–30 μm in size, which are composed of tightly held submicrometer crystals, which are further composed of metallic nanocrystals, typically at the range of few nanometers up to 30 nm, depending on the dopant and the metal, as determined by the Scherer equation applied on XRD data. An important feature of the XRD data, which helped in proposing the mechanism of entrapment (below), is that the diffraction angles remain precisely the same as in the pure fcc or bcc metal crystal; that is, the doping does not represent penetration into the dense metal lattice. Densities are

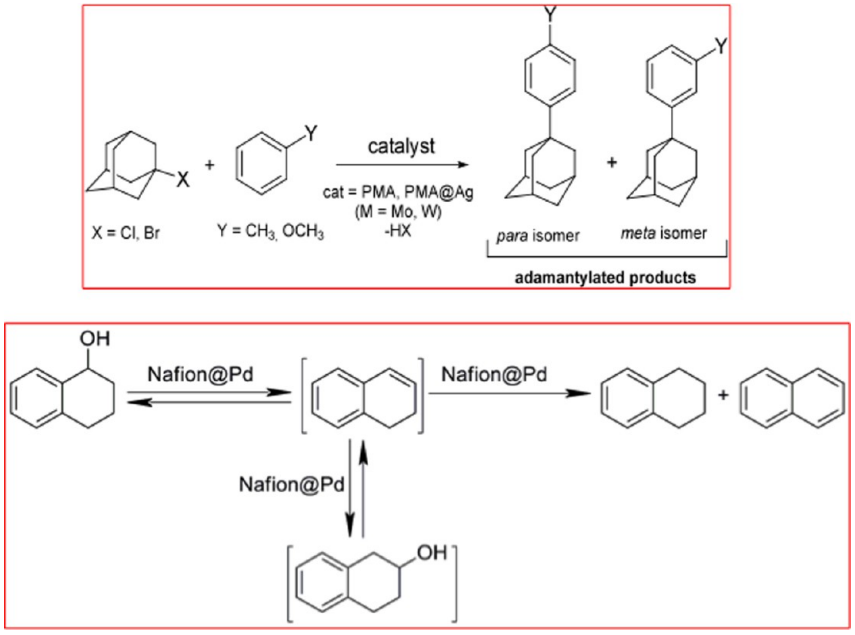

FIGURE 6. (top) Metals as heterogenization matrices for homogeneous catalysts: Adamantylation catalyzed by polyoxometallates@silver. (bottom) Entrapment of a catalyst in a catalytic metal, Nafion@Pd: The direct dual catalytic dehydration-disproportionation reaction.

indeed low compared with the native metal. For instance, Ag has a bulk density of 10.5 g/cm^3, but Congo-red@Ag has a density of 2.3 g/cm^3 (and the undoped powder a density of 3.6 g/cm^3).[1] Typical N_2–BET surface areas are few m^2/g, typical average pore sizes (by the BJH analysis) are 10–20 nm, and the adsorption–desorption isotherm has its narrow hysteresis loop at very high P/P_0 values (~0.9), all of which strongly support an interstitial porosity structure of an aggregate. It should also be noted that the compliance of the adsorption–desorption isotherm data to the BET equation is perfect,[1] and this is usually an indication of high homogeneity of the analyzed material.

2.4. Proofs That the Dopant Is there: 3D Entrapment Is Very Different from 2D Adsorption. There are quite a number of features that distinguish the 3D entrapment from 2D adsorption. The most elementary one is the following: A solution of Congo-red (CR) is prepared; in one experiment that solution is used for the entrapment process in Ag, and in another experiment, it is exposed to Ag prepared in the same way but without a dopant. The entrapment proceeds to 100%, but only 1% is adsorbed.[1] Visually this difference is very clear, as seen in Figure 2, top, for the entrapment of thionine in an alloy of Cu–Pt. Yet another indication for the entrapment is the behavior in the solvent of the doped molecule. Thionine, for instance, which is water-soluble and entrapped in a water-based reaction, is easily washed away when adsorbed on silver but can hardly be extracted at all from thionine@Ag with water.[2] It takes a very strong solvent such as DMSO to extract the dye (Figure 2, bottom). Such extractions not only prove that the dopant is caged inside the metal but also provide an important test to see whether anything happened to dopant in the process of entrapment. It was found that in the vast majority of the doping processes, the dopant remains intact (for a detailed explanation of why DMSO is capable of efficient extraction while water is not, see ref 3). Then, a classical test for the existence of an organic component in a hybrid material is thermal gravimetric analysis (TGA, Figure 4). Whereas extraction provides quantification of the amount dopant that is accessible to the extracting solvent, TGA (or total metal dissolution[5]) provides a full evaluation of that amount, and these populations need not be the same.[5] Note in the TGA traces[2,23,24] (detailed in the caption of Figure 4) that the full oxidative decomposition of the dopant ends at significantly lower temperatures compared with the free molecule, that it is narrower, and that it is cleaner. All of these observations indicated are the result of the oxidative catalytic action of the metal, and thus provide additional proof of the entrapment. Yet another indication comes from SEM. In Figure 3, bottom (the catalytic rhodium complex@Ag), we see an interesting "before-and-after":[15] the same circled spot is shown at the start of observation, and after a short while, the oozing-out of the organic materials is clearly seen; we have observed this phenomenon in other cases as well.

