Metal−Organic Composites: The Heterogeneous Organic Doping of the Coin Metals−Copper, Silver, and Gold

Itzik Yosef and David Avnir*

Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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We have continued the development of the novel family of organically doped metals. Two new aspects are described for these metal−organic composites: first, the doping is extended beyond silver to copper and gold, showing the generality of the concept; and second, a heterogeneous method of entrapment has been developed, in which the metal cation (of copper, silver, or gold) is reduced in the presence of the molecule to be entrapped using another metal that is higher in the electrochemical series (zinc for copper and silver cations, and copper for the gold cation). The three coin metals were doped with either a dye, thionin, or a polymer, Nafion. The procedure proved to be simple and quick. Characterization of these new composite materials included X-ray diffraction measurements, scanning electron microscopy, energy dispersive spectroscopy, surface area, porosity, thermogravimetric analysis, and density measurements. An outlook for potential application of these metal−organic composites is provided.

1. Introduction

We have recently introduced a new family of materials: Metal−organic composites, namely, organically doped metals.[1−4] The methodology of their preparation enables one to incorporate and entrap small or polymeric organic molecules within metals, thus creating this new family of composite materials, which, to the best of our knowledge, has been unknown so far. Various useful applications have already been demonstrated, including physical alteration of metal properties,[1−3] formation of new catalysts with superior performances,[3,4] and induction of new, unorthodox qualities to the metals.[1−4] Besides the basic motivation, namely, that these composites are largely unknown,[5] the practical motivation is based on the potential ability to tailor metals with any of the properties of the vast library of organic molecules and the potential of creating materials that are "in between" metal and, say, plastics.

The feasibility of these ideas has indeed been proven in our earlier reports.[1−4] The methodology of the preparation of the new metallic composites involves room-temperature metal synthesis by the chemical reduction of the metal-cation, carried out in the presence of the desired organic molecule. In our earlier reports, we used a carefully selected water-soluble reducing agent, sodium hypophosphite,[6] and concentrated on the entrapment in silver. Here, we move forward in two important aspects: First, we show that the composites can be generally prepared with other metals, and describe here the doping of two more metals, copper and gold. Second, we have developed an entrapment methodology that is based on a heterogeneous system, namely, the dispersion of a sacrificial reducing metal. We apply it to silver doping as well, thus showing that the two routes, the homogeneous and the heterogeneous, are open for metal doping. In fact, the heterogeneous approach was found to be quicker and simpler compared to the homogeneous one. Specifically, solutions of silver and copper salts were treated with metallic zinc powder and gold salt solution was treated with copper powder in the presence of the dopants, either the polyacid Nafion as an example of the entrapment of a polymeric organic molecule or the cationic dye thionin (Th) as an example of a smaller one (see Scheme 1 for their structures), thus creating Nafion@Cu, Nafion@Ag, Nafion@Au, Thionin@Cu, Thionin@Ag, and Thionin@Au (Figure 1). An outlook of possible applications of these composites is provided in the conclusions.

2. Experimental Section

Chemicals. $CuCl_2$, $AgNO_3$, $HAuCl_4$, Nafion (5 wt %, hydrogen-ion form, repeating unit 1100 g/mol), thionin (Th) acetate, zinc granules (20 mesh (∼840 μ)), and copper powder (3 μ) were purchased from Aldrich.

Entrapment Procedures (Scheme 2). *A. Entrapment of Nafion.* I. Entrapment of Nafion in Copper. A solution of 0.85 g of $CuCl_2$ (0.005 mol) in 25 mL of distilled water was poured into a stirred solution of 0.55 g of Nafion (0.025 mmol of the repeating monomer unit) in 25 mL of H_2O. After 5 min of stirring, 0.35 g of zinc powder was added and the combined slurry was stirred (750 rpm on a Heidolph MR 3000D stirrer, here and below) at room temperature (RT) for 6 h. Copper is formed while the polymer is entrapped according to $Zn(s) + Cu^{2+}(aq) + Nafion \rightarrow Zn^{2+} + Nafion@Cu(s)$ (redox balanced).

Precipitation of Nafion@Cu begins immediately and is clearly apparent. The precipitate was filtered and washed with 3 10 mL

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* Corresponding author. E-mail: david@chem.ch.huji.ac.il.

