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ペロブスカイト接合面におけるエキシトンの電荷分離

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Charge Separation of Excitons on the Heterojunction of a Perovskite Thin Film

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【Abstract】Transient luminescence from the photoelectric conversion electrode of the perovskite solar cell was investigated by time resolved dispersed fluorescence spectroscopy. A TiO_2 compact layer c-TiO_2 was deposited by aerosol spray pyrolysis on a cleaned transparent conductive glass FTO. The dimethylformamide solution of PbI_2 was dropped on the c-TiO_2 film followed by spin coating. The substrate was dipped in a 2-propanol solution of CH_3NH_3I, resulting in change into $CH_3NH_3PbI_3$ crystal. Three different materials were interfaced to the perovskite by spin coating: Poly(methyl methacrylate), phenyl-C_{61}-butyricacid methyl ester (PCBM, the electron-transporting material), or spiro-OMeTAD, the hole-transporting material. We performed time-resolved single photon counting for observing luminescence at ~ 800 nm from the excitons produced by 470 nm laser irradiation. The results suggest that the excitons generated in the perovskite layer have sufficient diffusion length to reach the interface where the excitons are quenched either by the electron- or hole-transporting materials.

【概要】光電変換効率の急速な増加に伴い、ペロブスカイト太陽電池の実用化に向けた開発研究が各所で進められている[1]。本研究ではヨウ化鉛ペロブスカイト中のエキシトンの拡散長およびその寿命を測定する目的で、エキシトンからの光ルミネッセンスを時間分解分光法によって観測した。試料は石英基板、緻密酸化チタン薄膜、ペロブスカイト結晶、電荷輸送物質の 4 層構造を持つ。電荷輸送物質として、電子輸送体のスピロ化合物またはホール輸送体の PCBM を用いると、800 nm 付近の発光の寿命が 1 ns 程度まで減少した。この結果から、平面ヘテロ接合面でエキシトンが電子とホールに分離すると予想された。

【Introduction】

Because of the rapid increase in their photovoltaic conversion efficiencies, a number of groups are hastening research and development on perovskite solar cells [1]. It has been accepted that the mesoporous TiO_2 layer is not essential for high-efficiency solar cells, since the carrier lifetime and diffusion length of lead halide perovskite are expected to be long enough to realize charge separation at the heterojunction. In the present study, transient luminescence from the photoelectric conversion electrode of the perovskite solar cell was investigated by time resolved dispersed fluorescence spectroscopy to determine the diffusion lengths and lifetimes of lead halide perovskite.

【Experimental methods】

Transparent conductive glass (FTO) substrates were cleaned by ultrasonication in deionized water and ethanol. A TiO_2 compact layer c-TiO_2 was deposited on FTO by aerosol spray

pyrolysis at 500°C using 2-propanol solution of titanium diisopropoxide bis(acetylacetonate), TPA.

For the cell fabrication a mesoporous TiO_2 layer containing 15- and 25-nm-sized particles was deposited by spin coating of a TiO_2 paste diluted in ethanol. This TiO_2 layer was subjected to calcination at 500°C. For luminescence spectroscopy deposition of the mesoporous TiO_2 layer was omitted.

The dimethylformamide solution of PbI_2 was dropped on the TiO_2 film followed by spin coating at 6500 rpm. After drying at 70°C for 30 min. we dipped the substrate in a 2-propanol solution of CH_3NH_3I to synthesize $CH_3NH_3PbI_3$. Three different materials were interfaced to the perovskite by spin coating chlorobenzene solution of (1) poly(methyl methacrylate), PMMA, (2) phenyl-C_{61}-butyricacid methyl ester, PCBM, or (3) spiro-OMeTAD, that is the hole-transporting material.

Part of a TCO[*1] was protected by a masking polyimide sheet
(Reserved for an anode contact area)
↓
Aerosol spray-pyrolysis of TPA[*2] on a hot TCO surface
↓ Remove the masking and Sintering at 500°C
Spin coating of TiO_2 paste[*3] diluted in ethanol at 1000 rpm
↓ Sintering at 500°C
Mesoporous TiO_2 film was infiltrated with PbI_2[*4] by spin coating
↓ Annealing at 70°C for 30 min.
TCO glass was dipped in a CH_3NH_3I solution[*5]
↓ Rinsed with 2-propanol and dried
HTM[*6] was deposited by spin coating at 4000 rpm
↓
Gold was deposited by vacuum evaporation on the top of the cell to form the back contact (cathode)
↓
Remove the masking and give a solder as the anode contact

Scheme 1. Fabrication process of perovskite solar cells.

We performed time-resolved single photon counting for studying luminescence from exciton generated in the perovskite layer. A 470 nm laser beam with an 86 ps pulse width was impinged on a photovoltaic electrode at 45 MHz repetition rate. Luminescence was dispersed by a monochromator and detected with a streak camera synchronized with the laser. The photon counts were accumulated as a function of the luminescence wavelength and delay time after photoexcitation. The fluorescence decay curve was obtained by integrating the counts over the wavelength range of from 780 to 820 nm.

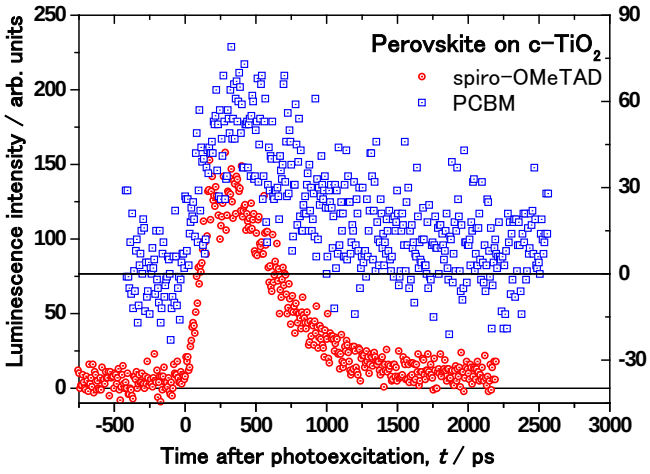

Fig. 1. Time-resolved photoluminescence decay of the perovskite on compact TiO_2 layer interfaced with spiro-OMeTAD and PCBM.

【Results and Discussion】

Fig. 1 shows the decay curves for the photoemission from perovskite on c-TiO_2 covered with PCBM (upper) and spiro-OMeTAD (lower). In the case of the perovskite covered with PMMA, laser impinging the sample gave rise to a rapid increase in the luminescence intensity but it leveled off and no transient decay has been found until at least 5 ns. These results suggest that the excitons generated in perovskite have sufficient diffusion length to reach the interface where they are quenched either by electron- or hole-transporting materials.

【Reference】

[1] J. Burschka *et al*. *Nature* **499**, 316-319 (2013).