Metal−Polymer Composites: Synthesis and Characterization of Polyaniline and Other Polymer@Silver Compositions

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Received March 6, 2008. Revised Manuscript Received April 17, 2008

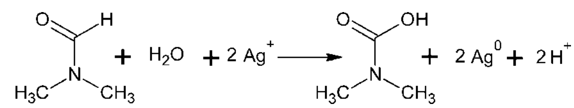
A method was developed for the entrapment of water-insoluble hydrophobic polymers in a metallic matrix, thus generalizing further the routes for obtaining the novel organics@metal composite materials. The reaction took place in an organic phase using the reduction of metal ions by DMF in the presence of water. The reductive entrapment of polyaniline was studied in detail using XRD, SEM, BET, TGA, UV−vis, XPS, and density measurements, and the mechanism of the entrapment was established. The scope of this approach is demonstrated by entrapment of two additional hydrophobic polymers, polystyrene and polyacrylonitrile.

Introduction

Whereas the number of metal elements is small and limited, that of organic and biological molecules is vast and virtually unlimited. Naturally, hybridization of these two parent families can enrich the property library and widen the application scope offered by each of them individually. Recently, this principle has been behind a series of studies[1–6] that introduced a new family of materials, designated as organic compound-doped metals. The methodology of their preparation enables one to incorporate small or large (polymeric) organic molecules within metals, thus creating a new family of metal matrix composites. Various useful applications have been already demonstrated, such as formation of metallic catalysts[5] and induction of unusual properties to metals, such as acidity[1] and chirality in bulk gold and silver.[2] The methodology of preparation of those metal matrix composites involves metal synthesis by chemical reduction of a metal cation in the presence of the selected organic molecule. The reductive entrapment can be carried out either homogenously,[1–4] with water-soluble reducing agents, or heterogeneously,[6] with a powder of metal. Most of our studies have been carried out on copper, silver, and gold, for which a variety of metal salts can be used. The composite is obtained in a powder form, which can be hot pressed to create films or discs.

Special attention has been devoted in our studies to the entrapment of polymers because intimate polymer@metals composites represent novel materials, which, to the best of our knowledge, have not been presented before. Thus far, water-soluble polymers could be entrapped because the of the aqueous reduction conditions. Thus prepared were poly(styrenesulphonic acid)@Ag, poly(vinylalcohol)@Ag, poly(vinylbenzyltrimethylammonium hydroxide)@Ag, Nafion@Ag, Nafion@Cu, and Nafion@Au. However, since most of the widely used polymers are hydrophobic and in order to enlarge the family of polymer@metal composites to encompass these additional polymers, a new entrapment methodology is required.

Scheme 1. Reduction Reaction of Silver Ions by DMF



Of the various reduction processes of metal cations in an organic phase,[7–12] one method emerged as particularly attractive, namely, use of *N*,*N*-dimethylformamide (DMF) due of its dual action. DMF is an excellent solvent for many polymers ("good solvent"), while at the same time it is a potent reducing agent for some metal cations.[13] Its activity can be triggered at will by adding an equimolar amount of water (small enough not to affect the dissolution properties) according to Scheme 1.

The main focus of this study is the entrapment of electrically semiconductive polyaniline (PANI) in silver, for which detailed analyses are presented and a mechanism of entrapment is established. Furthermore, the commonalty of the method is proven by showing its applicability to two other polymers, namely, polyacrylonitrile (PAN) and polystyrene (PS). Whereas PAN can be converted to a semiconductive conjugated "ladder" polymer via polymerization of

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10.1021/cm800657j CCC: $40.75
Published on Web 06/11/2008