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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

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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

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

[1] ISE member.

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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.

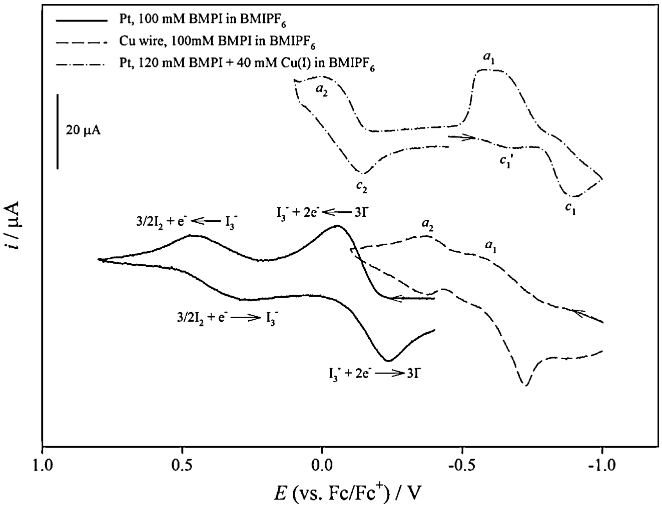

Fig. 1. CVs recorded at Pt disk or Cu wire electrode in the solutions indicated in the plot. The arrows indicate the initial direction of potential scan. Scan rate: 50 mV s^{-1}.

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).

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 $E_{\text{p},a1}$ = −0.536 V and $E_{\text{p},a2}$ = −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$^-$ → 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

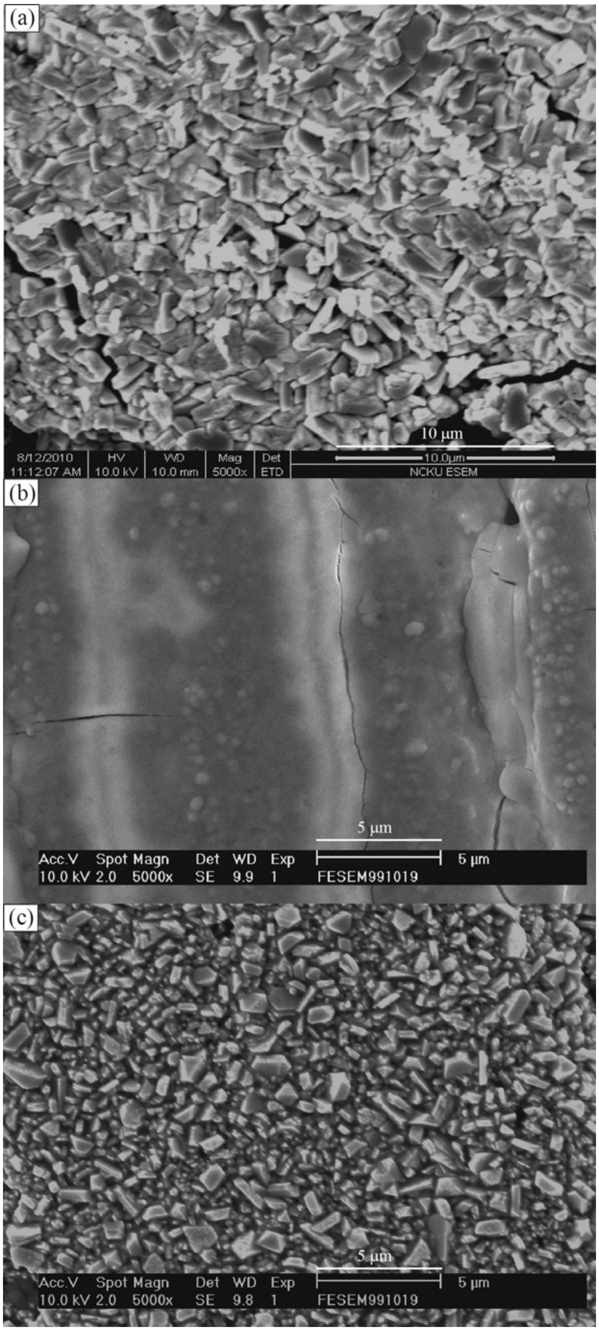

Fig. 2. SEM micrographs of (a) CuI/Cu formed by anodizing Cu wire at −0.2 V in BMI-PF$_6$ containing 100 mM BMP-I, (b) Cu/W formed by electrodepositing Cu onto W wire at −1.9 V in BMP-DCA with 50 mM CuCl, and (c) CuI/W converted from the Cu/W of (b) by using the same iodination procedure indicated in (a).

