J|A|C|S COMMUNICATIONS

Published on Web 04/14/2009

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 TiO_2 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 TiO_2 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−e] PbS,[4f,g] InP,[4h] and InAs[4i] 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 $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$ 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 TiO_2 as n-type semiconductors. Solar energy was converted with an efficiency of 3.8% on a $CH_3NH_3PbI_3$-based cell, while a high photovoltage of 0.96 V was obtained with a $CH_3NH_3PbBr_3$-based cell.

Each photoelectrode was prepared on a fluorine-doped SnO_2 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 $TiCl_4$ aqueous solution at 70 °C for 30 min to form a thin TiO_2 buffer layer. A mesoporous film of TiO_2 (n-type semiconductor) was prepared on the above-treated FTO by coating with a commercial nanocrystalline TiO_2 paste (see the Supporting Information) using a screen printer and sintering at 480 °C for 1 h in air. The resultant TiO_2 film had a thickness of 8−12 μm. Nanocrystalline particles of $CH_3NH_3PbX_3$ (X = Br, I) were deposited on the TiO_2 surface by a self-organization process starting with the coating of a precursor solution containing stoichiometric amounts of CH_3NH_3X and PbX_2. CH_3NH_3Br and CH_3NH_3I were synthesized from HBr and HI, respectively, by reaction with 40% methylamine in methanol solution followed by recrystallization. Synthesis of $CH_3NH_3PbBr_3$ on the TiO_2 surface was carried out by dropping onto the TiO_2 film a 20 wt % precursor solution of CH_3NH_3Br and $PbBr_2$ in *N*,*N*-dimethylformamide; subsequent film formation was done by spin-coating.[8] For $CH_3NH_3PbI_3$, an 8 wt % precursor solution of CH_3NH_3I and PbI_2 in γ-butyrolactone was employed. The liquid precursor film coated on the TiO_2 gradually changed color simultaneously with drying, indicating the formation of $CH_3NH_3PbX_3$ in the solid state. A vivid color change from colorless to yellow occurred for $CH_3NH_3PbBr_3$ and from yellowish to black for $CH_3NH_3PbI_3$. X-ray diffraction analysis (Rigaku RINT-2500) for $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$ prepared on TiO_2 showed that both materials have crystalline structures that can be assigned to the perovskite form. $CH_3NH_3PbBr_3$ 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] $CH_3NH_3PbI_3$ 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 $CH_3NH_3PbBr_3$-deposited TiO_2 showed nanosized particles (2−3 nm) that existed here and there on the TiO_2 and/or $CH_3NH_3PbBr_3$ surface (Figure 1).

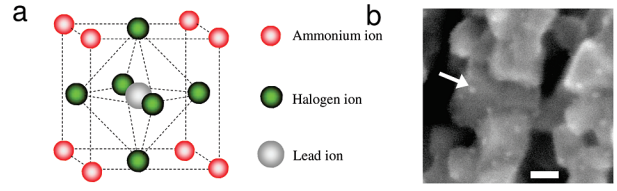

Figure 1. (a) Crystal structures of perovskite compounds. (b) SEM image of particles of nanocrystalline $CH_3NH_3PbBr_3$ deposited on the TiO_2 surface. The arrow indicates a particle, and the scale bar shows 10 nm.

A photovoltaic cell was constructed by combining the $CH_3NH_3PbX_3$-deposited TiO_2 electrode ($CH_3NH_3PbX_3/TiO_2$) 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 $CH_3NH_3PbBr_3/TiO_2$-based cell employed an electrolyte consisting of 0.4 M LiBr and 0.04 M Br_2 dissolved in acetonitrile, while the $CH_3NH_3PbI_3/TiO_2$-based cell employed 0.15 M LiI and 0.075 M I_2 dissolved in methoxyacetonitrile. A sandwich-type open cell had an effective light-exposure area of 0.238 cm^2 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

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10.1021/ja809598r CCC: $40.75

a solar simulator (PEC-L10, Peccell Technologies), respectively, the latter irradiating simulated sunlight of AM 1.5 and 100 mW/cm^2 intensity.