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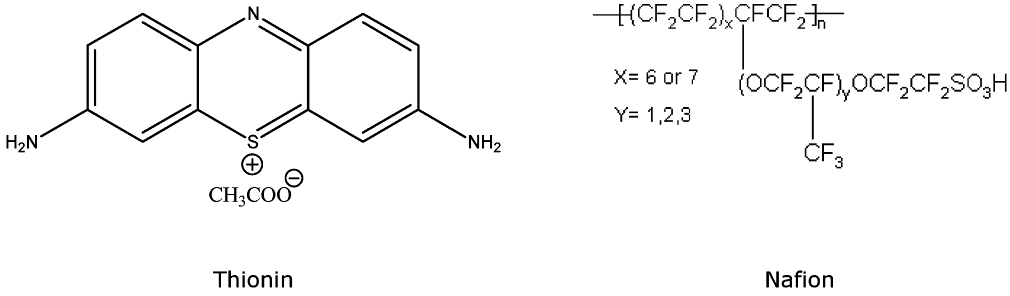
Scheme 1. Structures of Nafion and Thionin



portions of water and dried overnight under a vacuum. The sample was then washed with 15 mL of 37% w/w hydrochloride acid to dissolve and wash out zinc residues. The resulting material, 0.3 g of Nafion@Cu, contained ~100% of the initial polymer used in the reaction mixture, as determined by TGA analysis. The color and shine of the precipitate is that of typical copper (Figure 1c). Copper oxidation is a feature to be avoided: longer periods of stirring the slurry may result in some copper oxidation.

II. Entrapment of Nafion in Silver. Nafion@Ag (Figure 1b) was prepared similarly, according to Nafion + Zn(s) + $2Ag^+(aq) \rightarrow Zn^{2+}$ + 2Nafion@Ag(s) (redox balanced), except for the initial quantities taken (Table 1), resulting in ~100% entrapment.

III. Entrapment of Nafion in Gold. Taking here copper as the reducing agent (Table 1), we employed a similar procedure to prepare Nafion@gold at ~80% entrapment yield (which did not increase by stirring beyond 6 h, up to 24 h), according to Nafion+ 3Cu(s) + $2Au^{3+}(aq_{)} \rightarrow 3Cu^{2+}$ + 2Nafion@Au(s) (redox balanced).

In this case, nitric acid was used to wash out the copper residue.

B. Entrapment of Thionin. In a typical procedure, 0.25 g (0.635 mmol) of $HAuCl_4$ was dissolved in 25 mL of water. The solution was then poured into another stirred solution of 0.001 g (0.0035 mmol) of Th in 25 mL of water. After 5 min of stirring, 0.065 g (1.02 mmol) of copper powder was added and the combined solution was stirred at room temperature for 6 h. Precipitation was apparent immediately. The precipitate was filtered and washed with 3 10 mL portions of distilled water and dried overnight under a vacuum. We then used 15 mL of 70% nitric acid to wash the sample again, followed by water (3 × 10 mL) portions and drying, resulting in 0.12 g of Th@Au (Figure 1a). Spectral analysis of the filtered solution (Th in water is characterized by the 599 and 283 nm absorption peaks) indicated that 50% of the initial dye was entrapped in the metal. The entrapment procedures of Th for silver and copper (Figure 1c) were carried out similarly, except for the initial quantities taken and the percentages of entrapment, which were higher (Table 1).

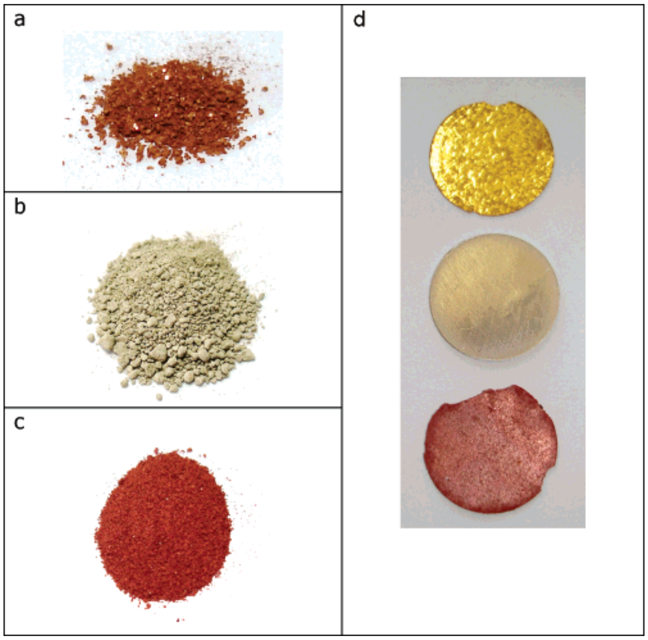


Figure 1. Doped metal powders and pressed coins of gold, silver, and copper: (a) Thionin@Au, (b) Nafion@Ag, and (c) Thionin@Cu; (d) gold, silver, and copper, from top to bottom.

