Electrochimica Acta 65 (2012) 204–209

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical preparation of photoelectrochemically active CuI thin films from room temperature ionic liquid

Hsin-Yi Huang, Da-Jean Chien, Genin-Gary Huang, Po-Yu Chen*,[1]

Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung City 807, Taiwan

ARTICLE INFO

Article history:
Received 27 October 2011
Received in revised form 11 January 2012
Accepted 12 January 2012
Available online 20 January 2012

Keywords:
Cuprous iodide
Electrodeposition
Anodization
Photocurrent
Compound semiconductor

ABSTRACT

Cuprous iodide (CuI) thin films with photoelectrochemical activity were prepared by anodizing copper wire or copper-electrodeposited tungsten wire in the room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF_6 RTIL) containing *N*-butyl-*N*-methylpyrrolidinium iodide (BMP-I). A copper coating was formed on the tungsten wire by potentiostatic electrodeposition in BMP-dicyanamide (BMP-DCA) RTIL containing copper chloride (CuCl). The CuI films formed using this method were compact, fine-grained and exhibited good adhesion. The characteristic diffraction signals of CuI were observed by powder X-ray diffractometry (XRD). X-ray photoelectron spectroscopy (XPS) also confirmed the formation of a CuI compound semiconductor. The CuI films demonstrated an apparent and stable photocurrent under white light illumination in aqueous solutions and in a RTIL. This method has enabled the electrochemical formation of CuI from a RTIL for the first time, and the first observation of a photocurrent produced from CuI in a RTIL. The coordinating strength of the anions of the RTIL is the key to the successful formation of the CuI thin film. If the coordinating strength of the anions of the RTIL is too strong, no CuI formation is observed.

1. Introduction

Cuprous iodide (CuI) is an important photoelectric semiconductor with a band gap of 3.1 eV and is often used for visible light-assisted photoelectrochemical and solar energy conversion systems. CuI is a convenient *p*-type semiconductor used for constructing fully solid-state dye-sensitized photovoltaic cells because it is optically transparent and has good hole conductivity [1,2]. Several methods have been developed to prepare CuI nanocrystallites [3–5]. Appropriate immobilization of these semiconductor nanocrystallites on a solid surface is, however, usually required for practical applications. It would be thus more convenient to directly form CuI thin films on a surface of interest. The most frequently used procedures for the direct formation of CuI on a solid surface involve three key steps developed by Penner [6]. The first step is the electrodeposition of Cu nanocrystallites on a conductive surface. Second, the Cu nanocrystallites are oxidized to Cu_2O. The final step involves the displacement of the oxide with iodide (from Cu_2O to CuI). Zen and co-workers applied the same procedures in Tris-buffer solution, and the formation of Cu_2O was more controllable [7]. A few studies have reported the direct electrodeposition of CuI [8] or the electrochemical conversion from Cu to CuI [9], and one report discussed the conversion of Cu to CuI on Cu(1 1 1) [10].

Room temperature ionic liquids (RTILs) have been recognized as unique solvent systems and employed for many purposes, including the electrodeposition of metals, alloys, and semiconductors [11,12] because they have many special properties such as nonvolatility, (electro)chemical and thermal stability, a wide temperature range over which they are liquid, and adjustable physicochemical properties. The electrochemical formation of CuI has never been carried out in RTILs, however. Herein we report the electrochemical preparation of CuI thin films converted from surface Cu by simply anodizing Cu at a constant potential in the RTIL 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF_6) containing *N*-butyl-*N*-methylpyrrolidinium iodide (BMP-I). This process can be called iodination. Compared with the published literature in which direct formation of CuI on an electrode surface was reported [6,8], the method mentioned here involves fewer steps (the Cu surface can be directly converted to CuI without the transition from Cu to Cu_2O). In addition, no volatile organic solvents such as acetone are required because the RTIL is nonvolatile. Two types of Cu substrate, Cu wire electrodes and Cu-coated W wire electrodes, were employed in this study. For the Cu wire electrode, the Cu surface could be directly converted to CuI in one step. Two steps were essential for the Cu-coated W wire electrode: electrodeposition of Cu and then iodination. The Cu layer coated on the W wire electrode was formed by electrodeposition at a constant potential in the RTIL BMP-dicyanamide (BMP-DCA) containing CuCl

---

* Corresponding author. Tel.: +886 7 3121101x2587; fax: +886 7 3125339.
E-mail address: pyc@kmu.edu.tw (P.-Y. Chen).

