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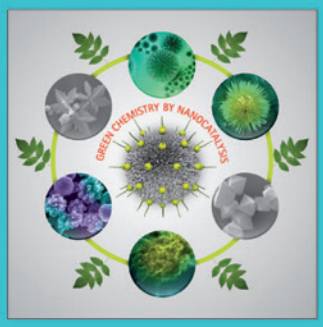

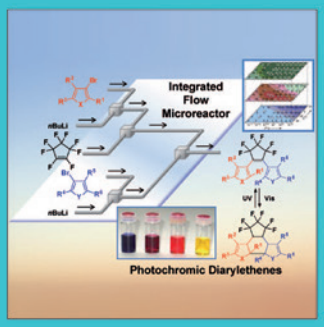

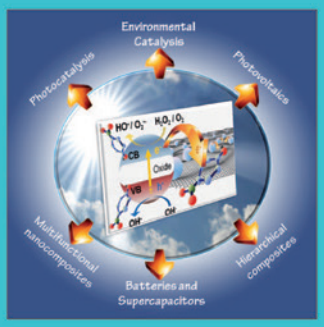

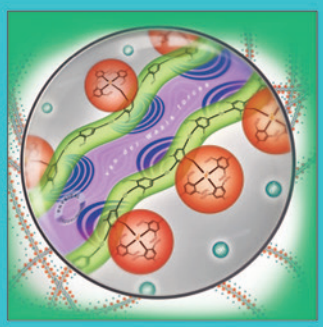

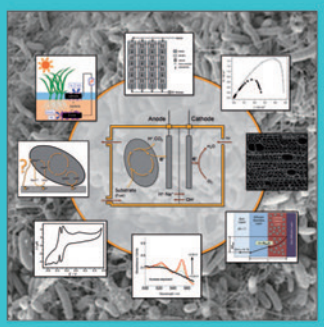

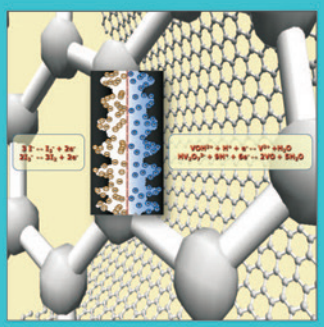

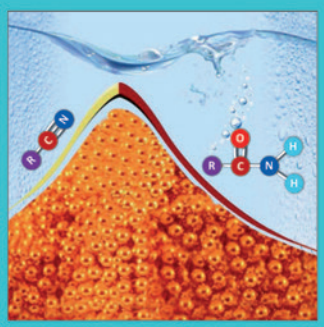

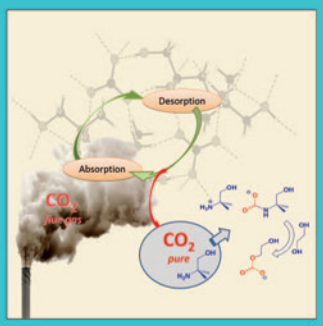

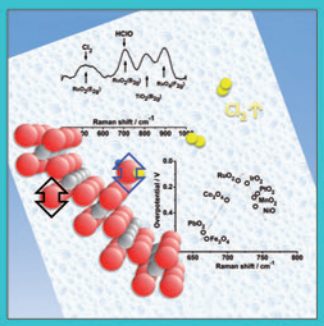

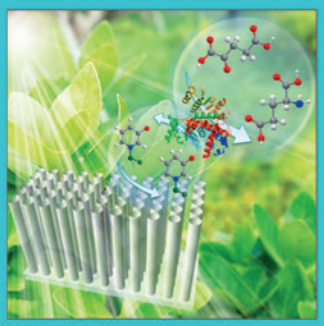

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Solar Water Splitting Utilizing a SiC Photocathode, a $BiVO_4$ Photoanode, and a Perovskite Solar Cell

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We have successfully demonstrated solar water splitting using a newly fabricated photoelectrochemical system with a Pt-loaded SiC photocathode, a CoO_x-loaded $BiVO_4$ photoanode, and a perovskite solar cell. Detection of the evolved H_2 and O_2 with a 100% Faradaic efficiency indicates that the observed photocurrent was used for water splitting. The solar-to-hydrogen (STH) efficiency was 0.55% under no additional bias conditions.