Additional Experiments. *Adsorption vs Entrapment.* For comparing entrapment to adsorption, we carried out the following experiments: The pure metal was prepared as described above except for the presence of the organic molecule. The resulting metal powder was then stirred for 6 h in a water solution of the organic molecule (Th or Nafion), using the conditions and concentrations of the entrapment procedure. The amount adsorbed was determined by UV−vis spectroscopy of the filtered solution in the case of Th and by weight analysis of the filtered solution (after evaporation) for the case of Nafion (Table 3).

Leaching and Extraction Experiments. Leaching into water of the entrapped molecules was tested by stirring 0.1 g of the doped metal with 30 mL of water for 24 h. Extraction of the dopants is possible with DMSO. Typically (e.g., for Nafion@Cu and Th@Ag), 0.1 g of the composite were suspended in 25 mL of DMSO under constant stirring for 6 h, and the solid was then filtered and washed.

Stability of the Dopants to the Reaction Conditions. The stability of Nafion and of Th to the reducing metals was checked in solution by following the entrapment procedure described above but without adding the metal cation; no chemical modifications were observed. In another test, Th was extracted from, for example, Th@Ag, with DMSO by the above procedure, and the spectra before and after the extraction were compared.

Experiments on the way to the Final Procedures. We briefly mention here the results of experiments that led to the final recommended procedures, which have been useful in understanding the dopant@metal system. In one such experiment, the effect of the metal counteranion was tested and indeed found to be an important parameter. For instance, when copper sulfate was taken instead of copper chloride, the efficiency of entrapment dropped, for example, for Th. In another experiment designed to compare the already developed homogeneous entrapment procedure[1] to the heterogeneous one reported here, entrapment of Congo Red (CR), an anionic dye, was attempted, because it was fairly well entrapped with a soluble reducing agent.[1,4] It was found, however, that it is less suitable for the heterogeneous method. Thus, in the case of entrapment in copper and silver, a large amount of the initial dye was not entrapped while separate precipitates, apparently of the metal salts of CR, were still forming. In the case of gold, there was another problem one should pay attention to routinely, and that is that CR was oxidized by the gold cation.

Instrumentation. SEM was carried out on a Sirion (FEI) HR-SEM instrument (operating voltage is indicated for each picture).

Scheme 2. Entrapment Procedure

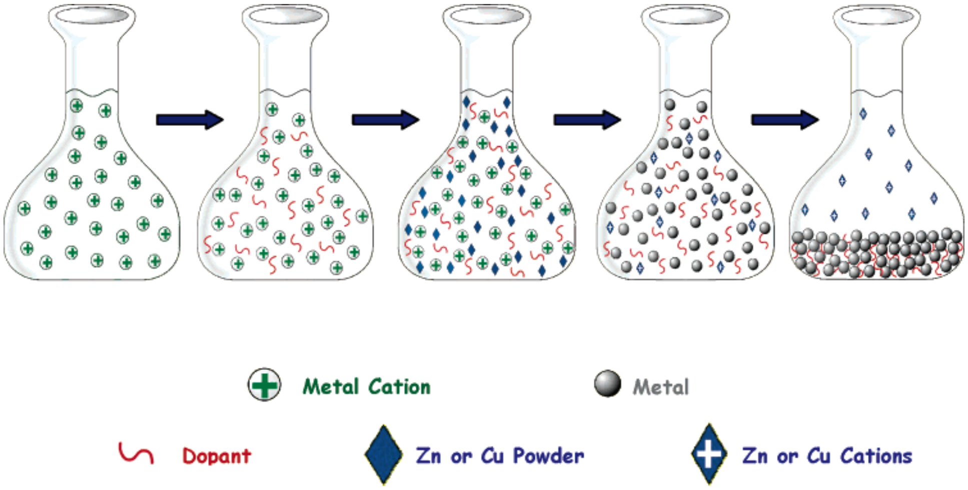


Table 1. Summary of Entrapment Procedures[a]

sample	weight (g) reducing metal	metal salt	dopant	starting dopant:metal molar ratio	% of all nonmetallic atoms in the product	wt % ratio (dopant:sample)
Thionin@Cu	Zn 0.35	$CuCl_2$ 0.85	Thionin 0.004	1:360	7.3	1.1
Thionin@Ag	Zn 0.5	$AgNO_3$ 1.7	Thionin 0.006	1:500	5.0	0.4
Thionin@Au	Cu 0.065	$HAuCl_4$ 0.25	Thionin 0.001	1:180	8.3	0.4
Nafion@Cu	Zn 0.35	$CuCl_2$ 0.85	Nafion 0.55	1:200	23.9	8.0
Nafion@Ag	Zn 0.5	$AgNO_3$ 1.7	Nafion 0.285	1:770	7.5	1.3
Nafion@Au	Cu 0.065	$HAuCl_4$ 0.25	Nafion 0.20	1:70	41.9	6.0

[a] All samples were stirred for 6 h in a total volume of 50 mL of distilled water.