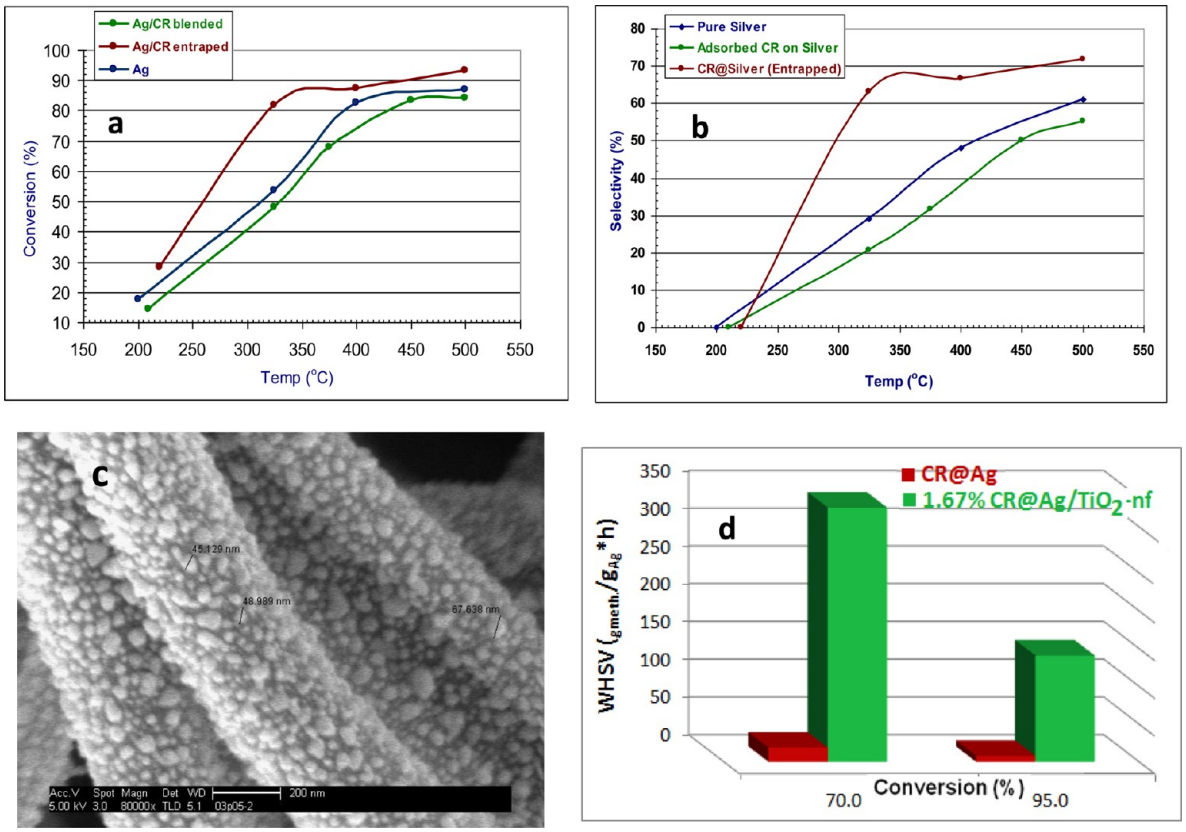

FIGURE 7. A superior silver catalyst for methanol oxidation to formaldehyde is activated Congo-red (CR)@Ag: (a) the maximal conversion is reached at 100 °C lower compared with pure silver or with adsorbed CR on silver; (b) a 200 °C temperature lowering is obtained for the maximal selectivity; (c) CR@Ag nanocrystal aggregates dispersed on titania nanofibers provide a huge jump (d) in the weight-hourly space-velocity.

The challenge of probing the molecule from within the metal was met recently. Both Raman (SERS) and fluorescence spectra of dopant molecules from within the 3D metallic cages of thin films obtained by the newly developed doping-electroless method have been observed.[22] More proofs of the doping appear below, which relate to fact that one gets metals with unorthodox properties: the induction of chirality in gold, the conversion of palladium into an acidic metal, the lowering of conductivity of silver, and more.

2.5. The Mechanism of Entrapment. We propose that the entrapment mechanism is as follows (Figure 5): In the mixture of the metal cations, the reducing agent molecules and the dopant molecules, tiny nucleating nanocrystals of the metal form immediately. Once they form, dopant molecules are adsorbed, even if with a small equilibrium constant. If the reduction and aggregation rates are faster than the adsorption residence time of the dopant, then entrapment will take place by shifting the adsorption/desorption equilibrium. Helping this process are functional groups with substantial interaction with metal surfaces (sulfonates, amines, carboxylates, etc.), but we find that these are not critical; it is enough to have even weak transient interactions to facilitate the entrapment. In the case of polymers, it is even simpler. Once a portion of the molecule is entrapped, say its tail, this anchor ensures full entrapment. The resulting aggregated material (Figure 5) has then a continuum of populations of dopant molecules: those that are easily washed away in the cleaning procedure (adsorbed molecules in the classical sense); those that are entrapped in narrow bottleneck pores and are not washed away but are still accessible to diffusing incoming molecules (such as substrate molecules for entrapped catalysts or enzymes); and those that are totally buried with no access to the outside world. The distribution among the populations varies among the different entrapping methodologies. For instance, in electrochemical entrapment, the inaccessible population is relatively high (see ref 5 for analysis). The interactions of the molecule with the surrounding metal can thus be of various types: from strong ionic interactions (such as with carboxylates) to coordinative bonds (such as with the lone electron pair of amines) to π-interactions and even

