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Electrochemistry of Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ Crystals

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Abstract: Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ is an ionic crystal with suitable band gap and conductivity for optoelectronic applications. The sensitivity of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal and its derivatives to chemical composition, film-forming process, and even moisture lead to difficulties in evaluating its electronic structure and redox behavior using electrochemical techniques. Nevertheless, full understanding of the electrochemical behavior of the perovskite crystal is certainly beneficial for tuning its redox properties and chemical stability, especially for device fabrication. We show that the band structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ can be successfully evaluated based on electrochemical square wave voltammetry. The energy level of the bottom of the conduction band of the perovskite crystal was determined directly from the onset reduction potential with reference to the onset oxidation potential of ferrocene, and estimated to be -3.56 eV; the top of the valence band, at -5.07 eV, was determined indirectly after taking into consideration the bandgap, because the oxidation current of the iodide ions shields that corresponding to the valence band of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal. The overlap of the oxidation currents from the iodide ions and the valence band of the crystal suggests that there are excess iodide ions in $\text{CH}_3\text{NH}_3\text{PbI}_3$ not involved in the development of the valence band. In addition, the alternating current (AC) impedance spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ indicate that the iodide ions are not completely immobilized. These imply that the defects in the crystal are related to the iodide ions to a large extent. The electrochemistry of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in an organic electrolyte reveals its coupling degradation during the redox processes in square wave and cyclic voltammetry. The degradation reactions result from the reduction of lead ions and oxidation of iodide ions in the perovskite crystal. In electrochemical reduction, along with the reduction that occurs in the conduction band, the lead ions in the crystal are reduced to metallic lead, which introduces a phase change in the crystal, as revealed in cyclic voltammetry; the metallic lead can be re-oxidized electrochemically. In the case of electrochemical oxidation, the iodide ions, as well as the valence band of $\text{CH}_3\text{NH}_3\text{PbI}_3$, lose electrons. The electrochemically generated iodine diffuses into the organic electrolyte gradually, which results in the loss of iodide ions in the crystal. Such loss of iodide ions continues during the cyclic redox reaction. Apparently, the electrochemical investigations on perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ show that the crystal is extremely reactive during the redox process; attention should be paid on controlling the excess iodide ions and the irreversible phase change resulting from the oxidation of lead ions.

Key Words: Perovskite; Solar cell; Electrochemistry; Band gap; Redox reaction

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钙钛矿 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 晶体的电化学

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摘要: 电化学方波伏安及循环伏安测量表明, 钙钛矿 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 晶体在有机电解质中的氧化还原过程伴随着化学降解。该化学降解源于 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 晶体中铅离子的还原以及碘离子的氧化。通过电化学伏安法可以测定晶体的能带。

关键词: 钙钛矿; 太阳能电池; 电化学; 能带; 氧化还原反应

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1 Introduction

Perovskite methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$, MAPbI₃) has shown its potential as one of the most promising candidate materials for the low-cost high-performance solar cells¹⁻³. Over 19% of light-to-electricity conversion efficiency was achieved with halide-mixed MAPbI₃ thin-film photovoltaic devices⁴, while more than 22% conversion efficiency has been reported recently for the solar cells based on formamidinium lead iodide which is chemically inspired by MAPbI₃⁵. However, the fully understanding on the relationship between the chemical structure and the optoelectronic properties of perovskite materials, e.g. MAPbI₃, is still unattained⁶⁻⁸. The electronic/band structure of the perovskite MAPbI₃ is crucial to its light-to-electricity conversion efficiency in solar cells⁹⁻¹⁴. It is revealed that the bottom of the conduction band mainly consists of *p* orbital of Pb^{2+} ions while the top of the valence band contains the contribution of *s* orbital of Pb^{2+} ions and *p* orbital of I^- ions, which results in the band gap of ~1.5 eV (~-3.93 eV for bottom conduction band and ~-5.43 eV for top valence band) for MAPbI₃^{13,15-20}. The organic component CH_3NH_3^+ does not create gap states but stabilize the crystal structure.

However, the chemical degradation and defects of MAPbI₃ will damage the long-term device stability when exposed to moisture and high temperature^{7,21-24}. In addition, the current-voltage hysteresis found in perovskite solar cells is still lack of reasonable explanation²⁵⁻²⁷. The full understanding on the chemistry of solid MAPbI₃ is desired.

In this paper, we report the electrochemical redox behaviors of MAPbI₃ crystal in the nonaqueous electrolyte. The irreversible electrochemical redox reactions and the chemical degradation of MAPbI₃ crystal are revealed, which implies the instability of MAPbI₃ in devices is mostly related to the coupling side reactions of crystal.

2 Experimental

MAPbI₃ is soluble in highly polar solvents, such as dimethylsulphoxide (DMSO), *N,N*-dimethylmethanamide (DMF), and etc. due to its ionicity. Instead, it is insoluble in less

polar and nonpolar organic solvents, e.g. chloroform, dichloromethane, hexane, and etc. The electrochemical measurements was then conducted in degassed dichloromethane with ~0.05 mol·L⁻¹ TBAP (tetrabutylammonium hexafluorophosphate) as the supporting electrolyte reasonably. Glass carbon electrode (ϕ ~1 mm), Pt wire, and Ag wire was employed as the working electrode, the counter electrode, and the quasi-reference electrode (-0.4 V vs Fc^+/Fc in solid state), respectively. MAPbI₃ crystal film on glass carbon electrode was formed at 60 °C by drop-casting with a 1 : 1 molar ratio of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 in DMF solution.

3 Results and discussion

The possible reactions of perovskite occurred in the electrochemical process may include:

the reduction of perovskite crystal, e.g. one cell,

the oxidation of the cell in perovskite crystal,

Besides, the reduction of lead ions and the oxidation of iodide ions in the crystal matrix should also be taken into considerations,

The existence and possible redox reactions of other complex ions from the crystal, such as $[\text{PbI}_6]^{4-}$ found in organic electrolyte solutions^{28,29}, could be excluded because perovskite crystal is solid and insoluble in our experiments. The redox of CH_3NH_3^+ group could be barely observed, because the reduction/oxidation potential will be much larger than that of the above reactions³⁰. The further oxidation of Pb^{2+} ions in crystal matrix is possible, but it should occur out of the electrochemical windows that we set.

Fig. 1a shows the reduction of perovskite crystal (potential scans from 0.0 to -1.5 V) and re-oxidation (potential scans from -1.5 to 0.0 V) of the reduced perovskite crystal in the square wave (SW) voltammetric measurements. The onset potential of the reduction of perovskite crystal is ~-0.84 V. In contrast to one

Fig. 1 Linear SW voltammetric curves of MAPbI₃ on GC electrode in organic electrolyte.

(a) The linear SW potential scans from 0.0 to -1.5 V, then immediately scans back from -1.5 to 0.0 V. (b) The linear SW potential scans from 0.0 to $+1.5$ V at first, then scans back. These two measurements were conducted on two freshly prepared crystal films in order to avoid the involvement of I^0 , Pb^0 , and phase transition on the SW voltammetry.

The amplitude of 25 mV, frequency of 15 Hz, and potential step of 4 mV were set in SW measurements.

broad reduction peak, there are two peaks in the re-oxidation process of the reduced perovskite crystal. Fig. 1b shows the oxidation process of intrinsic perovskite crystal (potential scans from 0.0 to $+1.5$ V). Two oxidation processes are observed in the SW curve, while the reduction of oxidized perovskite crystal (potential scans from $+1.5$ to 0.0 V) shows one peak at $\sim +0.9$ V clearly.

The bottom of conduction band of perovskite crystal can be evaluated from the onset reduction potential with reference to the onset oxidation potential of ferrocene (~ 0.40 V vs Ag wire, which corresponds to the energy level of 4.8 eV in vacuum)³¹. The bottom of conduction band of perovskite crystal is then calculated to be -3.56 eV ($E(\text{conduction band}) = -(4.8 + (-0.84 - 0.40))$ eV). 0.4 eV difference between the bottom conduction band of TiO_2 and MAPbI₃ has been reported¹⁴. Given the bottom conduction band of TiO_2 is -4.0 eV, the bottom conduction band of MAPbI₃ should be -3.6 eV, very close to -3.56 eV from our electrochemical evaluation, which indicates the reliability of our electrochemical evaluation. From the reported band gap of perovskite crystal, 1.51 eV^{11,20}, we can obtain the top of valence band is -0.07 eV ($E(\text{valence band}) = -3.56 \text{ eV} - 1.51 \text{ eV}$) which

derives the onset oxidation potential of perovskite crystal in voltammetry should be $+0.67$ V ($E_{\text{ox}}(\text{vs Ag}) = 5.07 - 4.8 + 0.40$). Apparently, there is only one of the two oxidation peaks in Fig. 1b relates to the electron loss of the valence band of the perovskite crystal, the oxidation peak at $\sim +1.1$ V should be ascribed to the oxidation of MAPbI₃, the reaction (2), while the oxidation with shoulder-like peak from $\sim +0.30$ to $\sim +0.90$ V could be reasonably attributed to the reaction (4), the oxidation of iodide ions, because the onset oxidation potential of the first oxidation process ($\sim +0.30$ V to $\sim +0.90$ V) is too lower than the calculated $+0.67$ V. This conclusion is further confirmed by the cyclic voltammetric (CV) results, vide infra.

In contrast to the clear and interpretable SW voltammograms, typical CV curves of MAPbI₃, shown in Fig. 2, are more

Fig. 2 Cyclic voltammograms of perovskite MAPbI₃ crystal on GC electrode in organic electrolyte.

(a) Two typical successive cycles. The potential scans from 0.0 V to negative at the scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$. (b) After long-time repeated potential scanning at $100 \text{ mV} \cdot \text{s}^{-1}$. (c) the oxidation of perovskite in CV at $100 \text{ mV} \cdot \text{s}^{-1}$, the arrow indicates the current decreases with the potential cycling.

complicated. As the potential scans to negative, the reduction current rises dramatically at ~ -0.67 V, see Fig. 2a, there are current loops in CV curves, indicated by the arrows in the figure, which is a sign of phase transition introduced probably from the break-in of the electrolyte or the conduction change of perovskite crystal film. Along with the potential scan, the cross potential, at which the reduction-current loop forms, shift to negative from ~ -0.55 V in 1st scan to ~ -0.70 V in the 2nd scan. Gradually, the current loop disappears after repeated potential scan, which leads to CV curve given in Fig. 2b.

The oxidation curves shows normal redox behaviors of the crystal, see Fig. 2c, no current loops are observed when the initial potential scans to positive and the electrochemical window is limited within $0.0 \sim +1.5$ V, the oxidation of perovskite crystal shows clear oxidation peak at $\sim +0.70$ V which will surely disappear in the following potential cycles. The gradual decrease of the oxidation peak current at $\sim +0.70$ V in Fig. 2c, shows the unstability of perovskite crystal upon oxidized electrochemically. It is noted that the oxidation reaction with peak at $\sim +0.7$ V and the reduction process with peak at ~ -0.2 V are always observed when the potential scan spans -0.5 to $+0.8$ V (see Fig. 2a). In addition, no reduction peak at ~ -0.2 V appears if the potential scans between 0.0 and -1.5 V. This indicates these two process comes from a redox couple, $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{CH}_3\text{NH}_3\text{PbI}_2^0$ (reaction (4)). The second oxidation with peak at $\sim +1.0$ V comes from the oxidation of the perovskite crystal itself. The oxidation onset potential of the crystal is defined to be $\sim +0.67$ V which is exactly the onset potential of perovskite crystal oxidation derived from SW voltammetry and the band gap of perovskite crystal. The reduction peak at $\sim +0.60$ V should then be assigned to the reduction of the oxidized perovskite crystal reasonably. The reduction of $\text{CH}_3\text{NH}_3\text{I}_2^0$ is suppressed since the limited electrochemical window, the re-oxidation of $\text{CH}_3\text{NH}_3\text{I}_2^0$ is then restrained, which results in the disappearance of the oxidation peak of I^- in $\text{CH}_3\text{NH}_3\text{PbI}_3$, as shown in Fig. 2c.