Table 2. X-ray Diffraction Patterns and Crystallite Size

	lit. data[a] Ag		Nafion@Ag		lit. data[a] Au		Thionin@Au		lit. data[a] Cu		Nafion@Cu	
plane (*hkl*)	*d* (Å)	intensity	*d* (Å)	intensity	*d* (Å)	intensity	*d* (Å)	intensity	*d* (Å)	intensity	*d* (Å)	intensity
111	2.359	100	2.357	100	2.355	100	2.352	100	2.088	100	2.087	100
200	2.044	40	2.042	34	2.039	52	2.037	32	1.808	46	1.808	33
220	1.445	25	1.444	14	1.442	32	1.441	12	1.278	20	1.279	11
crystallite size[b] (nm)			30.1				26.3				35.6	

[a] 2003 JCPDS, International Center for Diffraction Data. [b] Calculated from the XRD patterns using Scherrer's equation.

Table 3. Adsorption vs Entrapment Values of Thionin and Nafion for The Three Metals[a]

metal	adsorption of Th (%)	entrapment of Th (%)	adsorption of Nafion (%)	entrapment of Nafion (%)
Cu	7.5	86	15	100
Ag	6.5	76	12	100
Au	2.5	50	3	80

[a] Percentage of the initial concentration.

XRD measurements were carried out with Philips automated powder diffractometer (with PW1830 generator, PW1710 control unit, PW1820 vertical goniometer, 40 KV, 35 mA, Cu KR (1.5405 Å)). Energy-dispersive analysis of X-rays (EDAX) was carried out with an attachment to the same SEM instrument. UV−vis absorption spectroscopy was carried out with a Hewlett-Packard 8452A diode-array UV−vis spectrophotometer. Thermogravimetric analysis (TGA) was performed on a TA instrument SDT 2960 from 25 to 1100 °C at a heating rate of 5 °C/min in flowing dry air (or under nitrogen for the copper samples (100 cm^3/min)). For a more exact analysis of the TGA graphs, the derivative of weight loss was calculated using the supplied software. Surface area and porosity were determined from nitrogen adsorption/desorption isotherms with a Micromeritics ASAP-2000 physisorption instrument, using the BET and BJH equations, respectively. Density was determined from weight/volume analysis.

3. Results and Discussion

Visual Observations. Figure 1 provides macroscopic pictures of the composites. Significantly, the copper and silver alloys are not oxidized and retain their characteristic metal color and shine (after pressing). Going down to the microscopic level, some typical pictures are collected in Figure 2. For instance, for copper, one can see (Figure 2a) that Th@Cu is composed of ∼1 μm aggregates of crystallites ∼35 nm in size. A similar overall morphology characterize Nafion@Cu as well (Figure 2b). The effect of the dopant on morphology is seen by comparison with pure Cu (Figure 2c): the nanocrystallites are larger, and the roughly spherical growth, apparently around the sacrificial Zn nucleus, is evident. In the other metals, the aggregation features are