assigned as Cu(I) + e$^-$ ↔ Cu ($E_{p,c1}/E_{p,a1}$ = −0.900/−0.600 (V)) and Cu(II) + e$^-$ ↔ Cu(I) ($E_{p,c2}/E_{p,a2}$ = −0.145/0.000 (V)), respectively. The reductive wave $c_{1'}$ corresponds to the under potential deposition (UPD) of Cu at the Pt surface. No CuI film was formed in this solution no matter what oxidative potential was applied. Thus, the mechanism mentioned in the literature is not involved in the CuI formation in this system [8]. In that study, CuI was formed from the decomposition of CuI_3^{2-} ($CuI_3^{2-} \rightarrow CuI + I_2 + 2e^-$) in acetone. Additionally, the a_1 wave of the dashed curve overlaps with the a_1 wave of the dash-dot curve, indicating that both oxidative waves involve the same reaction (Cu → Cu(I) + e$^-$). The a_2 wave observed in the dashed curve may be due to the formation of a CuI film, leading to a current fluctuation.

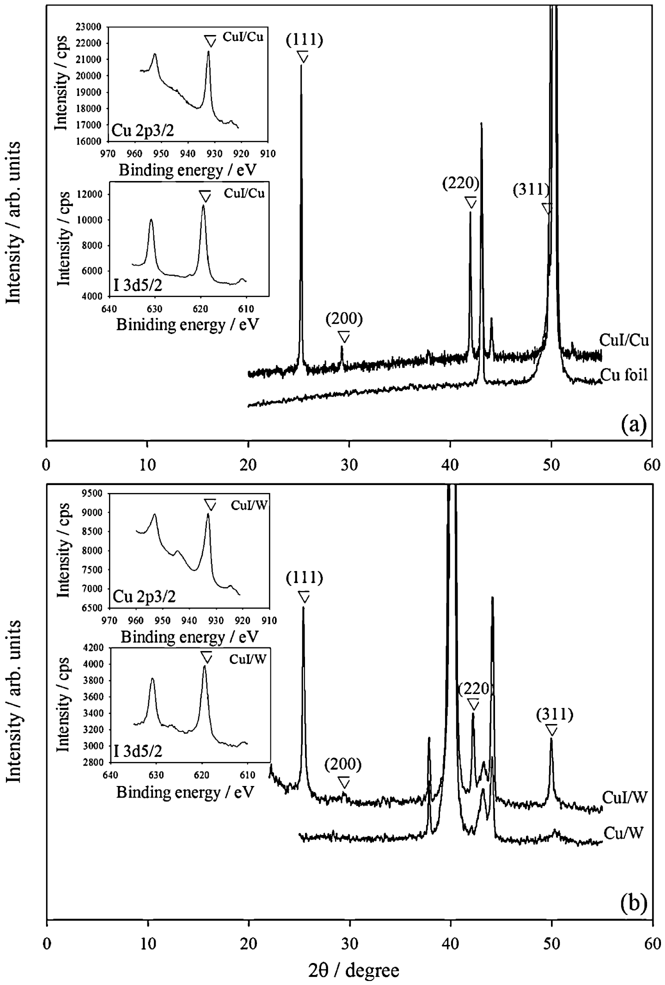

Fig. 3. XRD patterns of (a) Cu foil and CuI/Cu formed from the conversion of Cu foil, and (b) Cu/W and CuI/W formed from the conversion of Cu/W. Cu/W and CuI film were prepared by following the procedures indicated in Fig. 2. Insets show the XPS spectra for the relevant CuI film.