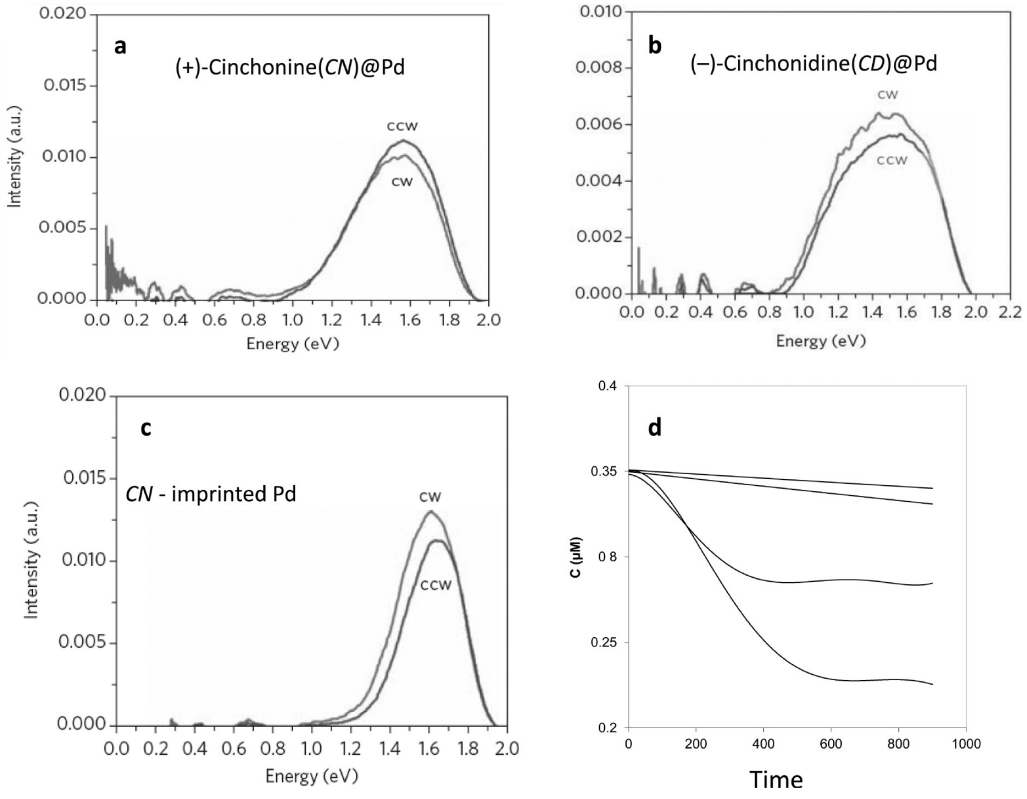

FIGURE 8. Chiral metals: (a) Enantioselectivity is observed when clockwise (cw, bottom curve) or counterclockwise (ccw, top curve) circularly polarized light hit Pd within which (+)-cinchonine (CN) is entrapped: different energy-distribution profiles are obtained. (b) The authenticity of this observation is provided by doping with the enantiomeric (−)-cinchonidine (CD): the trend is reversed. (c) The trend is also reversed when CN is extracted leaving behind CN-imprinted Pd. (d) The chiral imprinting of Pd is detected also by enantioselective readsorption. Shown is the kinetics of adsorption of (from top to bottom) CD on Pd, CN on Pd, CD on CN-imprinted Pd, and CN on CN-imprinted Pd.

weak Van-der-Waals interactions. In fact, various portions of the molecule can interact differently with the surrounding metal.

3. Properties and Applications

In looking for properties and applications of molecule@metal hybrids, four general types of questions are *a priori* open for exploration: Is the dopant affecting the properties of the metal? Are the dopant molecules affected by residing within the metallic matrix? Can one extract a dual functionality from both components? Are there instances where properties and activities of the hybrid are synergetic, that is, the performance is more or different than the combined activities of the separate components? A decade in the running, positive answers and examples to all of these options have emerged, as briefly described next.