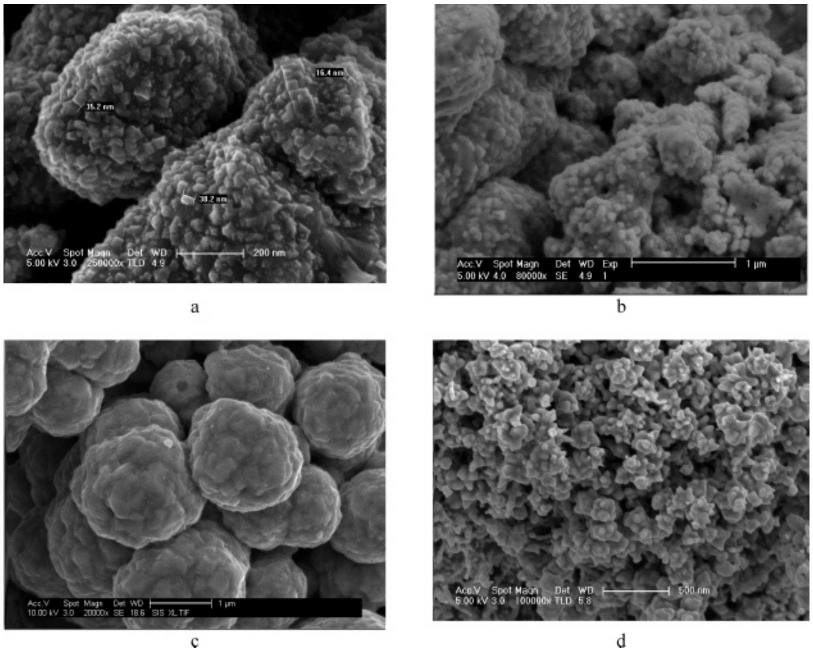


Figure 2. High-resolution SEM images: (a) Thionin@Cu (bar = 200 nm), (b) Nafion@Cu (bar = 1μ), (c) pure copper (bar = 1μ), and (d) Nafion@Au (bar = 500 nm).

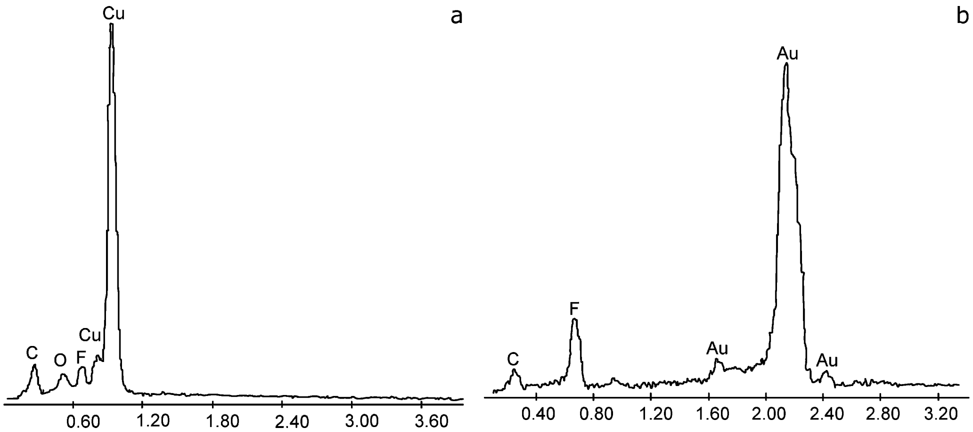


Figure 3. EDAX analysis of (a) Nafion@Cu and (b) Nafion@Au.

similar, and Nafion@Au is shown as a typical example in Figure 2d.

XRD Measurements. XRD analysis (Table 2) confirms the SEM observations: Application of the Scherer equation[7] indeed indicates that the elementary building blocks of these composites are metal fcc nanocrystals (for all three metals), ~25−35 nm in size. It is significant for the consideration of the mechanism of entrapment to note that the entrapment does not change the crystal characteristic typical diffraction lines in all three metals.

EDAX. The composite nature of the new materials is evident in a number of analyses, one of which is EDAX (and the others are detailed below). Some typical EDAX profiles are given in panels a and b of Figure 3 for Nafion@Cu and for Nafion@Au, respectively. The appearance of the indicative F signals is clearly seen.

Expressing the Composite Nature of Dopant@Metal. There are several ways to express the composite nature of these materials. First, as is customary for metal alloys,[8] one can use the atom percent. For the metal−organic composites, that would be the percent of all nonmetallic atoms, including hydrogen. For instance, for Nafion@Cu, it is 23.9%. Another possibility is then to use the molar ratio, organic repeating unit:metal, which for our example is 1:200 (or 0.5%). Finally, one can use the weight percent ratio, which for our example is 8.0% w/w. Each of these carries different information, and all are needed because of the large difference between the atomic weights of the metal and of the atoms of the organic molecule. However, the value that gives the real "feeling" of the composite nature is the 23.9% non-metal atoms. The various comparative entrapment values are collected in Table 1.

Adsorption from Water vs Entrapment. It is important to emphasize that adsorption on the surface of the metal powder and the entrapment within it are very different processes. This is clearly shown in Table 3. There is a major

