Optoelectronic Properties of CuI Photoelectrodes

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Supporting Information

ABSTRACT: Detailed mechanistic understanding of the optoelectronic features is a key factor in designing efficient and stable photoelectrodes. In situ spectroelectrochemical methods were employed to scrutinize the effect of trap states on the optical and electronic properties of CuI photoelectrodes and to assess their stability against (photo)electrochemical corrosion. The excitonic band in the absorption spectrum and the Raman spectral features were directly influenced by the applied bias potential. These spectral changes exhibit a good correlation with the alterations observed in the charge-transfer resistance. Interestingly, the population and depopulation of the trap states, which are responsible for the changes in both the optical and electronic properties, occur in a different potential/energy regime. Although cathodic photocorrosion of CuI is thermodynamically favored, this process is kinetically hindered, thus providing good stability in photoelectrochemical operation.

Photocathodic (PEC) methods hold the promise of uniting the functions of solar cells and electrolyzers, thus directly converting sunlight to fuels. At the same time, after almost five decades of research on different semiconductor systems (e.g., metal oxides and chalcogenides), the magic bullet to attack the problem is still to be found. Both new chemical, electrochemical, and new methods are needed to develop photocathodes with enhanced PEC performance. The recent wave of excitement triggered in the solar energy community by lead halide perovskites has generated an interest in employing the same time, chemical, electrochemical, and photoelectrochemical corrosion remains a major issue that needs to be better understood and circumvented.

Notably, the oxide counterpart (Cu2O, cuprous oxide) of CuI is frequently studied as a promising photocathode material for solar cells, or even for photocatalytic CO2 reduction. At the same time, it is prone to photocorrosion, which severely limits its applicability, unless some protection strategy is employed. Some protection strategies are discussed in the literature where spectroelectrochemistry provided valuable insights into the energetics, defect sites, and charge-transfer properties of semiconductors.

For example, the redox transformation of conjugated polymers (organic semiconductors) was investigated by applying the combination of two in situ techniques at the same time, to follow both spectroelectrochemical and conductance changes. As for inorganic semiconductors, the presence of electrons in the accumulation layer of TiO2 was probed through spectroelectrochemistry. The flatband potential of semiconductors can be conveniently estimated from the onset potential of the absorbance change. The difference in spectral response and onset potential can also be used to distinguish the flatband potential and trapping of electrons at the defect sites. Spectroelectrochemical diffuse reflectance spectroscopy is also appropriate to seek information on electron traps and distinguish different chemical species generated during photoexcitation of the semiconductor. As discussed above, the existing literature is oxide- (and especially TiO2) centric. However, there are precedent spectroelectrochemical studies on other nonoxide materials as well (e.g., CdSe, CsPbBr3, CsIn2S3, and Cu:ZnSe/CdSe). Here, we present how the combination of two methods can furnish new insights on the optoelectronic properties of CuI.

UV–visible spectra were recorded for the spin-coated CuI layers before and after annealing at 150 °C for 10 min (Figure 1A). The annealed layers showed sharp features at 407 and 337 nm, which correspond to the excitonic peaks of CuI. The...
bandgap, which was calculated from the Tauc plot derived for a direct allowed transition, gave a value of 3.01 eV (Figure S1), in close agreement with values reported in the literature. SEM images demonstrated that a homogeneous film developed on the surface of the ITO supports (Figure 1B). The coverage, however, was not perfect because small holes formed within the film. The layer thickness was 700–750 nm as determined from side-view SEM images (not shown here).

PEC measurements were performed to probe the photoactivity of the prepared layers under simulated sunlight (Figure 1C) in both argon- and oxygen-saturated 0.1 mol dm$^{-3}$ Bu$_4$NPF$_6$ dichloromethane electrolyte, using a solar simulator as the light source (AM1.5), with an additional UV cutoff filter (<400 nm) operated at 100 mW cm$^{-2}$. The sweep rate was kept at 1 mV s$^{-1}$, while the light-chopping frequency was 0.05 Hz.

In the first set of spectroelectrochemical experiments, we determined the stability window of CuI electrodes. The potential was scanned from 0.0 V with a sweep rate of 5 mV s$^{-1}$ in both cathodic (Figure 2A) and anodic directions (Figure 2B) on two separate layers. Under negative bias, a reduction peak appeared with the onset of $\sim-0.6$ V, related to the Cu(I) $+ e^- \rightarrow$ Cu(0) reaction. In the case of oxidation, the onset potential was measured at $\sim+0.8$ V, corresponding to the reaction 2 CuI $\rightarrow$ 2 Cu(I) $+ I_2 + 2 e^-$. These redox events have a clear effect on the optical features of the CuI film deposited on ITO electrodes (Figure S2).