3.1. Catalysis. Catalysis opens several possibilities for the use of the metal doping methodology:

3.1.1. Using the Metal for Heterogenization of Homogeneous Catalysts. There are three major classes of solid materials: polymers and plastics, crystalline and amorphous oxides and ceramics, and metals. The first two have been used massively in catalysis as supports of catalytic entities and as standard methods for heterogenization of homogeneous catalysts. To the best of our knowledge, metals have never been used for that purpose (a rather astonishing fact). So the first use of the metal doping methodology we developed for catalysis is the introduction of this elementary class of materials as heterogeneous support for catalysis. This was made possible by three features of molecules@metals: the entrapped molecules (or a high portion of them) are accessible to external diffusing substrate molecules; the dopant is capable of displaying either its characteristic chemical reactivity or (sometimes strongly) modified activity; despite its accessibility to reaction, the dopant is tightly held within the narrow pores and cages and either does not leach at all or leaches out to a negligible level. Examples of the successful use of this methodology for metal heterogenization of homogeneous catalysts are the acid-catalyzed pinacol−pinacolone rearrangement with Nafion entrapped in silver (Nafion@Ag) and the dehydration of 2-phenylethanol to styrene with the same catalyst.[17] This

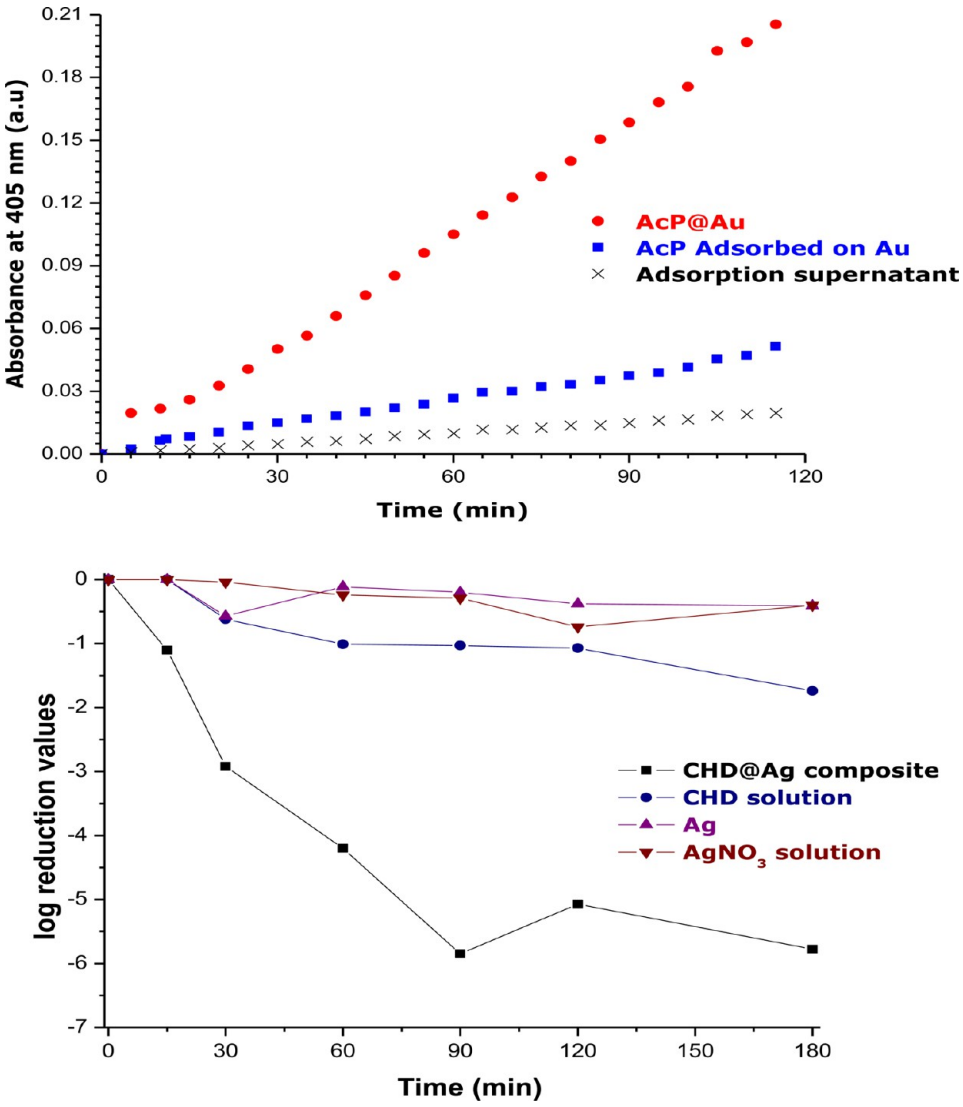

FIGURE 9. Bioapplications: (top) activity of acid-phosphatase entrapped in gold (as determined from the absorbance of the product (*p*-nitrophenolate), compared with the activity of the adsorbed protein; (bottom) very high synergetic biocidal activity is observed when antibacterial chlorhexidine is entrapped in silver, itself an antibacterial metal (note the logarithmic scale of reduction). Shown is the activity toward *E. coli*; similar high activities were obtained for wound pathogenic bacteria.

specific example indicates another interesting outlook: the material, which looks like the parent metal and behaves like it, displays a new unorthodox property that is induced by the dopant. Thus, Nafion@Ag provides "acidic silver"; and when the silver is doped with the polybase poly(vinylbenzyltrimethylammonium hydroxide), "basic" silver is obtained: immersing it in a NaCl solution raised the pH to 10.0.[17]

Heterogenization with a metallic matrix proved in a number of cases to be beneficial for the stability of the molecular catalyst, for increasing yield, and for obtaining products not obtained under homogeneous conditions. For instance, the Friedel–Crafts alkylation of toluene with either 1-bromoadamantane or the less reactive 1-chloroadamantane (Figure 6, top) proceeds to >99% yield with the metal-heterogenized $H_3[P(Mo_3O_{10})_4]$@Ag, compared with only 2–3% yield with free $H_3[P(Mo_3O_{10})_4]$ in solution.[18] In yet another example, the hydrogenation of styrene or of diphenylacetylene with the heterogeneous catalyst RhCl(COD)($Ph_2P(C_6H_4SO_3Na)$)@Ag proved to be efficient and recyclable, whereas in solution the catalytic complex decomposes after one cycle at 50% conversion.[15]

3.1.2. Catalytic Dopant Entrapped in a Catalytic Metal. The ability to entrap within a metal opens yet another very interesting possibility, namely, obtaining heterogeneous catalysts in which *both* the dopant and the entrapping,

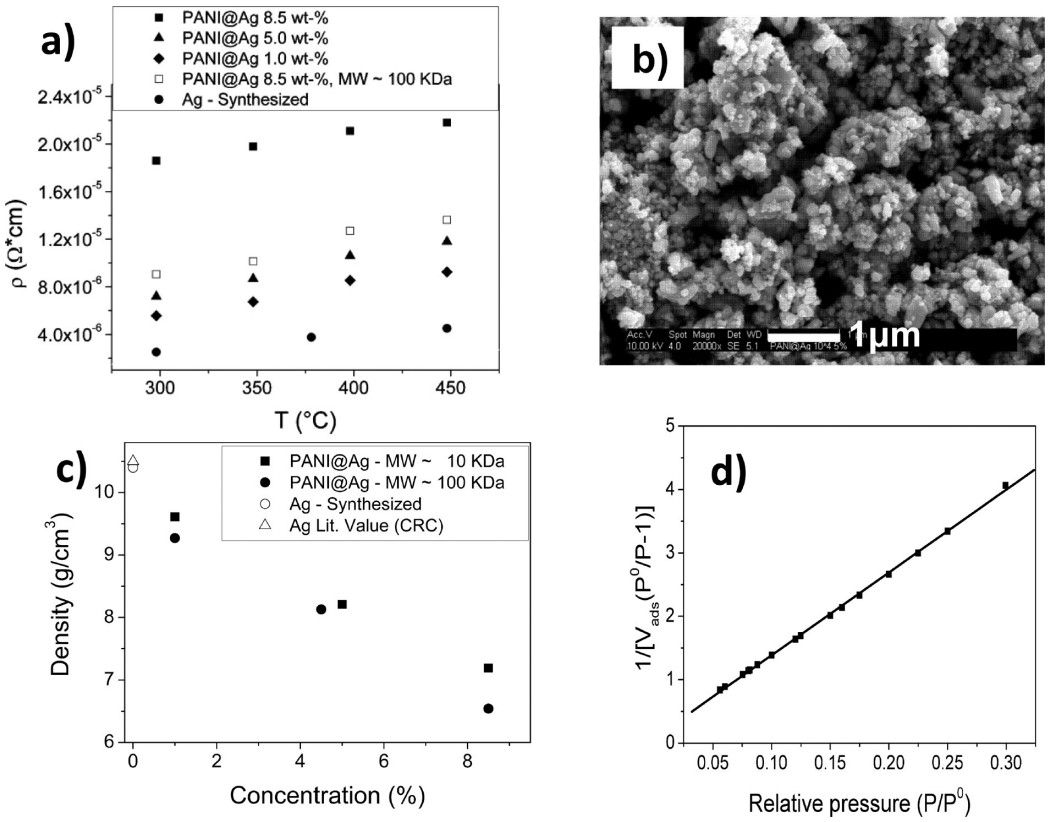

FIGURE 10. Doping effects on silver conductivity: (a) temperature dependent resistivity of polyaniline@Ag with different concentrations of the polymer (M_w = 10 kDa); (b) the porous morphology of the 5 wt %, 10 kDa composite; (c) this morphology translated to densities that are below that of pure silver; (d) an indication of the homogeneity of the polyaniline@Ag composite is the excellent compliance with the surface-area-determination of BET equation (5 wt %, 10 kDa).

heterogenizing metal are catalytic. Such materials may show then multiple catalytic activities, where usually two catalysts and separation steps are needed. This was indeed recently achieved with Nafion@Pd, and significantly, only the hybrid catalyst but not its separate components could pull three dual reaction schemes to completion.[10]

The reactions with which the one-step, one-pot, one-hybrid material dual catalytic activity have been demonstrated are the dehydration/disproportion of 1,2,3,4-tetrahydro-1-naphthol directly to naphthalene and tetralin (Figure 6, bottom), the dehydration/hydrogenation of 1,2,3,4-tetrahydro-1-naphthol directly to tetralin, and the dehydration/hydrogenation of 1-phenyl-2-propanol directly to 1-propylbenzene.

3.1.3. Affecting the Catalytic Activity of the Metal. It turns out that an organic dopant can have beneficial effects on the catalytic activity of the metal itself. An example is the thermally activated Congo-red (CR)@Ag for which we have found significant improvement of the performance of Ag as a catalyst for the widely used industrial process of methanol oxidation to formaldehyde[23,25] (Figure 7).

