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COMMUNICATION

Fine-tuning of metal work function by molecular doping

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A new approach for fine tuning of metal work (WF) function in the range of 1 eV is described. The WF control is achieved by 3D molecular doping of the metal rather than the classical 2D adsorption. Small molecules (Congo red, thionine) and polymers (Nafion, poly(vinylbenzyltrimethylammonium) chloride) were both shown to affect the work function of gold and silver. The in-situ reaction of the dopants within the metallic matrix is a further tool for altering the WF, confirming that this effect is dopant-dependent. We attribute this effect to the charge transfer interactions between the dopant molecule and the surrounding 3D metallic cage.

The work function (WF) is a fundamental characteristic of all matter which governs many applications of metals, semimetals and semiconductors. Controlling the WF is used to modulate photo- and thermionic electron emissions, to affect the material catalytic performance, to control organic electronics properties and the performance of laser diodes, and more¹. Many of these applications are dependent on the ability to tailor the WF, and by-far the most common method to achieve it is by adsorbing of (self-assembled) polar molecules on the surface². Here we propose and demonstrate a completely different approach to affect the WF of metals: Molecular doping of the metal, that is, incorporating the WF-modifying molecule within the 3D metallic matrix. Molecular doping of metals is a relatively new materials methodology³ which has already proved useful in a wide range of applications ranging from catalysis⁴ to medicine⁵. Such molecular doping offers new properties which are the result of synergism between the dopant and the metal, or which are the result of one affecting the other. This, in turn, is made possible because of the intimate interaction between the dopant and the metal in the inter-crystallite cages which define the entrapment; 2D adsorption is a different process, usually using only one moiety of the molecules, and usually affecting only the metallic atoms at the interface, not the bulk. By careful selection of the dopant and its concentration, fine-tuning of the dopant@metal properties

can be tailored – the huge library of organic molecules is all available for that purpose. Examples include the alteration of the conductivity of silver⁶, affecting the inherent catalytic behavior of silver^{7a}, palladium^{7b} and gold^{7c}, affecting the electrode behavior of silver⁸, enhancing the corrosion-resistance of iron⁹, alteration of electrocatalytic behavior of copper^{10a}, palladium^{10b}, silver^{10c} and copper-palladium alloy^{10d}, stiffening of gallium¹¹ and more. Many of these applications are made possible because the entrapped molecules cannot be easily washed away as in adsorption and yet they are accessible to reaction with external reagents by diffusion through the interstitial pore-network. Furthermore, the entrapped molecules have a much better stability and are protected from harsh environmental conditions; molecules which cannot be adsorbed are easily entrapped; much higher concentrations of the organic molecule are obtained by 3D doping compared with 2D adsorption; and the doped metals offer better compliance with device construction restrictions. A preliminary observation that the organic dopants are capable of affecting the WF of gold films¹² prompted us to carry out a full study of this new way to affect the WF. This is a unique observation because, as mentioned above, classically the WF of a metal is altered by placing a molecular barrier on the surface, not inside the metal. Here we report that the WF of metals are affected and tuned by using both small molecules and by polymers, and furthermore, that this WF control can also be achieved by reactions with the entrapped dopant. Two metals at two architectures were examined: Discs obtained by pressing powders of the doped silver or gold into discs; and doped gold thin films. Specifically Congo red (CR)@Ag, CR@Au, Nafion@Ag and poly(vinylbenzyltrimethylammonium hydroxide) (PVBA)@Ag discs have been prepared by reducing the silver or gold cation with sodium hypophosphite in the presence of the molecule to be entrapped (see Experimental Details in the Supplementary Material (SM)). The resulting metallic powders (Fig. 1 and Fig.