To visualize the changes in the optical properties occurring under applied electrochemical bias, the first electrochemical reduction and oxidation half cycles were plotted together with the absorbance change at the excitonic peak. The green circle indicates a regime where an abrupt change in the excitonic peak is observable without a Faradaic process.

Further spectroelectrochemical studies were conducted within the boundaries of the stability window of $\sim$0.2 to 0.6 V vs Ag/AgCl (Figure 3A–B). The cathodic current seen inside the stability window (around +0.2 V) in the cyclic voltammogram (Figure 3A) is related to the electron injection into the trap states close to the valence band. When more electrons are present in these shallow trap states, there is a higher probability to form excitons. This process is accompanied by optical changes, as shown in Figure 3B. The absorbance of the excitonic peak was monitored over three cycles, and reversible change was seen in the excitonic peak absorbance (Figure 3C). The constant baseline shift, observed...
at all wavelengths, is attributed to the light-scattering effects arising from possible changes in the morphology. The reversibility in the absorption, however, was visible only in the case of the excitonic peak (Figure S4). More interestingly, the evolution of the excitonic peak in unannealed samples occurs after applying the cathodic bias, as shown in Figure S5.35 In situ Raman spectroelectrochemical experiments were carried out to tie the absorbance changes to alterations in the electronic structure of the CuI layers. During these experiments the applied potential was varied in a nonorderly manner in the range of \(-0.2\) to \(-0.6\) V vs Ag/AgCl. A gradual change was seen in the Raman spectra as a function of the applied potential (Figure 3D). These studies further confirmed the reversibility of charge carrier injection/removal to/from the CuI electrodes. The sharp peak at \(\sim 130\) cm\(^{-1}\) corresponds to the transverse optical (TO) phonon mode of CuI, while the other two bands at \(\sim 167\) and \(\sim 99\) cm\(^{-1}\) show the longitudinal optical (LO) phonon mode and the transverse acoustic (TA) phonon modes, respectively.36,37 When a positive bias was applied, the gradual change in the intensity of the LO and 2TA Raman modes was observed. These changes occurred in the same potential region as the optical changes (between 0.2 and 0.5 V) observed in the previous section. Temperature can have a similar effect on the Raman spectra of CuI as demonstrated in a previous study.36 The spectrum recorded at low temperature was similar to the reduced spectrum in our study, while the one recorded at higher temperature resembled the oxidized one. This change was attributed to the increase in
the disorder, which allows features in the density of states to become Raman active.\textsuperscript{36}

To examine the electrical properties of the CuI electrodes, electrochemical impedance spectroscopy experiments were performed. The charge-transfer resistance changed as a function of the potential, as qualitatively reflected in the shape of the Bode plots in Figure 4A (the equivalent circuit shown in Figure S6 was employed for semiquantitative analysis). At negative potentials, there was a sharp increase in the charge-transfer resistance (Figure 4B). This is caused by the electron injection into the layer, which in turn hinders transfer of majority carriers (holes) to the electrolyte. This change, however, occurred in a different potential region (between −0.10 and 0.15 V) compared to those observed on the UV–vis and Raman spectra.

To determine the flatband potential of CuI, Mott–Schottky analysis was performed at three different frequencies within the stability window (Figure 4C). The determined flatband potential was +0.14 ± 0.03 V, which is close to the onset potential of the photocurrent (Figure 1C). Notably, at potentials more positive than the flatband, the majority charge carriers can reach the surface; therefore, the resistance remains unchanged after this point (Figure 4B).

To accurately determine the band diagram of CuI and position the observed phenomena, Kelvin probe microscopy was performed on the CuI electrodes. The valence band energy was at −5.24 eV, as shown by the corresponding ambient pressure photoelectron spectroscopy (APS) data in Figure S7B. The Fermi level (−5.09 eV, determined from Kelvin probe measurements shown in Figure S7A) lies very close to this energy, which is typical for p-type semiconductors. Using the optical bandgap value (3.01 eV) obtained from the Tauc analysis, the conduction band energy was calculated (−2.23 eV) and the energy band diagram was constructed (Scheme 1).\textsuperscript{31,38,39}

On the basis of the comparison in Scheme 1, several important conclusions can be drawn. Reversible population/depopulation of the trap states occurred around the flatband potential (near the Fermi level). The density of these states in a CuI film is also presented in Scheme 1. The population level of these states dictates the optical and electronic properties of CuI. The deeper traps are primarily responsible for the electronic properties, while the shallow traps dictate the optical absorption at the excitonic peak. We note that these insights are also important for solar cell research where CuI is often employed as a hole-transporting material. Such studies are in progress in our laboratories focusing on perovskite solar cells containing CuI hole-transporter and will be reported soon.

From a PEC stability perspective, if we compare the values of the corrosion potentials to the valence band (VB) and conduction band (CB) positions, one can see that there is a high thermodynamic driving force for the cathodic corrosion (i.e., CB is much more negative compared to the reductive corrosion potential). According to our experimental results, however, CuI is stable as a photocathode, and no decrease in its performance was seen during an 8 h photoelectrolysis (in fact, a slight increase was seen in the photocurrents in Figure S8A because of surface roughening). Furthermore, the optical properties (UV–vis and Raman), XRD pattern (Figure S8B–D), and elemental composition (Table S1) of the electrodes before and after photoelectrolysis were almost identical. This is indeed a surprising observation, considering the similarity to its oxide counterpart (see band position comparison in Scheme S1), which suffers from rapid photocorrosion under similar circumstances.\textsuperscript{15,33} Kinetic factors are major contributors here, which might be explained by solid-state chemistry considerations. Cu has a face-centered cubic (fcc) crystal structure, which is very similar to cubic Cu$_2$O, where Cu atoms arrange in the fcc sublattice. In contrast, the studied CuI has a wurtzite structure, which has a different symmetry. This hypothesis still has to be validated, but we suspect the structural similarity of Cu$_2$O and the corrosion product Cu facilitates the corrosion process, whereas the dissimilar structure in the case of CuI makes the corrosion process kinetically sluggish.

\section*{EXPERIMENTAL SECTION}

Details of the synthetic process are presented in the Supporting Information, but briefly, the synthesis of CuI was carried out in aqueous solution. Copper(II) acetate monohydrate and hydrogen iodide were used as precursors. The copper acetate solution was added dropwise into the dilute hydriodic acid solution under continuous stirring. The white precipitate was separated by vacuum filtration, washed several times with deionized water, and finally dried. The CuI layers were spin-coated from a 0.15 mol dm$^{-3}$ CuI solution in acetonitrile. Immediately after spin-coating, the layers were subjected to two drying/heat treatment steps.

All electrochemical experiments were performed with a Metrohm Autolab PGSTAT302 type potentiostat/galvanostat in a standard three-electrode setup. The ITO/CuI electrodes functioned as the working electrode, a platinum mesh or platinum wire as the counter electrode, and a Ag/AgCl wire as a pseudoreference electrode ($E_{\text{Ag/AgCl}} = +0.36$ V vs Ag/AgCl). All measurements were carried out in a 0.1 mol dm$^{-3}$ Bu$_4$NPF$_6$ in dichloromethane. For the Mott–Schottky analysis, full impedance spectra were recorded at different potential values in the 100 kHz to 0.1 Hz frequency range, using a sinusoidal excitation signal (10 mV RMS amplitude). For photoelectrochemical studies, a Newport LCS-100 type solar simulator was used as the light source (AM1.5), with an additional UV cutoff filter (<400 nm) with a power density of 100 mW cm$^{-2}$. For the spectroelectrochemical experiments, an Agilent 8453 UV–visible diode array spectrophotometer was
used in the range of 300–1100 nm. Scanning electron microscopy (SEM) images were captured using a FEI Helios NanoLab DualBeam instrument. Raman spectroscopic measurements were carried out by a SENTERRA II Compact Raman microscope, using a 532 nm laser excitation wavelength. In situ Raman spectroelectrochemistry was performed using an ECC-Opto-Std electrochemical cell (EL-CELL GmbH) equipped with a sapphire window and a potentiostat/galvanostat (Metrohm Autolab PGSTAT204). The valence band position and the Fermi level of the CuI films were determined by ambient pressure photoelectron spectroscopy and Kelvin probe measurements, using a KP Technology APS04 instrument. Further details about the experimental techniques are presented in the Supporting Information.

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