[1] ISE member.

0013-4686/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2012.01.044

as the source of Cu(I) ions. The obtained CuI thin films were characterized with a scanning electron microscope (SEM) couples with an energy dispersive spectrometer (EDS) that was employed for the semi-quantitative elemental analysis. A powder X-ray diffractometer was used to determine the crystalline structure of the CuI film and an X-ray photoelectron spectrometer (XPS) was used to determine the surface state of the CuI films. The CuI thin films also exhibited a stable photoelectrochemical response in aqueous media and in an RTIL under the illumination of a halogen light bulb.

2. Experimental

2.1. Materials and instrumentation

Electrochemical experiments were performed either inside a glove box (MBRUAN, UNI-LAB B) using a Princeton Applied Research potentiostat/galvanostat (PAR 263A) or outside a glove box with a CH Instrument electrochemical analyzer (CHI 660C). A traditional three-electrode electrochemical cell was employed, and the detailed configuration has been described previously [13]. A platinum disk electrode (1.6 mm Ø) was used for the voltammetric study in a glove box. For the electrochemical formation of CuI, Cu wire (Alfa Aesar, 99.9%, 1 mm Ø) or W wire (Alfa Aesar, 99.95%, 0.5 mm Ø), the latter of which was electrodeposited with a Cu layer (Cu/W), was used as the working electrode. A reference electrode fabricated by immersing a piece of platinum wire in a ferrocene (Fc)/ferrocenium (Fc^+) solution (the molar ratio of $Fc/Fc^+ = 1$) in a glass tube with a porous Vycor tip was employed. Therefore, the potential was reported with respect to the redox potential of Fc/Fc^+ for the electrochemical experiments carried out inside a glove box. A platinum spiral immersed in the IL and separated from the bulk solution by a porosity E glass frit was used as a counter electrode. Outside the glove box, an Ag/AgCl (NaCl saturated) reference electrode and a platinum wire counter electrode were used in aqueous solutions.

The room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF_6 RTIL) [14] and *N*-butyl-*N*-methylpyrrolidinium iodide (BMP-I) [15] were prepared by following the published procedures. BMP-dicyanamide (BMP-DCA) RTIL was also prepared by following the procedure published in the literature [15].

2.2. Formation of CuI thin films

CuI thin films were prepared in a glove box via conversion of surface Cu at a copper wire electrode or a Cu-coated W wire electrode (Cu/W) by anodization at −0.2 V (vs. Fc/Fc^+) in BMI-PF_6 containing 100 mM BMP-I. The obtained CuI-coated electrodes are denoted as CuI/Cu and CuI/W, respectively. The Cu layer coated on a W wire electrode (Cu/W) was formed by potentiostatic electrodeposition (at −1.9 V vs. Fc/Fc^+) from firmly stirred BMP-DCA RTIL containing 50 mM CuCl. The as-prepared CuI films were cleaned by soaking the CuI/Cu or CuI/W electrodes in acetone to remove residual RTIL and then dried under nitrogen.

2.3. Characterization and photoelectrochemical measurements

The CuI films were characterized using SEM (FEI Quanta 400F or Philips XL-40 FEG) and XPS (JEOL JAMP-9500F). The crystalline structure of the CuI films was analyzed by XRD (Shimadzu Model XD-D1). The photocurrent produced from the CuI films under the illumination of a 50 W (Watt) halogen light bulb was studied using cyclic voltammetry and chronoamperometry (the latter was performed at different potential biases (E_{bias} vs. Ag/AgCl or Fc/Fc^+)) in pH 8 phosphate buffer solution (PBS) containing 10 mM KI under an air atmosphere or in BMI-PF_6 containing 30 mM BMP-I under a nitrogen atmosphere in a glove box. The obtained CuI films were mixed and ground with an appropriate amount of dry and pure KBr salt to form transparent CuI-KBr disks for study by UV–vis spectroscopy using UV–vis spectrophotometer (Thermo GENESYS 10S BioUV-Vis).