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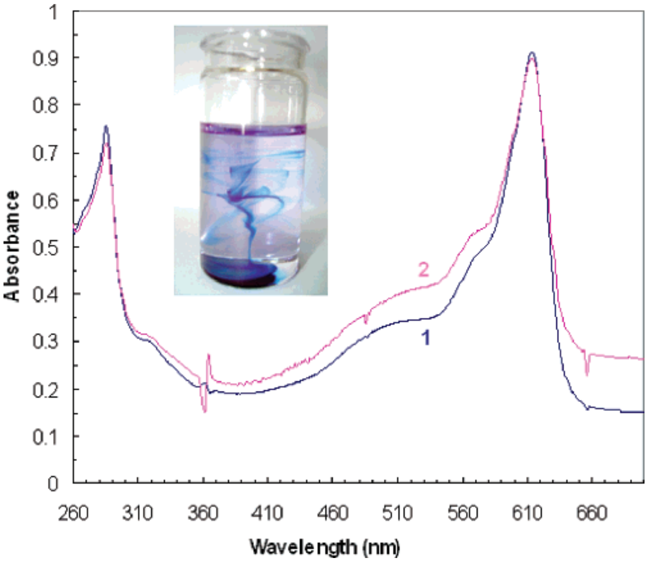

Figure 4. Spectra of thionin in DMSO before entrapment (line 2) and after extraction from Thionin@Ag (line 1). Inset shows the extraction process.

different between adsorption and entrapment: whereas adsorption is of the order of few molar percent, entrapment of these water soluble molecules is very high. And, whereas adsorption occurs on the surface of aggregated metal, the entrapment occurs simultaneously with the formation of the metal, namely, during the early aggregation stages of the metal crystallites into bulk powder. Comparing adsorption to entrapment, one can think of the former as a 2D process and the latter as a 3D multiple-interaction process. It is also notable that although water easily washes away the adsorbed molecule, leaching into water is extremely small (below the limit of detection up to 1%); we return to the mechanism of the entrapment in the Summary.

Stability of the Dopants and the Metals to the Reaction Conditions. Only with DMSO was it possible to extract the dopant (Figure 4, inset). This is an important experiment, because it allows one to compare the spectra of the dopant before and after entrapment (and extraction); a typical result showing that the dopant remains intact is provided in Figure 4.

TGA. The TGA profiles of Nafion before and after the entrapment in copper are shown in panels a and b of Figure 5. A lowering of close to 100 °C in the temperature of decomposition is evident for Nafion@Cu, along with a narrowing of the decomposition range (Figure 5b), both indicating a catalytic action of the metal on the decomposition process (another catalytic effect of the metal on the degradation process has been reported for poly(styrene sulfonic acid) and poly(vinyl alcohol) entrapped in silver[2]). For comparison, the TGA of Nafion adsorbed on copper is shown in Figure 5c and provides an additional indication that entrapment is a distinctly different process compared to adsorption, showing an in-between behavior. Whereas the TGA analysis for the copper samples was carried out in nitrogen (because air causes oxidation of the copper and its weight increases), for Nafion@Au and Nafion@Ag, the analysis was carried out in air (panels d and e of Figure 5). The degradation process in this case is different; under air, it is mainly oxidative degradation of the Nafion, but under nitrogen, it is mainly nonoxidative graphitization. However, the catalytic effect of lowering the temperature of decomposition, compared to the pure Nafion, is seen here as well. Finally, it should be noted that oxidative TGA weight losses agree with the estimates on the quantities entrapped.

Surface-Area Measurements. It is quite indicative that the N_2 adsorption−desorption loops of these composites (a typical example is provided in Figure 6a) nicely obey the BET equation with an excellent correlation coefficient of >0.9998 (Figure 6b). Recalling the assumptions behind the BET equation, and in particular the condition of homogeneity of the adsorption sites,[9] this excellent compliance indicates the homogeneous nature of the composite. The shape of the isotherm and its high-pressure hysteresis range, the ∼20 nm pore sizes, the low surface areas, and the low pore volumes (Table 4) all support a conclusion that the composites are indeed mesoporous aggregates, the porosity of which is, by and large, interstitial. The variation in surface areas and in the other parameters agrees with the extraction experiments: there is an ∼10% increase in surface area after extraction of the polymeric dopant. The fact that the pore size basically remains around ∼20 nm shows that the new pores that have been freed because of the extraction are of the same nature and size, that is, the size domain of the polymer is perhaps on that order. Compared to blank Cu, it is seen that the doping causes an increase in all of the parameters. The polymer interferes with the aggregating packing of the crystallies, thus creating a more porous composite.

Density Measurements. Some typical density values are collected in Table 5. It is clearly seen that the doped metals are much less dense compared to the pure crystalline metal, indicating mainly the aggregate nature of the composites; note that the organic component pushes the density even lower.

4. Summary and Suggested Mechanism of Entrapment

We have shown here that entrapment of organic molecules within metals is achievable beyond the detailed studied silver[1−4] with the other (coin) metals, namely, copper and gold. We also showed that the preparation of the metal−organic composites is possible not only by the previously developed homogeneous method but also heterogeneously. How is it then that although the preliminary process in the entrapment sequence is adsorption on the forming metal nanocrystallites (an easily shifted equilibrium by washing), in the final product, water cannot extract these water-soluble molecules? We propose that the metal precipitation by the cation reduction shifts the adsorption equilibrium

$$\text{dopant (solution)} + \text{metal crystallite} \rightleftharpoons \text{adsorbed dopant}$$

as follows: This adsorption (which occurs through the nitrogen atoms in Th[10] and apparently through the sulfonate

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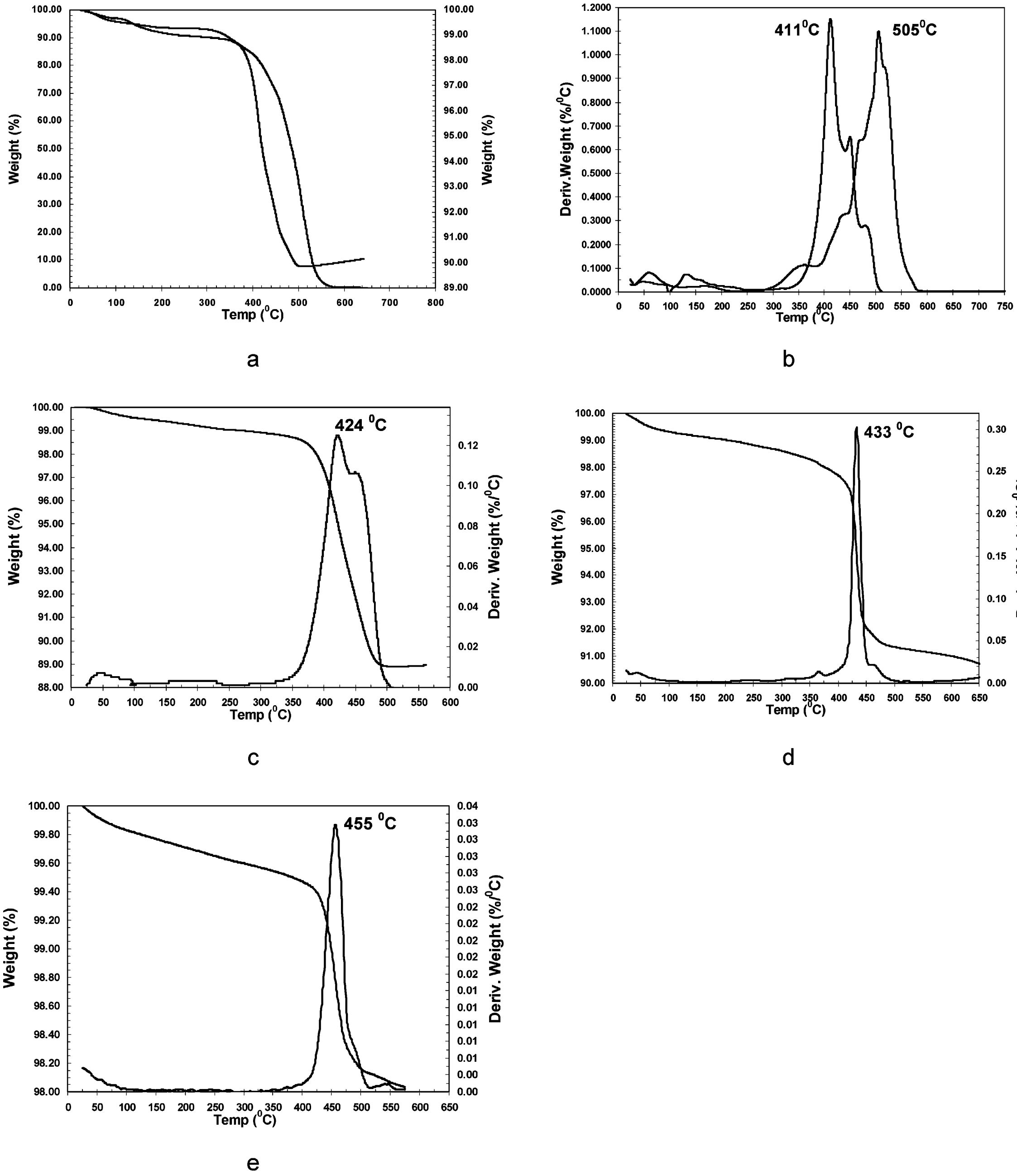