The polarographic half-wave potential of the reduction of Pb^{2+} in dichloromethane is -0.345 V vs Fc^+/Fc , i.e. -0.745 V vs Ag wire if converted³², which means the reduction of lead ions in crystal to Pb^0 and re-oxidation of the Pb^0 should be involved in the electrochemical measurements³³. The current loops in Fig. 2a and b indicate clearly the phase transition, which suggests that the reduction of lead ions in the crystal, reaction (3). Consequently, such a reduction of lead ions in the crystal will generate excessive unstable iodide ions in the crystal, and vice versa, which could seriously destroy the stoichiometry of perovskite MAPbI_3 .

It is interesting to observe the re-oxidation process of reduced perovskite $(\text{CH}_3\text{NH}_3\text{PbI}_3)^-$ in SW, indicated by the very broad peak at the range from -1.5 to ~ -0.6 V, while the other peak at ~ -0.3 V from $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{CH}_3\text{NH}_3\text{Pb}^0\text{I}_3$ couple is not recorded in the reduction process (potential scans from 0.0 to -1.5 V) in Fig. 1a. The absence of the reduction of lead ions in $\text{CH}_3\text{NH}_3\text{PbI}_3$ and the observable re-oxidation peak of $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{CH}_3\text{NH}_3\text{Pb}^0\text{I}_3$ at ~ -0.3 V also indicate that the

Fig. 3 Nyquist plot (a) and Bode plot (b) of MAPbI_3 crystal, measured at different bias potentials on GC electrode in organic electrolyte.

The amplitude in AC impedance measurements is 2 mV.

reduction of lead ions in MAPbI_3 occurs coupled with the reduction of perovskite MAPbI_3 in SW. It is not fully clear why the phase transition of the crystal is not detected by SW but unavoidable in CV. One of the possible reasons might be that the accumulation of Pb^0 or $\text{CH}_3\text{NH}_3\text{Pb}^0\text{I}_3$ in the crystal could be altered by the applying pattern of the biased potentials in SW.

AC impedance spectra of the perovskite crystal are presented in Fig. 3. The semicircles appear and no diffusion characteristics are observed at higher bias than $+0.2$ V when oxidation of the perovskite crystal occurs as shown in Fig. 3a, which indicates the charge transfer processes are kinetically controlled. It is much clear in Bode plot (Fig. 3b) that there are two time constants at low bias potential, such as 0.0 and $+0.2$ V. At these potentials, there are no electrochemical reactions from the perovskite crystal on the working electrode, both time constants should be attributed to the charging process. As the bias potential increases (e.g. at $+0.4$ V and $+0.6$ V), the oxidation of iodide ions in the crystal, reaction (4), occurs. The only time constant should be correlated with the reaction (4). At high potential, $+0.8$ V, the oxidation of the crystal should be detected. The time constant from 0.1 to 10 Hz is reasonably attributed to the charging from electrolyte on crystal film, while the time constant in the range from 10 Hz to 1 kHz, at 0.0 and $+0.2$ V, which should be from the charging from iodide ions in the crystal lattice on the film. This indicates that iodide ions in the perovskite crystal is not fully immobilized but flexible to some extent or the excess iodide ions exist as the crystal was formed^{25,27,34}.

4 Conclusions

The electrochemistry of perovskite crystal film in organic electrolyte reveals that lead ions and iodide ions in the crystal can be electrochemically reduced or oxidized separately apart from the redox process of the perovskite crystal. Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ is not electrochemically stable. The top of valence band and the bottom of conduction band are derived from the electrochemical measurements to be -5.07 and -3.56 eV.

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