Photoelectrochemical water splitting is an attractive reaction to convert solar energy to chemical energy, the so-called artificial photosynthesis. In a photoelectrode system, electric bias can be applied between a photoanode and a photocathode. Moreover, H_2 is obtained separately from O_2 in the photoelectrode system. There are many visible-light-driven photocathodes such as Cu^I-containing metal sulfides[1–6] and selenides,[7,8] Rh-doped $SrTiO_3$,[9] $CaFe_2O_4$,[10] and SiC;[11–13] and photoanodes such as WO_3,[14–16] $BiVO_4$,[17–24] Fe_2O_3,[25–27] $SnNb_2O_6$,[28] TaON,[29] Ta_3N_5,[30–33] $LaTiO_2N$,[34,35] $BaTaO_2N$,[36,37] and $SrNbO_2N$.[38,39]

Herein, we focused on SiC as a photocathode and $BiVO_4$ as a photoanode. To construct a photoelectrode system; the photocurrent density, onset potential of the photocurrent, and stability are important factors. Cu^I-containing metal sulfides and selenides give excellent cathodic photocurrents, although their onset potentials are not very positive.[1–8] Moreover, the chemical instability in water of metal sulfides and selenides still remains an issue.[2,6,7] Chemically stable metal oxides of Rh-doped $SrTiO_3$ and $CaFe_2O_4$ possess largely positive onset potentials, whereas the photocurrents are low.[9,10] From this point of view, the SiC with relatively positive onset potential (1.15 V vs. RHE), high photocurrent, and high stability is a suitable candidate as a photocathode in the photoelectrochemical water splitting system.[13] Regarding the photoanode candidate, $BiVO_4$ shows the most negative onset potential and high photocurrent under simulated sunlight irradiation.

To achieve high solar energy conversion efficiency, the use of a wide range of sunlight, especially visible light, is important. A weak point of the SiC and $BiVO_4$ is the relatively wide band gap of 2.4–2.5 eV (about 500 nm) as visible-light-responsive materials. Because transparent SiC and $BiVO_4$ photoelectrodes can be prepared,[12,20] we focus on their combination with a perovskite solar cell to overcome this issue.[40,41] In more detail, the perovskite solar cell can absorb transmitted light through the transparent SiC and/or $BiVO_4$ photoelectrodes, because it can utilize visible light up to about 800 nm. Moreover, the photovoltage of about 1.1 V can be used for the photoelectrochemical system to assist water splitting. Actually, there are some reports about the combined system of a perovskite solar cell with a $BiVO_4$ photoelectrode for water oxidation to

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O_2.[42–45] In all reports, Pt was used as a cathode for water reduction to H_2. Ideally, a photoelectrode should also be used for the cathode in the photoelectrochemical system. Here, we demonstrated photoelectrochemical solar water splitting using a SiC electrode as a photocathode. The SiC photocathode was combined with a $BiVO_4$ photoanode to split water without any external bias. A perovskite solar cell was also employed to utilize transmitted light through SiC and/or $BiVO_4$ photoelectrodes and to supply electric assistance for boosting water splitting.