Figure 5. Thermogravimetric analysis (TGA) of Nafion. (a) Right line, pure Nafion; left line, Nafion@Cu (both under N_2). (b) Derivatives of the lines in (a). (c) Nafion adsorbed on copper. (d) Nafion@Au. (e) Nafion@Ag.

moieties in the case of Nafion[11,12]), is not an isolated event; during the residence time of the adsorbed molecule, reduction and aggregation continue to take place in the immediate environment of the adsorbed species, thus affecting the back reaction in the above equilibrium. In the case of polymer entrapment, it is enough to have preliminary entanglement of portions of the molecules, to secure it in its adsorption position. Molecular level experiments for exploration of this and other propositions as to the entrapment mechanism are in progress; yet the accumulated previous work, and practically all of the observations detailed above, point to an entrapment picture in which tightly aggregated nanocrystallites hold the organic molecules within the interstitial porosity and cages. We have shown that although entrapment starts with adsorptive forces, in the final product, the organic molecules are held inside these aggregates in a much stronger way (physical encaging) to such an extent that water, a good solvent for the dopants, is not capable of extraction (but easily washes away adsorbed molecules).

The fact that these novel composite materials are obtainable by quite different reduction and entrapment mechanisms, homogeneous reduction of metal cations and heterogeneous metal reduction of these cations, seems to indicate that these

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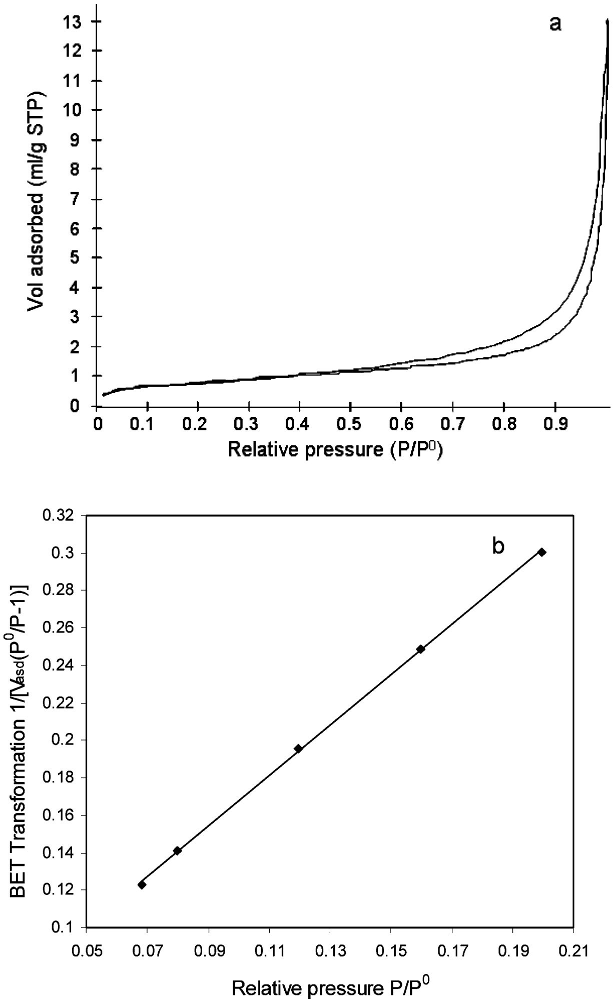

Figure 6. Adsorption/desorption isotherm and compliance to the BET equation of Nafion@Cu.

Table 4. Typical Surface Area and Pore Size Values

sample	surface area (m^2/g)	pore volume (mL/g)	pore size (nm)
Nafion@Cu	3.2	0.020	21
Nafion@Cu (after extraction)	3.5	0.025	23
Cu blank	1.2	0.005	15

Table 5. Typical Densities of the Metal−Organic Composites and Parent Metals

	density[a] (g/mL)
bulk Cu[b]	8.9
Cu powder	2.1
Nafion@Cu	1.1
Thionin@Cu	1.2
bulk Ag[b]	10.5
Ag powder	3.1
Nafion@Ag	1.6
Thionin@Ag	1.9
bulk Au[b]	19.3
Au powder	5.9
Nafion@Au	2.3
Thionin@Au	2.4

[a] By volume−weight determination [b] From the CRC Handbook of Chemistry and Physics, 81st ed.

new composites are inherently stable and that many more combinations of organics and metals are possible candidates for the preparation of new metal−organic composites. Although the field is still in its infancy, as the very ability to obtain these materials is still being researched, it is already clear that diverse applications are just around the corner, including modification of electronic properties and other physical properties of metals, modification of chemical reactivates of both the dopant and the metal, and catalysis; the latter will be reported shortly.[4]

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