Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells

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Light-energy conversion by photoelectrochemical cells has been extensively studied in the past 50 years using various combinations of inorganic semiconductors and organic sensitizers.1 Dye-sensitized mesoscopic TiO2 films have been established as high-efficiency photoanodes for solar cells.2 As cost-effective devices, dye-sensitized photovoltaic cells suit vacuum-free printing processes for cell fabrication; such processes enable researchers to design thin, flexible plastic cells by low-temperature TiO2 coating technology.3 With a thin photovoltaic film, optical management is an important key for harvesting light while ensuring high efficiency. Organic sensitizers often limit light-harvesting ability because of their low absorption coefficients and narrow absorption bands. To overcome this, researchers have examined quantum dots such as CdS,4a,b CdSe,4c InP,4h and InAs4i for photovoltaic cells in both electrochemical and solid-state structures. Intense band-gap light absorption by these inorganic sensitizers, however, has not allowed high performance in quantum conversion and photovoltaic generation; significant losses in light utilization and/or charge separation are found at the semiconductor−sensitizer interface. We have studied the photovoltaic function of the organic−inorganic lead halide perovskite compounds CH3NH3PbBr3 and CH3NH3PbI3 as visible-light sensitizers in photoelectrochemical cells. In addition to being synthesized from abundant sources (Pb, C, N, and halogen), these perovskite materials have unique optical properties,5 excitonic properties,6 and electrical conductivity.7 In this report, we show a photovoltaic function of the perovskite nanocrystalline particles self-organized on TiO2 as n-type semiconductors. Solar energy was converted with an efficiency of 3.8% on a CH3NH3PbI3-based cell.

Figure 1. (a) Crystal structures of perovskite compounds. (b) SEM image of particles of nanocrystalline CH3NH3PbBr3 deposited on the TiO2 surface. The arrow indicates a particle, and the scale bar shows 10 nm.

Each photodevice was prepared on a fluorine-doped SnO2 transparent conductive glass (FTO, 10 Ω/sq, Nippon Sheet Glass) as a substrate, the surface of which had been pretreated by soaking in a 40 mM TiCl4 aqueous solution at 70 °C for 30 min to form a thin TiO2 buffer layer. A mesoporous film of TiO2 (n-type semiconductor) was prepared on the above-treated FTO by coating with a commercial nanocrystalline TiO2 paste (see the Supporting Information) using a screen printer and sintering at 480 °C for 1 h in air. The resultant TiO2 film had a thickness of 8−12 μm. Nanocrystalline particles of CH3NH3PbX3 (X = Br, I) were deposited on the TiO2 surface by a self-organization process starting with the coating of a precursor solution containing stoichiometric amounts of CH3NH3X and PbX2. CH3NH3Br and CH3NH3I were synthesized from HBr and HI, respectively, by reaction with 40% methylamine in methanol solution followed by recrystallization. Synthesis of CH3NH3PbBr3 or CH3NH3PbI3 on the TiO2 surface was carried out by dropping onto the TiO2 film a 20 wt % precursor solution of CH3NH3Br and PbBr2 in N,N-dimethylformamide; subsequent film formation was done by spin-coating.8 For CH3NH3PbI3, an 8 wt % precursor solution of CH3NH3I and PbI2 in γ-butylrolactone was employed. The liquid precursor film coated on the TiO2 gradually changed color simultaneously with drying, indicating the formation of CH3NH3PbX3 in the solid state. A vivid color change from colorless to yellow occurred for CH3NH3PbBr3 and from yellowish black for CH3NH3PbI3. X-ray diffraction analysis (Rigaku RINT-2500) for CH3NH3PbBr3 and CH3NH3PbI3 prepared on TiO2 showed that both materials have crystalline structures that can be assigned to the perovskite form. CH3NH3PbBr3 gave diffraction peaks at 14.77, 20.97, 29.95, 42.9, and 45.74°, assigned as the (100), (110), (200), (220), and (300) planes, respectively, of a cubic perovskite structure with a lattice constant of 5.9 Å.9 CH3NH3PbI3 gave peaks at 14.00 and 28.36° for the (110) and (220) planes, respectively, of a tetragonal perovskite structure with a = 8.855 Å and c = 12.659 Å.9 Scanning electron microscopy (SEM) observation of the CH3NH3PbBr3-deposited TiO2 showed nanosized particles (2−3 nm) that existed here and there on the TiO2 and/or CH3NH3PbBr3 surface (Figure 1).