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S1, SM) are aggregates of a broad particle size distribution (0.1 - 1 μm) composed of elementary metal nanocrystals (about 40 nm in size, from Scherrer analysis of the XRD spectra – see Fig. S2, SM) which strongly encage the dopant molecules to the extent that even if it is a water soluble molecule which is easily washed away by regular adsorption, only very strong solvents such as DMSO can extract the doped molecule from its cage (see ref.'s 13 for detailed studies of the entrapment mechanisms and the structure of the doped metals). Thermal gravimetric analysis (TGA, Fig. 1 and Fig. S1, SM) of the obtained doped metals proved the successful entrapment within discs of 2.6%wt for CR@Ag, 1.7%wt for CR@Au, 0.55 %wt for Nafion@Ag and 1.3 %wt for PVBA@Ag. Resistivity measurements of the doped discs show that the conductivity is high, only marginally smaller than the pure metal - see Table S1. The entrapped dopants then underwent the following reactions within the entrapping metals Fig. 2(a):

* Reduction of entrapped CR with $\text{Na}_2\text{S}_2\text{O}_4$ ^{13a}

* Mg^{2+} - proton exchange of entrapped Nafion (“acidic silver”^{13b})

* Chloride exchange of hydroxide and back to chloride of PVBA (“basic silver”^{13b})

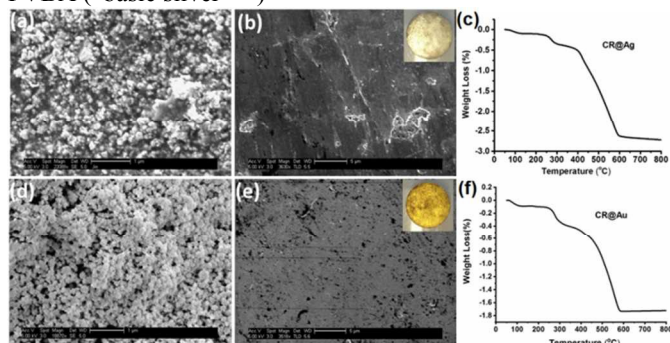


Figure 1. Congo-red doped silver and gold - CR@Ag (top row) and CR@Au (bottom row): SEM images before ((a), (d), bars: 1 μm) and after ((b), (e), bars: 5 μm) pressing the powders into discs, and the TGA profiles ((c), (f)). Insets: The compressed discs.

We begin with the CR systems: The reduction reaction of entrapped CR was performed in water, and then DMSO was used for extraction of the unreacted CR and the reaction products. Comparative spectra of absorption and FTIR are shown in Fig. S3 (b, c). The absorption spectra (Fig. S3(b)) show that ~80% of the entrapped CR has reacted; the remaining CR is apparently encaged in totally closed pores, inaccessible to the reducing agent. FTIR (Fig. S3 (c)) also confirms the N=N reduction reaction in that the 1430 cm^{-1} trans-azo band almost disappeared after reaction. For the WF measurements, 13 mm diameter disks were prepared by compressing 300 mg of the composite powder at 9,000 PSI for 5 min – see Fig. 1(b, e) for the resulting discs interface after compression (and Fig. S1(a, d) for additional SEM images of the powders described in this report).

Dopants abbreviations: CR – Congo red, PVBA - poly(vinylbenzyltrimethylammonium hydroxide), Th – thionine