A Pt-loaded SiC (Pt/SiC) photoelectrode gave excellent cathodic photocurrents in both aqueous phosphate (pH 6.8) and borate (pH 9.1) buffer solutions under simulated sunlight irradiation, as shown in Figure 1a. The onset potential versus reversible hydrogen electrode (RHE) and photocurrent density in the phosphate solution (pH 6.8) were almost the same as those in the borate buffer solution (pH 9.1). Thus, we have confirmed that the relative position between the band levels of SiC and the water redox potentials does not change depending on the pH, as previously reported.[11] The onset potential for the cathodic photocurrent was 1.2 V versus RHE, which is in agreement with the reported value of 1.15 V versus RHE.[13] This quite positive onset potential is favorable for fabricating a two-electrode photoelectrochemical cell for water splitting. An onset potential greater than 1.23 V versus RHE is the thermodynamic requirement to reduce water to H_2 without assistance of external bias for a photocathode material. In other words, only a small assistance is necessary for water splitting using the Pt/SiC photoelectrode. From this point of view, the photovoltage of about 1.1 V of a $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite solar cell is large enough.[46] Moreover, the absorption edges of SiC and the $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite solar cell were 500 and 800 nm, respectively (Figure S1 in the Supporting Information). Thus, it is expected that the solar cell can efficiently utilize the transmitted light in the range of 500–800 nm through the Pt/SiC photoelectrode. Actually, the perovskite solar cell showed a photovoltage of about 1.1 V, as shown in Figure 1b, even under irradiation of simulated sunlight through the Pt/SiC photoelectrode.

A two-electrode photoelectrochemical cell was constructed using the Pt/SiC photocathode and a counter electrode. Figure 2 shows the observed photocurrents under applied bias

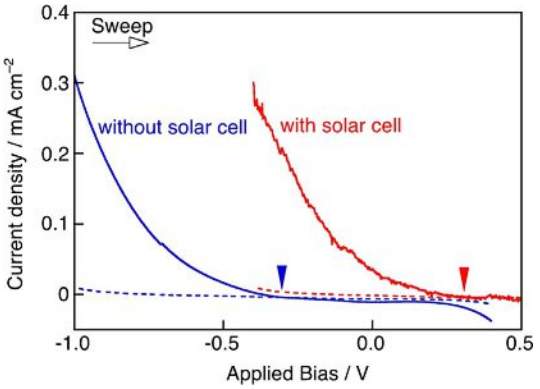

Figure 2. Measured current using a two-electrode system with a Pt/SiC photocathode and an oxygen-evolving anode in the presence and absence of a $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite solar cell. The solar cell was irradiated with transmitted light through the Pt/SiC photoelectrode. Solid and dashed lines represent the current under illumination and in the dark, respectively. The triangles indicate onset bias of photocurrents. Light source: solar simulator (AM 1.5G); electrolyte: aqueous borate buffer solution (pH 9.1).

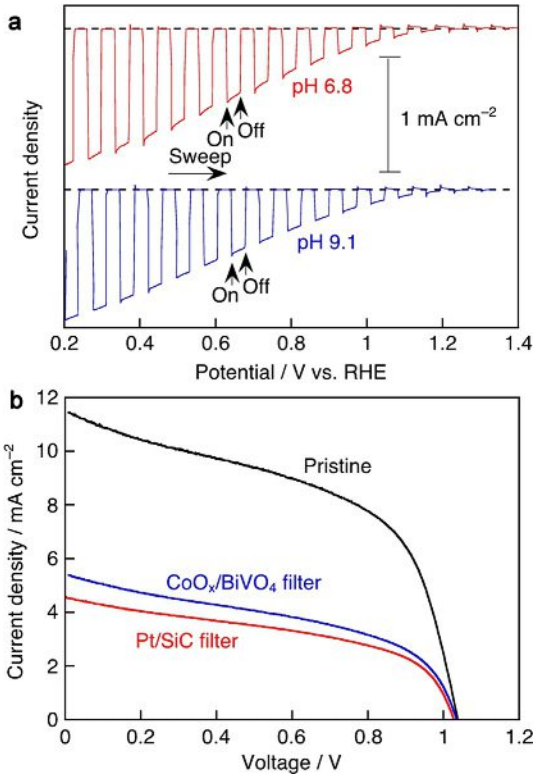

Figure 1. a) Current–potential curves of a Pt-loaded SiC photoelectrode in phosphate (pH 6.8) or borate (pH 9.1) buffer aqueous solutions under simulated sunlight irradiation. b) Current–voltage curves of a $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite solar cell under simulated sunlight irradiation with and without Pt/SiC or $CoO_x/BiVO_4$ filters. Light source: solar simulator (AM 1.5G).