A photovoltaic cell was constructed by combining the CH3NH3PbX3-deposited TiO2 electrode (CH3NH3PbX3/TiO2) as the photoelectrode (anode) and a Pt-coated FTO glass as the counter electrode (cathode) with insertion of a 50 μm thick separator film. The gap between the electrodes was filled with an organic electrolyte solution containing lithium halide and halogen as a redox couple; the CH3NH3PbBr3/TiO2-based cell employed an electrolyte consisting of 0.4 M LiBr and 0.04 M Br2 dissolved in acetonitrile, while the CH3NH3PbI3/TiO2-based cell employed 0.15 M LiI and 0.075 M I2 dissolved in methoxyacetoniitrile. A sandwich-type open cell had an effective light-exposure area of 0.238 cm2 with the use of a black mask. Incident photon-to-current quantum conversion efficiency (IPCE) and photocurrent−voltage (I−V) performance were measured on an action spectrum measurement setup (PEC-S20) and...
a solar simulator (PEC-L10, Peccell Technologies), respectively, the latter irradiating simulated sunlight of AM 1.5 and 100 mW/cm² intensity. Light irradiation of the photocells caused generation of anodic photocurrents with amplitudes of 5–11 mA/cm². After optimization of the average TiO₂ thickness for short-circuit photocurrent density (Jₚ), the maximum Jₚ occurred with 8 µm for CH₃NH₃PbBr₃/TiO₂ and 12 µm for CH₃NH₃PbBr₃/TiO₂. Figure 2a compares action spectra of the IPCE for the photocells based on CH₃NH₃PbBr₃/TiO₂ and CH₃NH₃PbI₃/TiO₂. With CH₃NH₃PbBr₃/TiO₂, the photocurrent occurred in the visible wavelength region (λ < 600 nm). The IPCE exhibited a sharp rise at ∼570 nm with saturation at <520 nm, which is characteristic of band-gap absorption. With a maximum of 65%, a plateau of IPCE indicates that incident photons are strongly absorbed by the 8 µm thin film of CH₃NH₃PbBr₃/TiO₂.

The perovskite iodide, CH₃NH₃PbI₃/TiO₂, resulted in a low IPCE (45%) but showed an extended spectral responsivity to λ ≈ 800 nm, reflecting the black color of the electrode. This bimolecular shift by halogen substitution is analogous to that for silver halide ionic crystals. The anodic photocurrent with high IPCE values corroborates that TiO₂ was efficiently sensitized by the nanocrystalline perovskite. Work function analysis by photoelectron spectroscopy of spin-coated polycrystalline films showed valence-band levels of CH₃NH₃PbBr₃ and CH₃NH₃PbI₃ at ∼5.38 and 5.44 eV versus the vacuum level, respectively (see the Supporting Information). Electrochemically, these valence-band levels are considered to be more positive than the oxidation potentials of the corresponding halides in the electrolyte, which, depending on halide concentration, are estimated to be 5.1–5.6 eV for Br₂/Br⁻ and 4.5–5.0 eV for I₂/I⁻. The conduction-band levels calculated from the wavelengths of the optical absorption edges are at ∼3.36 and 4.0 eV for CH₃NH₃PbBr₃ and CH₃NH₃PbI₃, respectively; such values allow electron injection to the TiO₂ conduction band (∼4.0 eV). As for the quantum confinement effect, the IPCE spectra show that it may not dominate the present perovskite system if it partially exists by sensitizing TiO₂ at shorter wavelengths.

Figure 2. (a) IPCE action spectra for photoelectrochemical cells using CH₃NH₃PbBr₃/TiO₂ (solid line) and CH₃NH₃PbI₃/TiO₂ (dashed line). (b) Photocurrent versus voltage characteristics for cells using CH₃NH₃PbBr₃/TiO₂ (solid line) and CH₃NH₃PbI₃/TiO₂ (dashed line) under 100 mW/cm² AM 1.5 irradiation.