CR@Ag was found to outperform both pure Ag and CR-coated Ag in terms of lowering the temperature needed for maximal conversion by 100 °C, lowering the temperature for maximal selectivity (aldehyde formation) by 200 °C (Figure 7, top). An even more significant improvement was found, when the CR@Ag nanoparticles were deposited on titania nanofibers[20,21] (Figure 7, bottom): a 12-fold increase in the weight hourly space velocity (WHSV) was found at a 70% conversion, and a 7-fold increase was found at a 95% conversion.

3.2. Inducing Chirality in the Metal. Except for some specific high Miller-index surface-cuts of metal crystals, which are chiral,[26] metal crystals are of course achiral because of the fcc or bcc lattice packing. The question we asked: Will the doping of a metal with a chiral molecule induce that structural property in the metal? Together with R. Naaman of the Weizmann Institute, we carried out an experiment, the rational of which is the following: Photoelectrons, that is, electrons that are emitted from a material by the action of light, have a certain typical distribution of energies of the emitted electrons. Suppose now that the

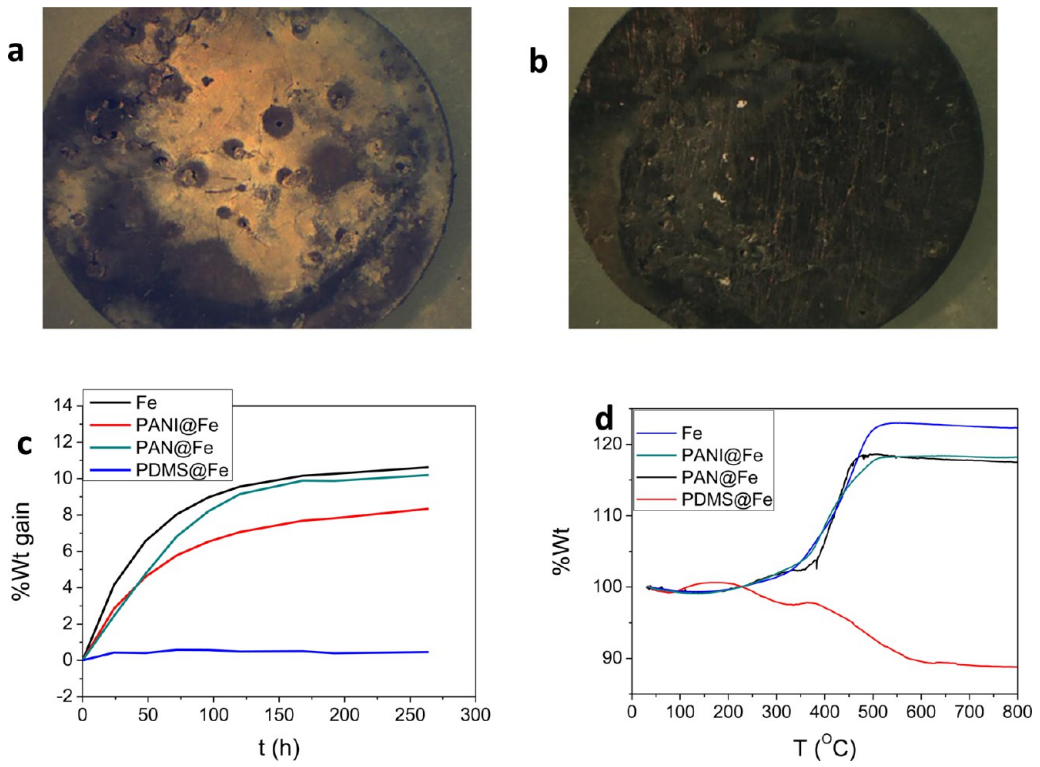

FIGURE 11. Iron doped with poly(dimethylsiloxane) (PDMS) does not rust: (a) When a coin of pure Fe is put in simulated seawater, it quickly rusts to the reddish oxide and disintegrates. (b) In contrast, PDMS@Fe remains intact to the level of seeing the grooves of the press used to make that coin. (c) This shows also by weight follow-up. Untreated Fe and two polymer@Fe coins gain weight because of iron-oxide formation, while PDMS@Fe maintains a constant weight. (d) This stability shows up also under oxidative TGA conditions: Only PDMS@Fe loses weight (because of the burning of the methyl groups), while the other samples gain weight.