in the presence and absence of a $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite solar cell. In the absence of the solar cell, a photocurrent was not observed under no-bias conditions, as expected from Figure 1a. When a negative bias smaller than −0.3 V was applied to the Pt/SiC photocathode, a photocurrent was generated. When the $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite solar cell was used, the solar cell was irradiated with transmitted light through the Pt/SiC photocathode. Upon using the solar cell, the onset bias drastically shifted toward positive from −0.3 to +0.3 V. The photoelectrochemical cell with the solar cell showed a photocurrent under no additional bias conditions, giving a solar-to-hydrogen (STH) efficiency of 0.04% calculated from the photocurrent.

To improve the water splitting efficiency, the oxygen-evolving anode was replaced with a CoO_x-loaded $BiVO_4$ doped with Mo ($CoO_x/BiVO_4$:Mo) photoanode, as depicted in Figure 3a. The $CoO_x/BiVO_4$:Mo showed anodic photocurrents at

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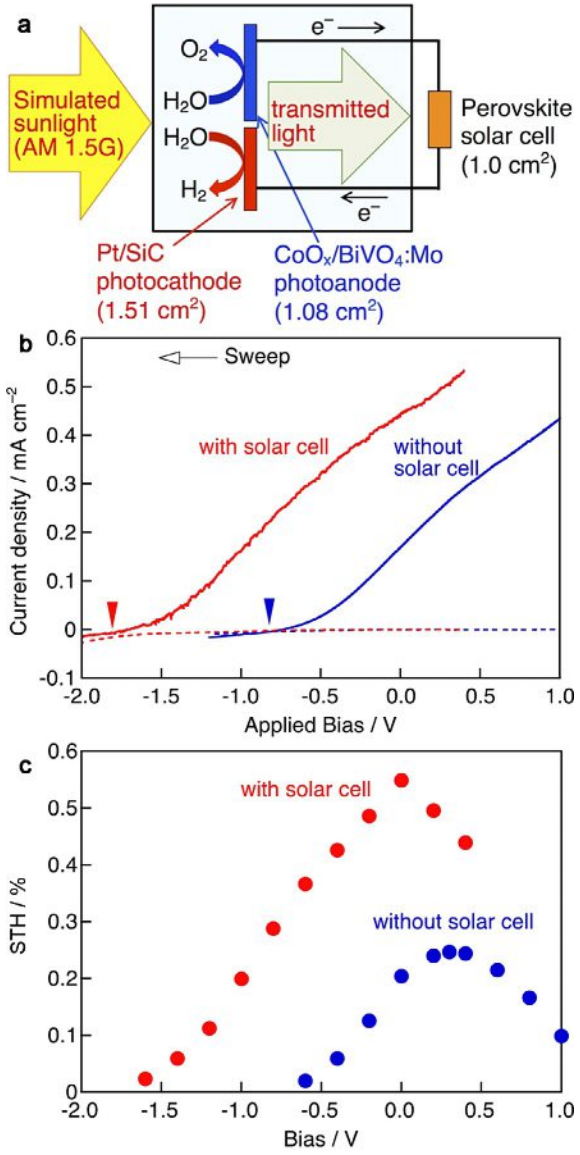

Figure 3. a) Layout of a two-electrode system with a Pt/SiC photocathode and a CoO_x/$BiVO_4$:Mo photoanode. b) Measured currents and c) STH efficiencies using a two-electrode system with a Pt/SiC photocathode and a CoO_x/$BiVO_4$:Mo photoanode in the presence and absence of a $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite solar cell. Solid and dashed lines represent the current under illumination and in the dark, respectively. The triangles indicate onset bias of photocurrents. The sum of the areas of the SiC photocathode and $BiVO_4$ photoanode (2.59 cm^2) was used for the calculation. Light source: solar simulator (AM 1.5G); electrolyte: aqueous borate buffer solution (pH 9.1).