We now analyse the WF measurement results, first for the case of metal entrapped CR (Fig. 2 and Table S2): CR was selected because of its functional groups: previously we have shown³ that the sulfonate groups are favorable for the entrapment process, which requires some adsorption residence time of the molecule on the forming metal crystallite in order to be entrapped (see ref.'s 8, 13a for a detailed account on the entrapment mechanism). It is first important to determine the effect of the classical method to affect the WF, that is, of adsorption of the WF modifier. It is seen (Table S2) that adsorption practically does not affect the WF (4.26 (entry 1), 4.30 eV (entry 2)). This is expected because CR neither forms a strong chemical bond with the metal nor self-assembles on the silver surface, both of which are necessary for the surface modification to control the WF. Doping, however, induces a significant increase to 4.71 eV (entry 3). Partial extraction of that dopant as described above, indeed provides an in-between value of 4.41 eV (entry 4). It is important to notice that this WF change is of a new category: It is not the classical interfacial barrier effect of adsorbed molecules, but a direct effect of the dopant on the metal from within it; in the discussion below we shall propose that the origin of this effect is of charge transfer in nature. An increase in the WF such as that observed here means that the dopant makes the detachment of electrons more difficult, that is, the dopant attracts the metallic electrons. We assumed that if this is the case, then reducing the same dopant *in-situ*, should result in the opposite effect, because reduction means enrichment in the electron charge. And this is exactly what happens: *In-situ* reduction of the CR as described above, leads now to a *decrease* of the WF to 4.09 eV (entry 5). Treatment of pure silver prepared by the same method with the reducing agent alone ($\text{Na}_2\text{S}_2\text{O}_4$) did not affect the WF (entry 6). This phenomenon is not unique for silver, and was observed also for gold, although with milder changes (entries 7-9): Again doping of gold with CR increase the WF, and reduction dropped it back. As thin films are particularly useful for large scale applications in opto-electrical devices, it was highly relevant to see if this WF-change methodology is applicable for thin film architectures. Thus, we have extended the study from the CR@gold discs to thin films of CR@gold (~100 nm). This thin film doping was carried out by the recently developed method of electroless deposition of molecularly doped metals, described in detail in ref.'s 12. Fig. 3(a) shows the compact dense granular morphology of the CR@Au film. It is seen (entries 10-12) that the changes of the WF of Au films are practically the same as for the discs (entries 7-9).

An important characterization which further proves the major difference between entrapment and adsorption, is Raman spectroscopy, which was carried out on CR@Au films – it is quite unique to be able to observe the Raman spectrum of CR in its doped state, that is, from a molecule surrounded all around by the metallic cage (Fig. S4). This is an extension of the widely used Surface Enhanced Raman Spectroscopy, only that the term SERS does not fit here, because it is not a 2D surface phenomenon, but a 3D metal cage enhancement (MCERS). Indeed, the fact that within the cage the molecule is interacting

with the metal through more than a main functional group (as is the case in 2D SERS), shows up in the variations between the SERS and MCERS spectra (Fig. S4 (a), (b)), such as appearances of new peaks (e.g., at 1250 cm^{-1}) and changes in relative intensity of peaks (such as at the 1350-1450 cm^{-1} range; see ref.'s 12a, b for a discussion of this phenomenon).

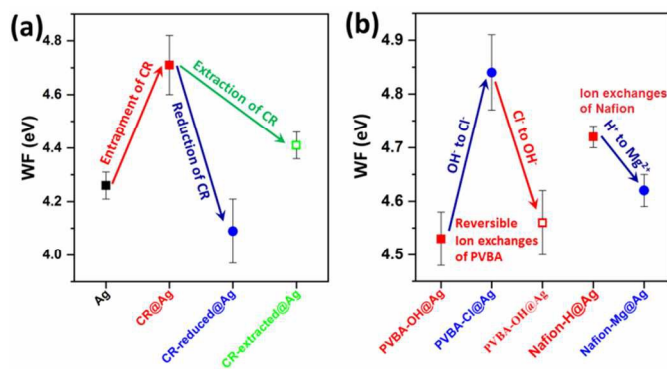


Figure 2. The sensitivity of the work function of silver to doping and to reactions of the dopant in (a) CR@Ag, (b) PVBA@Ag and Nafion@Ag.