material under study is chiral and that the light that illuminates it is circularly polarized, namely, it is chiral in its sense of propagation with two possible enantiotops, the clockwise (cw) and counter clockwise (ccw) polarizations. Two diastereomeric interactions are then possible: chiral material−cw light and chiral material−ccw light. In such a case one might expect to observe diastereomerism between the two options, that is, the cw and ccw will interact with the chiral material differently, and the energy distribution profiles of the emitted electrons might show differences in these two options. And indeed this was found to be the case.[11] When gold was doped with L-tryptophan, a clear difference between the energy profiles was observed for cw and ccw light: ccw light showed better interaction with the metal. To check for the authenticity of this observation, the enantiomeric D-tryptophan@Au was subjected to the same experiment, and the profiles of cw and ccw indeed reversed their order. The effect was observed with several chiral dopants and with additional metals, Ag[11] and Pd.[9] What then is chiral in the metal? Is it that the chiral dopant chirally distorts the orbitals at the Fermi level? Or is it that the geometry of the metal interfaces became chiral by tightly encompassing the dopant, forming a chiral metal cage? To answer that question one should repeat the photoelectron experiment also after removal of the dopant, that is on the pure metal. Together with Gadi Rothenberg (Amsterdam), we selected Pd for that experiment, since it is a hard metal, and one would expect minimal atom migration after extraction of the dopant.[9] (+)-Cinchonine (CN)@Pd and Pd obtained after extraction of CN from CN@Pd (Figures 8a,c) were subjected to the same comparative exposure to cw and ccw irradiation. Significantly, not only does one observe differences in the energy profiles of the *extracted* metal (Figure 8c), which shows that it is chiral, their order is reversed compared with CN@Pd. Furthermore, the extraction resulted in what we believe to be the first chirally imprinted metal[9] (Figure 8d). The readsorption ratio of NC/CD on CN-imprinted Pd was ~1.3; we recall that chiral materials with an enantioselectivity ratio of 1.05 are already used for choromatographic separation of enantiomers.

It is quite obvious that enantioselective catalysis has been a main applicative use of chiral Pd. Hydrogenation of ketones was tested with the doped catalysts.[9] Typically, the reduction of isophorone using a CD@Pd catalyst resulted in a

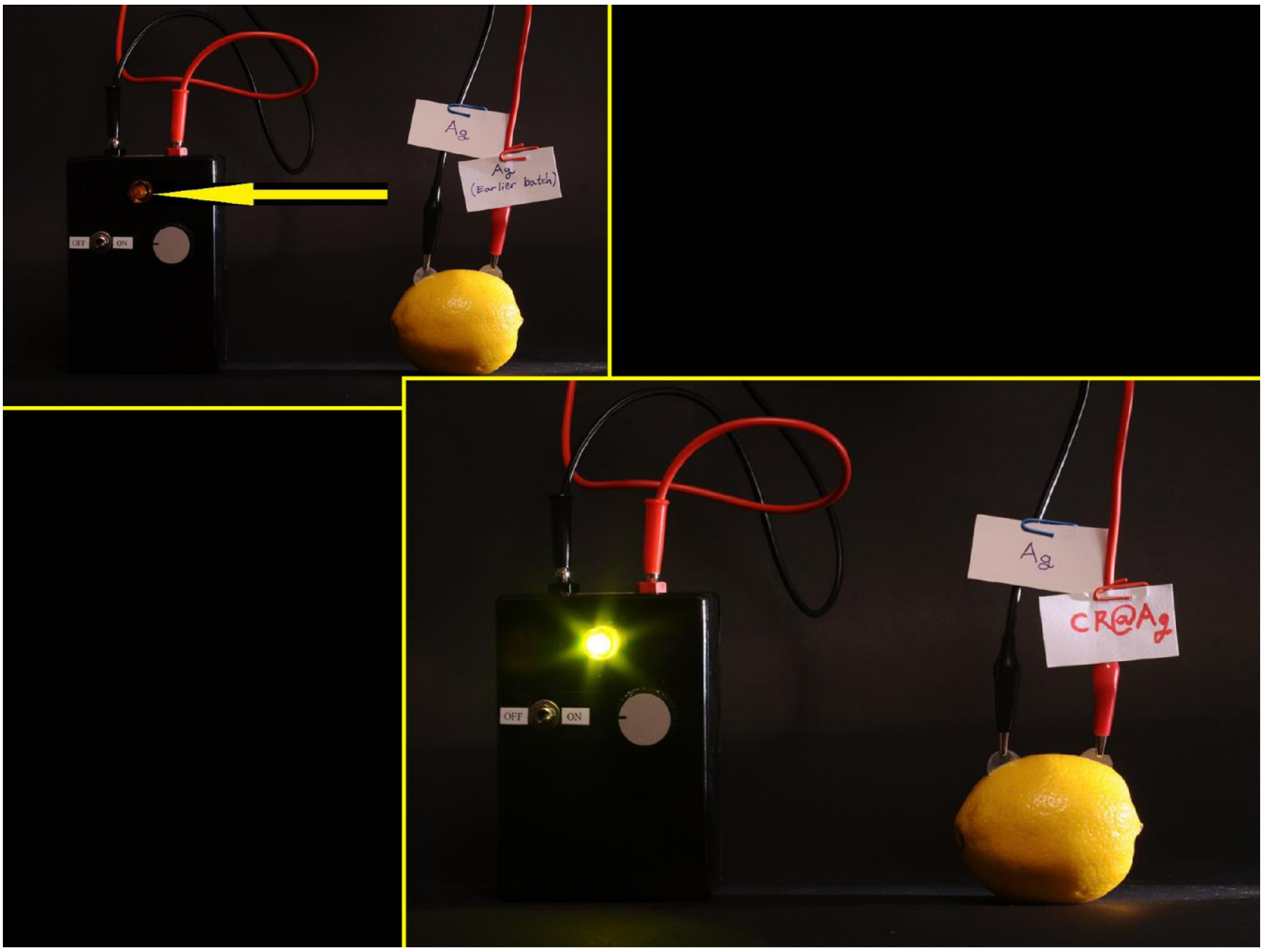

FIGURE 12. "Seeing the light". (top) When two silver electrodes are stuck in a lemon, the bulb (yellow arrow) is dark. (bottom) Replacement of one of the electrodes with CR-doped silver results in the light shining (see text for explanation).

small ee of 16%. The principle was proven, but the ee must of course be parametrized to higher values. The imprinted Pd (free of CD or CN) did not show catalytic enantioselectivity. Apparently the nonimprinted zones of the Pd overshadowed the catalysis from the imprinted cages. Surely, it is worth investing more efforts in this direction.