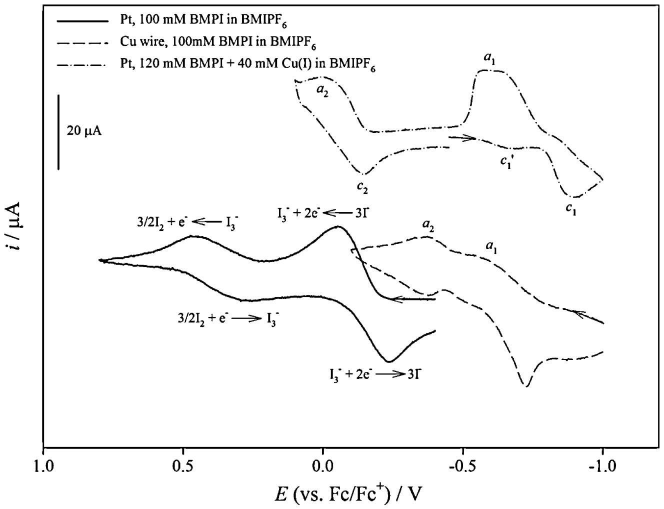

Fig. 1. CVs recorded at Pt disk or Cu wire electrode in the solutions indicated in the plot. The arrows indicate the initial direction of potential scan. Scan rate: 50 mV s^{-1}.

3. Results and discussion

3.1. Cyclic voltammetric study

Before formation of the cuprous iodide films (CuI films), evaluation of the behavior of BMP-I in BMI-PF_6 RTIL by cyclic voltammetry was necessary. The cyclic voltammogram (CV) recorded at a platinum disk electrode in BMI-PF_6 RTIL containing 100 mM BMP-I is shown in Fig. 1 (the solid curve). The potential was first scanned at an initial potential E_i of −0.400 V in the anodic direction, and two redox couples were observed. The relevant reactions of the two redox couples are indicated in the figure. The peak potentials of the two oxidative and the two reductive waves are −0.052 V/0.458 V and 0.274 V/−0.236 V, respectively. The same voltammetric behavior of the I^- ions in BMI-BF_4 RTIL (BF_4 is the abbreviation for tetrafluoroborate) has been reported [16].

The dashed curve ($E_i = -1.00$ V) in Fig. 1 shows the CV recorded at a Cu wire electrode in BMI-PF_6 containing 100 mM BMP-I. The electrode potential was initially scanned in the anodic direction. Apparently, Cu wire can be oxidized in the anodic scan because two broad oxidative waves were observed at $E_{p,a1} = -0.536$ V and $E_{p,a2} = -0.368$ V. However, these two oxidative waves do not demonstrate the typical behavior associated with anodic metal dissolution in a RTIL because rounded, rather than sharp oxidative waves with a steeply increasing current, are observed, indicating the formation of some insoluble layers. It was found that CuI thin films could be formed by holding the potential at these oxidative waves, which involved the production of Cu^+ cations (a detailed discussion follows). Thus, the formation of CuI should result from the reaction of $Cu^+ + I^- \rightarrow CuI$.

To provide a comparison, sufficient BMP-I was introduced into BMI-PF_6, and the bulk electrolysis of a Cu wire electrode was carried out to produce I^--coordinated Cu(I) ions (dash-dot curve in Fig. 1, with an initial potential E_i of −0.450 V). The applied potential was scanned from the initial potential in the cathodic direction, and two redox couples (c_1/a_1 and c_2/a_2) were observed. Based on the experimental results in the previous study [17], the relevant redox reactions for the two redox couples are