Next we studied whether other dopants can induce WF changes as well, and thionine (Th) was selected for that purpose because of its nitrogen and sulfur constituents, known to favor metal interaction¹⁷. Raman spectroscopy (Fig. S4 (c), (d)) confirms the successful entrapment of this molecule as well, and clearly shows even a larger MCERS compared with CR entrapped in gold, which should be ascribed to the stronger interaction towards gold of thionine. Interestingly, these stronger interactions as revealed by Raman spectroscopy, translate also to stronger WF alteration effect of Th compared with CR (entries 7 and 13). In a previous study we observed that Th greatly affects the metal grain size in gold films, decreasing it in the doped case compared to the pure gold film^{12a}: the sulfur atom in Th has a strong interaction with gold, slowing the growth of the Au grains in deposition process. This observation has opened the possibility for studying if yet another way to affect the WF of molecularly doped metals, is by tuning the elementary particle size through changing the dopant concentration. For instance, it was reported that the WF decreases with decreasing average grain size due to an increase in the grain boundary fraction, which is a non-equilibrium state in nanocrystalline metals^{15, 16}. Thus, the experiment with Th@Au film described above (entry 13, Table S2), was repeated with two additional, higher concentrations of doped Th. The decrease in grain size with increase in Th concentration is clearly seen by HR-SEM (Fig. 3 (b)-(d)), also as compared with CR@Au (Fig. 3 (a)). The actual grain sizes were obtained from the XRD patterns (Fig. 3 (e)); see Fig. S5, SM for EDS elemental analysis) using Scherrer's equation and these were found to be 41, 32 and 21 nm with increasing Th concentration, compared with 52 nm for the pure gold film. As clearly evident in Fig. 3 (f), decreasing grain size (increasing Th concentration) is accompanied with WF increase. An opposite trend was reported for gold, where it was found that the WF increases linearly with the grain size below 1 μm in the range of about 0.1 eV²⁰, indicating that the dopant is still the dominant factor in affecting the WF, through the mechanism suggested below.

Yet another useful family of molecularly doped metals that has been developed in recent years is the family of hybrid polymers@metals^{14,16,24}. For instance, the enhancing of corrosion-resistance of iron¹⁴ mentioned above, has been achieved by its doping with poly(dimethylsiloxane). Polymer doping was also used for introducing un-orthodox properties such as rendering the metal basic by entrapping the poly-base poly(vinyl benzyltrim ethylammonium) chloride, PVBA) and

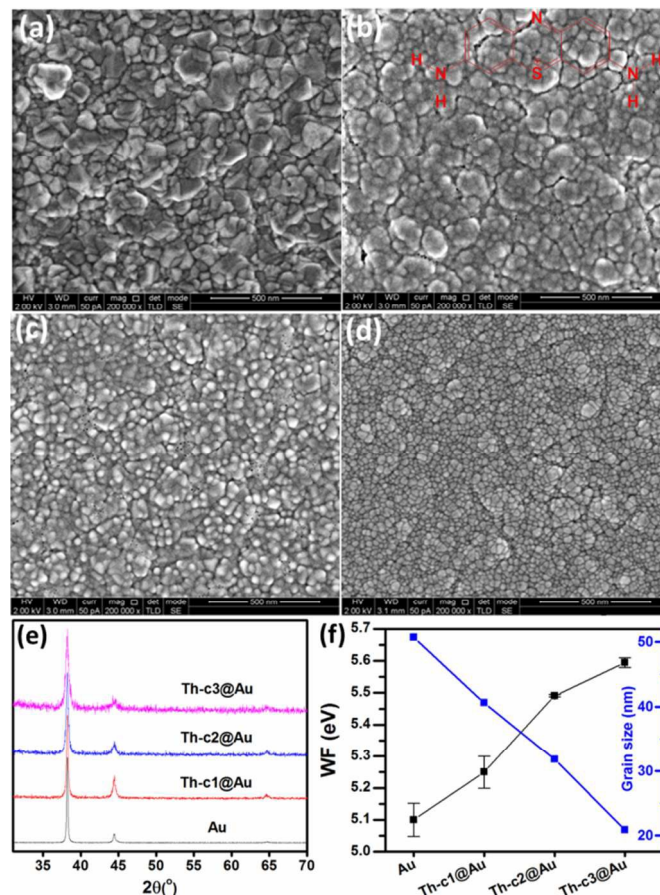


Figure 3. HR-SEM images of (a) CR@Au, (b) low concentration Th@Au, (c) medium concentration Th@Au and (d) high concentration Th@Au (bars: 500 nm); (e) The variations in the XRD patterns of the Th@Au films; (f) The reverse correlation between the work function and Au grains sizes of the Th@Au films.