potentials higher than 0.3 V versus RHE,[47] giving an overlapped range between potentials for the anodic photocurrent of the CoO_x/$BiVO_4$:Mo and the cathodic photocurrent of the Pt/SiC (Figure S2). Accordingly, the two-electrode photoelectrochemical cell with the Pt/SiC photocathode and the CoO_x/$BiVO_4$:Mo photoanode showed a clear photocurrent without assistance of external bias, giving a STH efficiency of 0.20% calculated from the photocurrent (Figure 3b,c). The open circuit voltage was 0.8 V, which corresponded well to the width of the overlapped potential range (Figure S2). When the solar cell was incorporated behind the Pt/SiC and CoO_x/$BiVO_4$:Mo photoelectrodes, the open circuit voltage became 1.8 V owing to the assistance of the photovoltage (1.1 V). The STH efficiency was dramatically improved from 0.04% (Figure 2) to 0.55% (Figure 3c) under no additional bias conditions by employing the CoO_x/$BiVO_4$:Mo photoanode.

To test the stability and the Faradaic efficiency of the system, the time dependence of the photocurrent was also measured under no additional bias conditions, as shown in Figure 4. The evolved gases were analyzed using GC every

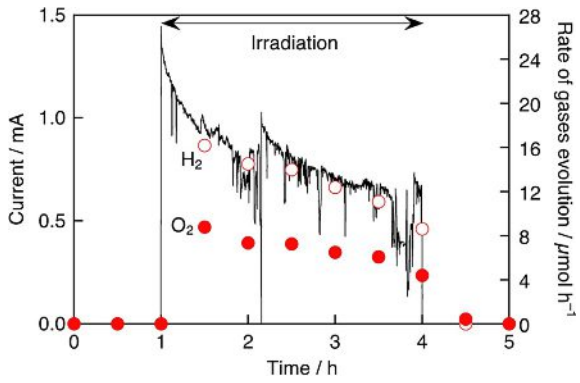

Figure 4. Photoelectrochemical H_2 and O_2 evolution using a two-electrode system consisting of a Pt/SiC photocathode (1.51 cm^2) and a CoO_x/$BiVO_4$:Mo photoanode (1.08 cm^2) with a $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite solar cell. The sum of the areas of the SiC photocathode and $BiVO_4$ photoanode (2.59 cm^2) was used for the calculation. Light source: solar simulator (AM 1.5G); electrolyte: aqueous borate buffer solution (pH 9.1). Layout of the system is the same as Figure 3a.

30 min. After a decrease in the photocurrent during the first 30 min from the start of photoirradiation, the decreasing rate became relatively slow for at least 2.5 h. The fluctuating photocurrent is probably owed to the solar cell, because such unsteady photocurrent was not observed in the absence of the solar cell (Figure S3). Moreover, stoichiometric H_2 and O_2 evolved under simulated sunlight irradiation. The actual rates of gas evolution matched with the theoretical rates calculated from the photocurrent measured. The almost 100% Faradaic efficiency indicates that the photocurrent was used for water splitting.

In conclusion, a Pt/SiC photoelectrode was successfully used as photocathode in a photoelectrochemical cell containing a CoO_x/$BiVO_4$:Mo photoanode. Although the Pt/SiC photoelectrode cannot reduce water to H_2 without assistance of an external bias, photoelectrochemical water splitting under simulated sunlight (AM 1.5G) irradiation without assistance of an external bias was achieved upon combination with the CoO_x/$BiVO_4$:Mo photoanode. The photocurrent was further improved by incorporating a $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite solar cell that efficiently utilized the transmitted light through the Pt/SiC or CoO_x/$BiVO_4$:Mo photoelectrodes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: bismuth vanadate · photocatalysis · silicon carbide · sustainable chemistry · water splitting

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