Figure 2b and Table 1 show the I–V characteristics of the CH₃NH₃PbBr₃ and CH₃NH₃PbI₃-sensitized photovoltaic cells under exposure to 100 mW/cm² AM 1.5 simulated sunlight. The Jsc value, which reflects the integrated area of the IPCE, was much larger for the CH₃NH₃PbI₃-sensitized cell than for CH₃NH₃PbBr₃ cell, the former yielding Jsc = 11 mA/cm², twice that of the latter. In contrast, the CH₃NH₃PbBr₃-sensitized cell showed a low open-circuit voltage (Voc) of 0.61 V, while the CH₃NH₃PbBr₃-sensitized cell yielded a notably high Voc of 0.96 V. The high Voc of the bromide (CH₃NH₃PbBr₃) is associated with the higher conduction band of the bromide relative to that of the iodide. This implies that the perovskite sensitizer electronically interacts with the surface conduction-band levels of TiO₂ that have distribution between particles. With Ru complex sensitizers and TiO₂, the maximum Voc ever reported is in the range 0.86–0.93 V. We assume that the origin of the high Voc is the bromide employed as a redox partner to couple with the perovskite bromide; the electrochemically more positive potential of bromide compared with iodide expands the range of photovoltage. As a result, however, the highest power conversion efficiency (η) of 3.81% was obtained with the iodide (CH₃NH₃PbI₃) backed by the high IPCE and Jsc. This efficiency is significantly higher than those obtained to date with nonorganic sensitizers and quantum dots. In studies of durability, continuous irradiation caused a photocurrent decay for an open cell exposed to air; this mechanism needs more study to improve the cell lifetime.

Table 1. Photovoltaic Characteristics of Perovskite-Based Cells

<table>
<thead>
<tr>
<th>Perovskite sensitizer on TiO₂</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃NH₃PbBr₃</td>
<td>5.57</td>
<td>0.96</td>
<td>0.59</td>
<td>3.13</td>
</tr>
<tr>
<td>CH₃NH₃PbI₃</td>
<td>11.0</td>
<td>0.61</td>
<td>0.57</td>
<td>3.81</td>
</tr>
</tbody>
</table>

* Measured with an incident area of 0.24 cm² under 100 mW/cm² AM 1.5 simulated sunlight irradiation.

In conclusion, the organolead halide perovskite compounds efficiently sensitize TiO₂ for visible-light conversion in photovoltaic cells. The materials are especially promising for realizing high photovoltages close to 1.0 V. A series of organic–inorganic perovskite materials CH₃NH₃MX₃ (M = Pb, Sn; X = halogen) exhibiting different energy gaps also are targets for optimizing the cell performance.

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Supporting Information Available: Preparation of TiO₂ materials, color of the perovskite compounds, and work function analysis for the perovskite crystals. This material is available free of charge via the Internet at http://pubs.acs.org.

References

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Materials for TiO₂ coating:

Preparation of a mesoporous film of TiO₂ (n-type semiconductor) on the surface of a TiCl₄-treated FTO substrate consisted of screen printing of a commercial nanocrystalline TiO₂ paste and subsequent sintering of a dried film at 480°C for 1 hour. Two kinds of commercial nanocrystalline TiO₂ pastes were used for the screen printing. PST-18NR supplied from JGC Catalysts & Chemicals Ltd, Kanagawa, Japan was used to prepare a 12 µm-thick TiO₂ film for fabrication of a CH₃NH₃PbBr₃/TiO₂ electrode. Solaronix Ti-Nanoxide T/SP, Switzerland was used to prepare an 8 µm-thick TiO₂ film for fabrication of a CH₃NH₃PbI₃/TiO₂ electrode. The thinner TiO₂ film was employed on the CH₃NH₃PbI₃/TiO₂ electrode so that the subsequent deposition of CH₃NH₃PbI₃ by way of casting an iodide-based liquid precursor solution requires a thin film to complete the absorption of the precursor solution.

Appearance of the perovskite sensitizers in the form of a grained power.

A powder of CH₃NH₃PbBr₃, optically absorbing in the visible region up to 520 nm, exhibits a vivid yellow color. A powder of CH₃NH₃PbI₃, optically almost entirely absorbing the visible light up to 800 nm, exhibits a black color.

Results of work function analysis by photoelectron spectroscopy for the spin-coated polycrystalline films of the two perovskites: