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 conducted the reaction in the presence of the desired organic molecule. 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.

2. Experimental Section

Chemicals. CuCl₂, AgNO₃, HAuCl₄, 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 CuCl₂ (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 H₂O. 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) + Cu²⁺(aq) + Nafion → Zn²⁺ + 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