Preparation of PEDOT/Cu composite film by in situ redox reaction between EDOT and copper(II) chloride

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Poly(3,4-ethylenedioxythiophene)/copper (PEDOT/Cu) composites were prepared by an in situ redox reaction of 3,4-ethylenedioxythiophene (EDOT) and copper(II) chloride. During the reaction, EDOT was oxidatively polymerized by Cu(II) chloride, while the Cu(II) ions were reduced to produce Cu metal particles. PEDOT/Cu composite films were also successfully prepared on CuCl\textsubscript{2}-coated poly(ethylene terephthalate) (PET) films by the vapor phase polymerization of EDOT. PEDOT/Cu films were characterized using UV–vis spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) to confirm the formation of PEDOT, and the presence of metallic Cu particles.

1. Introduction

Particles formed from the transition and noble metals, such as Cu, Ni, Pd, Ag, Pt, and Au, have been used in many applications, notably as catalysts [1], electronic and magnetic devices [2], nonlinear optical devices [3], and luminescence devices [4]. Due to the enormous practical potential of these materials, much work has been done on the preparation of metal particles [5,6]. In particular, Cu particles are expected to play a key role as a material in conductive inks, nonlinear optical materials, and electronic devices because of their low ionic migration characteristics and low cost.

However, little information is found in the literature about the preparation of Cu particles based on the chemical reduction method, and the practical feasibility of this approach has been questioned. Cu particles are not easily produced due to the comparatively low reduction potential of Cu ions as compared with that of noble metal ions: Cu\textsuperscript{2+} + 2e\textsuperscript{−} = Cu, 0.340 V; Ag\textsuperscript{+} + e\textsuperscript{−} = Ag, 0.799 V; Au\textsuperscript{3+} + 3e\textsuperscript{−} = Au, 1.52 V. Therefore, the identification of suitable reducing agents is necessary to allow for the reduction of copper ions under the mild conditions that are required to avoid particle damage [7]. Several reduction routes for the reduction of copper(II) chloride to Cu metal have been proposed [8,9], with classical methods requiring the use of strong reductants like hydrazine. Wu and Chen [8] reported that monodispersed Cu nanoparticles with mean diameters in a range from 5 to 15 nm were produced by the chemical reduction of copper(II) with hydrazine as a reducing agent and cetyltrimethylammonium bromide (CTAB) in alkaline water as a surface-modifying reagent. Pileni et al. devised a reverse micelle process using a sodium bis-2-ethylhexyl sulfosuccinate (AOT)/water/isooctane system to prepare Cu nanoparticles. Particle sizes were controlled in the range of 2–12 nm by changing the ratio of water to surfactant or by changing the concentrations of hydrazine or copper(II) [10].

Recently, conducting polymer/metal composites have attracted research attention because of their interesting physical properties and thus their potential for practical applications [11], Poly(3,4-ethylenedioxythiophene) (PEDOT) possesses remarkable transparent, conducting, and electrochromic properties, and is used in several applications including the ITO electrode modification of polymer light emitting diodes, antistatic transparent coatings, and the organic conductive electrode materials of several devices. Moreover, the oxidation potential of 3,4-ethylenedioxythiophene (EDOT) is similar to that of terthiophene, which means that it can be used as a reductant in the preparation of Au nanoparticles by the reduction of HAuCl\textsubscript{4} solution with alkylamine as the stabilizer [12]. We demonstrated that EDOT was easily oxidized with AuCl\textsubscript{4} to form PEDOT/Au composites by an in situ redox reaction [13]. In particular, Ilieva and Tsakova [14,15] showed that the galvanostatic reduction of Cu(II) ions in PEDOT layers results in copper crystallization on the...