Light irradiation of the photocells caused generation of anodic photocurrents with amplitudes of 5−11 mA/cm^2. After optimization of the average TiO_2 thickness for short-circuit photocurrent density (J_{sc}), the maximum J_{sc} occurred with 8 μm for $CH_3NH_3PbI_3/TiO_2$ and 12 μm for $CH_3NH_3PbBr_3/TiO_2$. Figure 2a compares action spectra of the IPCE for the photocells based on $CH_3NH_3PbBr_3/TiO_2$ and $CH_3NH_3PbI_3/TiO_2$. With $CH_3NH_3PbBr_3/TiO_2$, 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 $CH_3NH_3PbBr_3/TiO_2$. The perovskite iodide, $CH_3NH_3PbI_3/TiO_2$, resulted in a low IPCE (45%) but showed an extended spectral responsivity to λ = 800 nm, reflecting the black color of the electrode. This bathochromic shift by halogen substitution[6] is analogous to that for silver halide ionic crystals. The anodic photocurrent with high IPCE values corroborates that TiO_2 was efficiently sensitized by the nanocrystalline perovskite. Work function analysis by photoelectron spectroscopy of spin-coated polycrystalline films showed valence-band levels of $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$ 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 Br_2/Br^- and 4.5−5.0 eV for I_2/I^-. The conduction-band levels calculated from the wavelengths of the optical absorption edges are at ~3.36 and 4.0 eV for $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$, respectively; such values allow electron injection to the TiO_2 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 TiO_2 at shorter wavelengths.

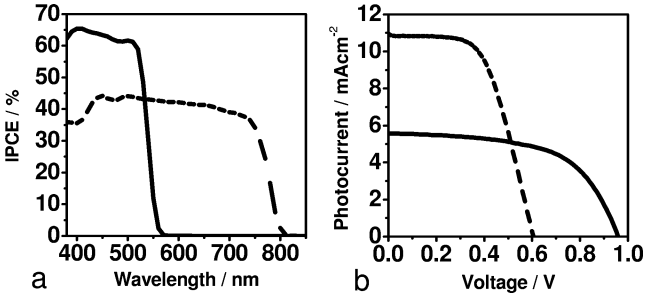

Figure 2. (a) IPCE action spectra for photoelectrochemical cells using $CH_3NH_3PbBr_3/TiO_2$ (solid line) and $CH_3NH_3PbI_3/TiO_2$ (dashed line). (b) Photocurrent−voltage characteristics for cells using $CH_3NH_3PbBr_3/TiO_2$ (solid line) and $CH_3NH_3PbI_3/TiO_2$ (dashed line) under 100 mW cm^{-2} AM 1.5 irradiation.

Figure 2b and Table 1 show the $I-V$ characteristics of the $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$-sensitized photovoltaic cells under exposure to 100 mW cm^{-2} AM 1.5 simulated sunlight. The J_{sc} value, which reflects the integrated area of the IPCE, was much larger for the $CH_3NH_3PbI_3$-sensitized cell than for $CH_3NH_3PbBr_3$ cell, the former yielding J_{sc} = 11 mA/cm^2, twice that of the latter. In contrast, the $CH_3NH_3PbI_3$-sensitized cell showed a low open-circuit voltage (V_{oc}) of 0.61 V, while the $CH_3NH_3PbBr_3$-sensitized cell yielded a notably high V_{oc} of 0.96 V. The high V_{oc} of the bromide ($CH_3NH_3PbBr_3$) 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 TiO_2 that have distribution between particles. With Ru complex sensitizers and TiO_2, the maximal V_{oc} ever reported is in the range 0.86−0.93 V.[10] We assume that the origin of the high V_{oc} 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 ($CH_3NH_3PbI_3$) backed by the high IPCE and J_{sc}. This efficiency is significantly higher than those obtained to date with nonorganic sensitizers and quantum dots.[4a−i] 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[a]

perovskite sensitizer on TiO_2	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
$CH_3NH_3PbBr_3$	5.57	0.96	0.59	3.13
$CH_3NH_3PbI_3$	11.0	0.61	0.57	3.81

[a] Measured with an effective incident area of 0.24 cm^2 under 100 mW/cm^2 AM 1.5 simulated sunlight irradiation.

In conclusion, the organolead halide perovskite compounds efficiently sensitize TiO_2 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 $CH_3NH_3MX_3$ (M = Pb, Sn; X = halogen) exhibiting different energy gaps[5] are also targets for optimizing the cell performance.

Acknowledgment. This work was supported by a Grant-in-Aid for Science from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. We thank Professor H. Segawa of The University of Tokyo for work function measurements.

Supporting Information Available: Preparation of TiO_2 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.

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JA809598R