As mentioned above, CuI thin films were converted from the surface Cu as long as the correct anodizing potential was applied. Therefore, an applied potential of −0.2 V was employed for the following experiments in order to convert surface Cu into CuI. In addition to the applied potential, another key factor for the successful formation of CuI is the coordinating strength of the anions of the RTIL. BMI-PF$_6$ was employed in this study because the interaction between Cu^I and PF$_6^-$ is very weak (the anodic dissolution of Cu is not feasible in a PF$_6$-based RTIL, indicating a very weak interaction between PF$_6^-$ and Cu^I) compared with other frequently used anions such as bis((trifluoromethyl)sulfonyl)amide (TFSA) and dicyanamide (DCA) [18]. The interaction between Cu^I and these two anions (TFSA and DCA) is too strong to allow formation of solid CuI films because more stable TFSA- or DCA-coordinated Cu(I) complex ions are formed in TFSA- or DCA-based RTILs. The formation of TFSA- or DCA-coordinated Cu(I) complex ions was confirmed because copper could be directly anodized and dissolved into TFSA- and DCA-based RTILs.

3.2. Electrochemical formation of CuI thin films and their characterization

As noted above, CuI films can be formed on Cu wire electrode (CuI/Cu) by anodization of the Cu electrode at −0.2 V in BMI-PF$_6$ containing BMP-I. Fig. 2a shows the SEM micrograph of

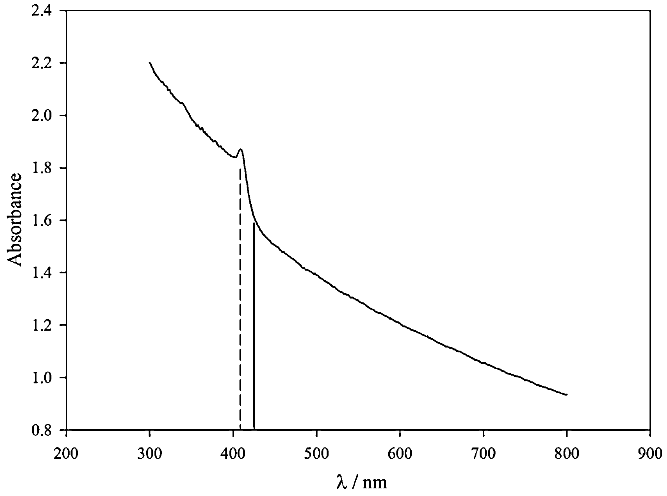

Fig. 4. UV–vis spectrum of transparent CuI-KBr disk. The dashed line indicates the abrupt absorption near 400 nm and the solid line shows the onset absorption near 420 nm.

the CuI/Cu electrode. During anodization, the smooth and mirror-like Cu surface was gradually converted to a white thin layer that was composed of compact and fine-grained crystalline prisms. To understand whether the CuI films could be formed on other conductive substrates, a W wire electrode was electrodeposited with a Cu thin layer (Cu/W) from BMP-DCA RTIL containing 50 mM CuCl, and the SEM micrograph of this Cu layer is shown in Fig. 2b. Apparently, the electrodeposited Cu layer is very compact and smooth. BMP-DCA RTIL was employed for the Cu electrodeposition because copper halides such as copper chloride (CuCl) have good solubility in BMP-DCA RTIL due to the strong ligand properties of the DCA anions. BMP-TFSA RTIL is also appropriate for Cu electrodeposition; however, the Cu ions, such as Cu(I) ions, must be introduced by anodic dissolution of copper metal because common copper salts such as copper halides are insoluble in this RTIL. For BMI-PF_6 RTIL, CuCl is insoluble and anodic dissolution of copper metal is unfeasible because of the very poor ligand properties of the PF_6^- ions. Additional Cl^- ions (ex. from BMI-Cl) have to be introduced to assist the CuCl dissolution. Electrodeposition of Cu in BMI-PF_6 is feasible but inconvenient.

After the electrodeposition of copper was accomplished at a W wire electrode (Fig. 2b), the Cu layer coated on the W wire electrode was converted to CuI (CuI/W) by employing the same iodination process mentioned in Fig. 2a, and the relevant SEM micrograph is depicted in Fig. 2c. Compared with Fig. 2a, the CuI film at the CuI/W electrode has a very different surface morphology, and the crystallites are smaller and more irregular in shape, but the CuI film has the same good adhesion as the film shown in Fig. 2a. The results shown in Fig. 2 demonstrate the advantages of preparing CuI thin films by Cu anodization in RTILs. For certain practical applications, some type of functional layer may need to be formed on the top of the CuI film. A fine-grained, rather than a rough, surface of CuI is essential for this purpose [1]. Therefore, the inhibitor of crystal formation is necessary. It can be observed that the CuI films formed in this study are compact and fine-grained. Therefore, they are appropriate for the formation of a top layer. In addition, preparation of a compact and smooth Cu coating for use in the formation of CuI thin films is very easy by electrodeposition in BMP-DCA RTIL, unlike in

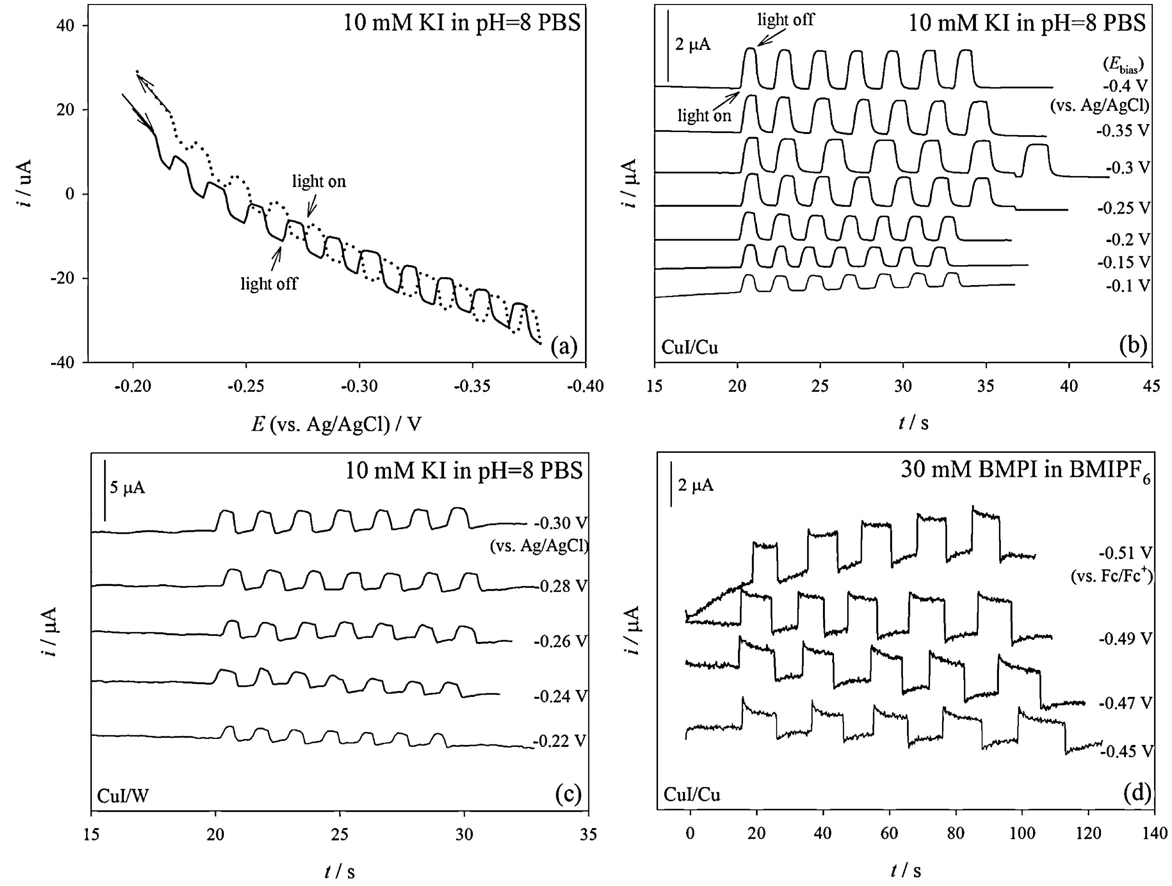

Fig. 5. The photovoltammogram of (a) CuI/Cu and the photochronoamperograms of (b) CuI/Cu, and (c) CuI/W at different E_{bias} in pH 8 PBS containing 10 mM KI. (c) Shows the photochronoamperogram of CuI/Cu in BMI-PF_6 plus 30 mM BMP-I in a glove box.

aqueous solutions, where Cu dendrites are always obtained unless additives such as environmentally harmful thiourea are used.

Although the surface morphologies of the CuI films converted from different Cu substrates were different to a certain degree, no noticeable differences could be found in their X-ray diffraction patterns. Fig. 3 shows that both of the CuI films converted from the different Cu substrates (Cu wire and Cu/W) were crystalline, and four characteristic diffraction signals of CuI were observed. The relative intensities of the diffraction peaks observed for the two CuI films were very similar to those reported in the literature [7]. Aside from the four apparent CuI signals, other signals observed in Fig. 3 are diffraction signals of the substrates, including copper foil and tungsten foil.

To further confirm the formation of the CuI films converted from the different Cu surfaces by iodination in BMI-PF_6 RTIL containing BMP-I, XPS analysis was carried out on the two CuI samples shown in Figs. 3a and b, and the experimental data are shown in the relevant insets. The binding energy (BE) of the Cu_{2p} electron observed for both of the CuI films (CuI/Cu and CuI/W) indicates that the oxidation state of the surface Cu is +1. The BE of the I_{3d} electron provides more solid evidence for CuI formation because its value is nearly identical to the database value for CuI (619 eV) [19].

The CuI film obtained by iodination of a copper wire electrode was carefully scraped off of the electrode and ground with an appropriate amount of KBr crystals to form a transparent disk under high pressure. The UV–vis spectrum of this disk was then acquired to investigate the electron absorption of the obtained CuI film. The characteristics of the spectrum (Fig. 4) are very similar to the literature data. Fig. 4 shows an abrupt absorption near 400 nm (~3.1 eV of the CuI energy gap) and an onset absorption near 420 nm [7]. This behavior is due to the excitation of electrons from the valance band to the conduction band. The experimental data indicate that the CuI film prepared in this study has a similar band gap as that of a regular CuI compound semiconductor. The aforementioned procedure was employed due to the lack of availability of a good reflective UV–vis spectrophotometer. The high background absorption (Fig. 4) was a disadvantage and possibly resulted from the absorption and/or scattering of KBr.

3.3. Photoelectrochemical examination of the obtained CuI films

CuI is a semiconductor demonstrating photoelectrochemical properties under visible radiation. Therefore, it is essential to study the photoelectrochemical properties of the CuI thin films obtained in this study. By modifying a system reported in the literature [7], a 0.1 M pH 8 phosphate buffer solution (PBS) containing 10 mM KI was employed as the electrolyte for studying the photoelectrochemical behavior of the CuI films. Cyclic voltammetry and chronoamperometry were carried out to study the photocurrent produced from illuminating the CuI films. A 50 W halogen light bulb was used as the light source for this study. The light bulb was turned on and off manually. Fig. 5a shows the typical photovoltammogram of a CuI/Cu electrode. The potential was scanned from the initial potential of −0.2 V in the cathodic direction and then reversed at −0.38 V. In order to make the voltammogram more readable, the anodic scan is shown as a dotted curve. The apparent photocurrents were observed with the light on and the light off. Fig. 5a also shows that the two curves (the cathodic and anodic scans) overlap to a significant degree.

In order to study in more detail the dependence of the photocurrent on the applied potential, photochronoamperometry was carried out at a series of potential biases (E_{bias}). Fig. 5b shows the typical photoresponses of the CuI film at the CuI/Cu electrode when different E_{bias} (from −0.10 to −0.40 V vs. Ag/AgCl) were applied. As can be seen, the photocurrents are very stable and increased with a shift of E_{bias} in the cathodic direction. A similar behavior is observed for the CuI film at the CuI/W electrode (Fig. 5c), but the stable photoresponses were observed within a narrower E_{bias} range (from −0.22 to −0.30 V vs. Ag/AgCl). The photoresponse of the CuI/Cu electrode was also studied in BMI-PF_6 RTIL containing 30 mM BMP-I in a glove box (Fig. 5d). A similar behavior as that shown in Fig. 5b was observed although more significant noise was detected (poorer mass transport and conductivity in the IL may be the cause of the noise), and the stable photoresponses were only observed within a very narrow E_{bias} range (from −0.45 to −0.51 V vs. Fc/Fc$^+$). This investigation is the first reported study of the photocurrent of CuI in a RTIL.

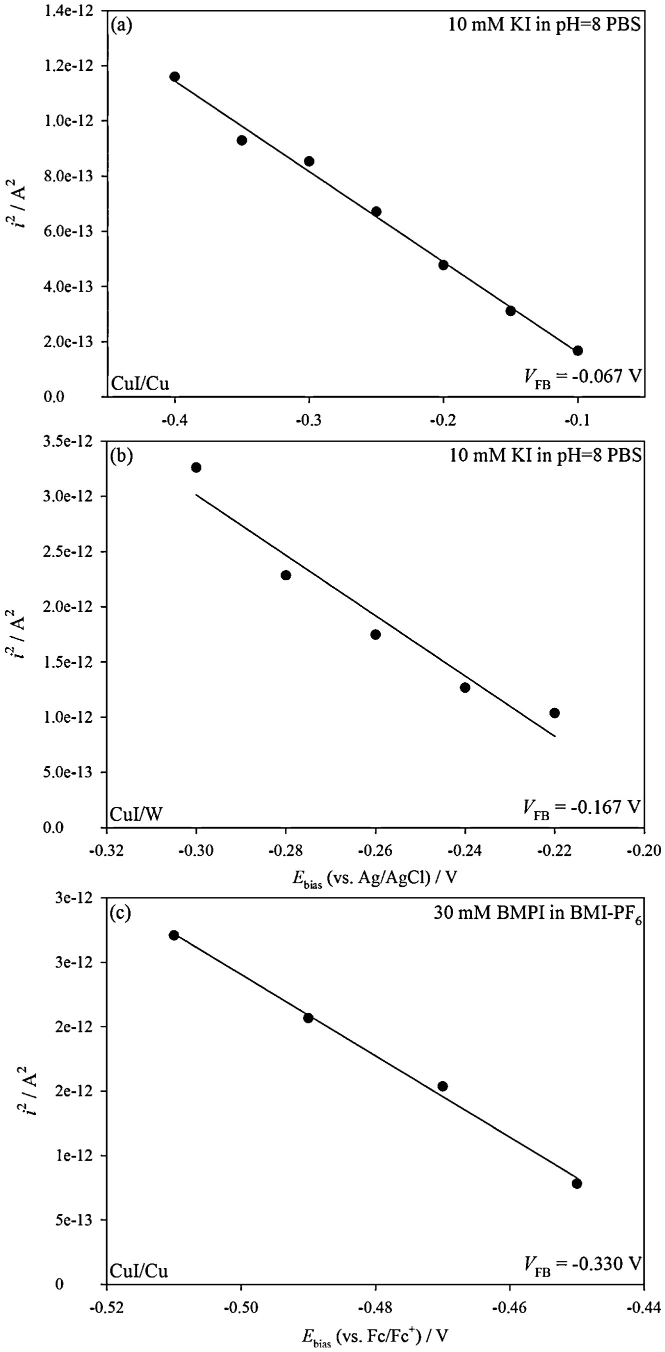

Fig. 6. The dependence of photocurrent square (i^2) on potential bias (E_{bias}).

The square of the measured photocurrent (i) was plotted as a function of the applied E_{bias}, and the plot is shown in Fig. 6. According to the equation [20]:

$$i^2 = \text{constant}(V - V_{\text{FB}}) \quad (1)$$

the flatband potential (V_{FB}; it has the same meaning as the zero charge potential of a metal electrode) of the obtained CuI films can be estimated from the intercept of i^2 on the E_{bias} axis, and the values are indicated in Fig. 6.

4. Conclusions

An electrochemical method was developed for the formation of CuI thin films. This method involves the conversion of Cu to CuI by anodizing surface Cu in the room temperature ionic liquid BMI-PF_6 containing BMP-I. The coordinating strength of the anions of the RTIL is critical for enabling CuI film formation because Cu(I) complex ions instead of CuI film will be produced if the coordinating strength of the anion is too strong. The CuI film obtained by this method had a crystalline structure and exhibited good photoelectrochemical responses. The CuI thin film may have potential uses in photoelectric devices, electrocatalysis, photosensing, and photochemical catalysis. The relevant experiments are underway in our laboratory.

Acknowledgement

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