acidic by entrapping the poly-superacid Nafion²⁴. It was therefore of interest to explore the possibility that doping of a metal with these reactive polymers affects the WF of the entrapping metal as well, and again to test the possibility that their reactivity within the metal, will show up in WF variation. PVBA@Ag and Nafion@Ag were prepared for that purpose (See experimental details in the SM) (Fig. S1), and it is seen (Fig. 2 and entries 14, 18 in Table 1) that doping of silver with these polymers, but not their simple surface adsorption (entries 15, 19) exert an increase in the WF of the metal. The ion-exchange properties of the two polymers (Fig. 2) were used to check for possible reactivity effects. For PVBA-OH@Ag, hydroxyl ions were exchanged with Cl⁻ using NaCl, and it was found, by following external increase in pH (Table S1) that the exchange was efficient and full (100%). As seen in Fig. 2 (and entries 14, 16) the exchange caused a drop-back of the WF, and furthermore, when the resulting PVBA-Cl@Ag was back

treated with OH⁻ using NaOH, the recovered WF was almost the same as in the original PVBA-OH@Ag (Fig. 2 and entry 17), confirming the fact that it is the reaction that affected these WF changes, and showing the reversibility of the process. Similar WF increase effect was found for the exchange reaction Nafion-H@Ag/Nafion-Mg@Ag, which was affected by equilibrating Nafion-H@Ag with Mg²⁺ (from MgSO₄) even though in this case about 40% of the entrapped protons were replaced (Table S3). The lower exchange in this case is attributed to the fact that Mg²⁺ can exchange protons only when it has access to two adjacent sulfonic acid groups that can replace two protons for one bridging Mg²⁺; in our case, therefore, about 20% of the sulfonate groups are conformationally aligned in the entrapped case to allow for the bridging of Mg²⁺.

What then is the origin of the observed dopants effects on the WF? We attribute the WF changes to the accepted interpretation of the effect of adsorptive surface modification, namely, induced charge transfer (CT) across the metal/dielectric interface creating a dipole, which shifts the position of the metal Fermi energy level³⁰. That 2D picture, is applicable we believe to our 3D entrapment situation, but with a crucial modification which relies on the known alteration of the WF of one metal by alloying with another³¹; it is again a CT effect which in an alloy originates from the nonzero potential difference between the two metals, that is, from the difference in the electron-per-atom ratio of the constituents^{31, 32}. Indeed, Pagliaro et al have proposed to treat the molecularly doped metals as a new type of alloys, coining the term MORALS (metal-organic alloys) for this new class of materials³³. Further justification of this view-point comes from a recent report on changes in the lattice parameters of gold by doping with amino acids³⁴. Thus, the mechanism we propose is a hybrid between the 2D CT interfacial mechanism and the alloy effect, that is, a 3D CT within the entrapping cages of the metal. Supporting this interpretation is our observation that when a reduction reaction has been performed with the dopant (CR), a decline in the WF was observed because of the formation of electron-richer products.

In conclusion, we demonstrated that WF of two metals can be affected by their molecular doping and tuned by the type of the dopant and by its concentration, within 1 eV by molecularly doping. Reactivity of the dopant is possible through the interstitial porosity of the aggregated matrix, and the reactivity affects WF again, and in a reversible way. In addition to the variety of potential applications listed in the introductory comments, this reversibility opens the possibility of designing sensitive stable chemical sensors³⁵.

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Notes and references

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† Full experimental details are provided in Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

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