3.3. Biological Applications. 3.3.1. Entrapped Enzymes[12]. As is the case with nonbiological catalysts, here too, whereas the use of organic polymers and oxides for the preparation of enzymatically active materials is well developed, the third principle enzyme–material combination, namely, protein–metal bulk, has not yet been reported. Again, plenty of studies have been carried out with 2D adsorption architectures, but as we shall see here too, adsorption and entrapment are very different processes. Our example is the entrapment of acid phosphatase in either gold or silver, resulting in acid-phosphatase@gold and acid-phosphatase@silver bioactive metals, both tested on the hydrolysis of the phosphate of *p*-nitrophenol. As seen in Figure 9, top, the entrapment procedure keeps the enzyme alive and active; note the much higher activity compared with adsorption, the residual activity of washings making sure that the activity is within the metal, and the similarity between Au and Ag as entrapment matrices, indicating the inert function of the metals. As the name of this enzyme implies, its optimal pH is on the acidic side of that scale. It is therefore not surprising that when exposed to basic conditions in solution, pH = 10.5, the free enzyme dies out instantly. In distinction, when entrapped in Au, it retains 32% of its activity. There are several reasons for the enhanced stability of the entrapped enzyme: First, the metallic cage is very rigid, not allowing the enzyme to undergo the conformational motions that lead to denaturation. Second, the tight cage poses significant limitation to constant bombardment with hydroxyls (as occurs in solution); and third, if a few hydroxyls do enter, then

they are titrated by the acidic amino acids on the surface of the protein.

3.3.2. Doped Silver as a Super-antibacterial Agent[13,14]. An interesting application where very high synergism between metal and dopant was observed is in the field of antibacterial agents. The idea was to form new bactericidal agents by the entrapment of an organic biocidal agent within a bactericidal metal. The concept was demonstrated for the entrapment of chlorhexidine (CH) within silver, a metal known for its own biocidal qualities. CH@silver's efficacy against wild-type *Escherichia coli* was evaluated and compared with the separate components. As can be seen in Figure 9, bottom, while the bactericidal efficacy of the individual ingredients (CH and metallic silver) is very low, CH@silver exhibits a markedly enhanced efficacy. This enhanced bactericidal effect is attributed to the simultaneous release and presence of the active biocidal ingredients in the solution. This powerful synergetic bactericidal action was recently found[14] also toward two opportunistic wound pathogenic bacteria, the Gram-negative *Pseudomonas aeruginosa* and the Gram-positive *Staphylococcus epidermidis*.

4. More Applications, Conclusion, and Outlook

More applications of doped metals have been developed, which due to the strict space limitation are briefly described in the figure captions. For instance, doping can be used to affect classical properties of metals, such as electrical conductivity, see Figure 10 and ref 24. Yet another observation of great practical value we made is that doping of iron with polydimethylsiloxane stops its corrosion and rust formation, see Figure 11 and ref 6.

We conclude this Account with the construction of a new electrochemical cell.[27] Classically, such cells are constructed from a pair of different metals. Our approach opens however the interesting possibility of constructing an electrochemical cell in which the two electrodes are made of the same metal, one doped and the other pure metal. On the basis of this, the potential difference between pure and doped silver electrodes was used to activate a light-emitting diode, and "we saw the light" (Figure 12).

Why is it that the concept of deliberate doping of metals has not been explored before as a general methodology?[28,29] A possible clue can be perhaps found in Primo Levi's, "The Periodic Table", where he writes (in the Zn chapter) about purity vs impurity in metals: "One could draw... two conflicting philosophical conclusions: The praise of purity, which protects from evil; and the praise of impurity, which gives rise to change, in other words, to life. I discarded the first: In order for the wheel to turn, for life to be lived, impurities are needed, and the impurities of impurities...".[30] Indeed, references with some relevance that we could cite in our first report in 2002[1] mention, in a *negative* context, that some electrochemical metal precipitations in organic media may result in entrapped organic impurities.[31] We have embraced Levi's philosophy and converted unwanted impurities into a new family of functional materials, the applications of which already cross chemistry from coast to coast.

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BIOGRAPHICAL INFORMATION

David Avnir's current scientific activities include, in addition to molecularly doped metals, theoretical and experimental aspects of chirality and symmetry, and sol–gel organic and bio-organic hybrid materials. Earlier major interests included fractal theory in chemistry and physics and far-from-equilibrium phenomena. He has coauthored 350 papers, many of which are highly cited, and holds several key patents in materials science. His latest recognitions are the Israel Chemical Society Prize (2011), his placement on the Hebrew University's "Wall of the Innovators Way" (2012), and the Life Achievement Award of the International Sol–Gel Society (2013).

FOOTNOTES

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The authors declare no competing financial interest.

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