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Supporting Information for

Saving electric energy by integrating a photoelectrode into a Li-ion battery

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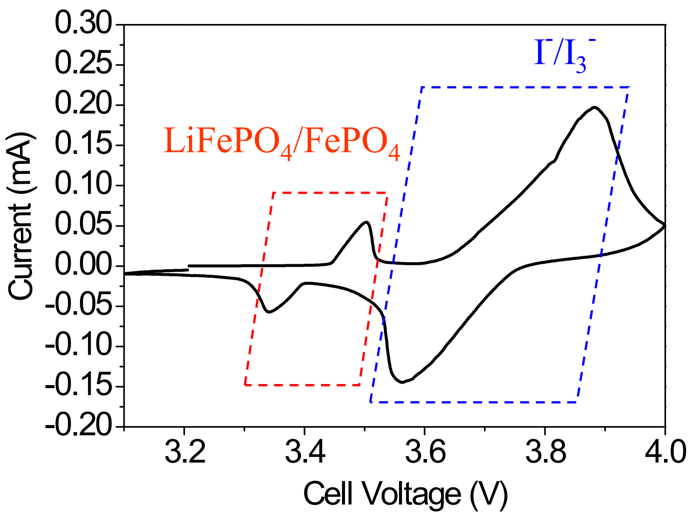
Experimental Section

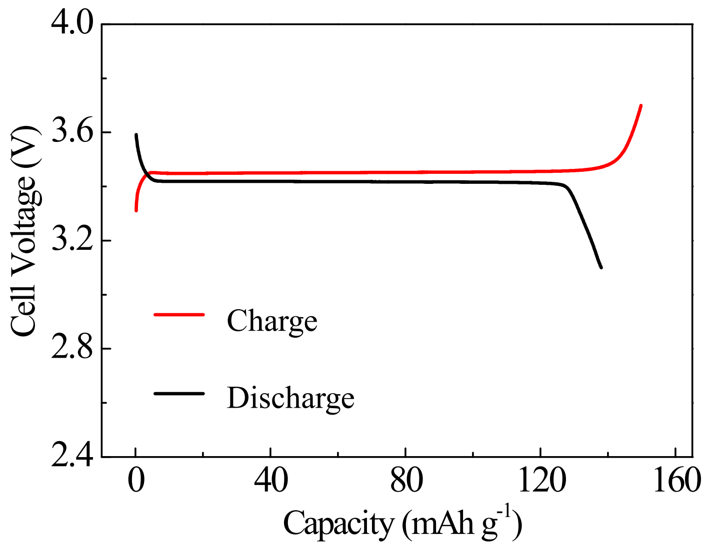
Preparation of the photoassisted chargeable LIB: The photoassisted chargeable LIB consists of a metallic Li anode with organic electrolyte, a LATP glass ceramic separator, a $LiFePO_4$ cathode with aqueous electrolyte, and a TiO_2 photoelectrode. The preparation of the anode side was conducted in an Ar-filled glove box (<1 p.p.m. of H_2O and O_2). The lithium foil with a thickness of 0.2 mm was cut to a rectangle of 8×40 mm, and then pressed onto a Cu mesh (Nilaco Cor., 100 mesh). An organic electrolyte of 1 M $LiClO_4$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) with a volume ratio 1:1 was added into this glass cylinder. LATP glass ceramic separator was supplied by Ohara Inc., Japan. The thickness and the electrical conductivity of the LATP plate at 25 °C was *ca.* 150 μm and 1.05×10^{-4} S cm^{-1}. The LATP was fixed on top of the glass cylinder thus sealing in the anode. The cathode ($LiFePO_4$) and photoelectrode (TiO_2) were stuck on the other cylindrical shape of the quartz shell. An aqueous electrolyte of 1 M Li_2SO_4 and 0.1 M LiI was added into this quartz cylinder. The $LiFePO_4$ cathode was prepared by mixing the $LiFePO_4$ with Super P carbon and polytetrafluoroethylene (PTFE) in a weight ratio of 8:1:1. The resulting slurry was then cast on a Ti mesh to achieve a loading of 0.5 mg cm^{-2}. For the photoelectrode, the nanorod TiO_2 was deposited on Ti mesh by a modified hydrothermal and thermal treatment.[1] In a typical procedure, the Ti mesh treated in air at 500 °C for 10 min was placed in an aqueous solution (28 ml) of 450 μl $TiCl_4$ (99.0%, Sigma-Aldrich) and 1.4 ml HCl (37%, Wako) and hydrothermally heated at 170 °C for 10 h. After reaction, the TiO_2 nanorod-decorated Ti gauze was washed with water, sintered at 450 °C for 2 h. The preparation and assembly of simple Li-ion battery was similar with above of solar Li-ion battery. The differences were that the photoelectrode was removed and the electrolyte is the 1 M Li_2SO_4 aqueous without LiI.

Electrochemical and photoelectrochemical measurements: The photoassisted chargeable LIB were tested using a Hokuto charging/ discharging machine, within a voltage range between 3.1 and 3.7 V, with discharge/charge current densities varying from 0.01-0.04 mA cm^{-2}. A XEF-501S Xe-lamp (San-ei Electric Co., Japan) was used as the light source. CV was tested using a Solartron instruments.

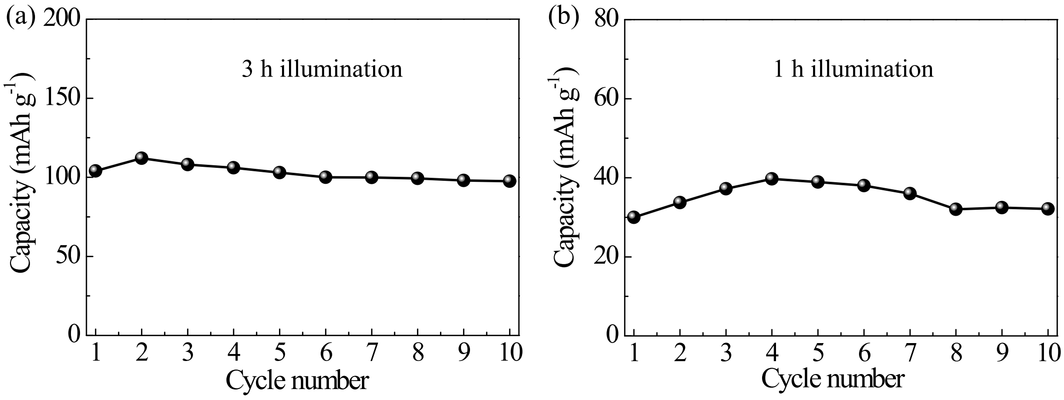
Characterizations: XRD was performed using a Bruker D8 Advanced diffractometer with Cu Kα (λ = 1.5406 Å) radiation. The UV-visible absorption spectra measurement was performed using Shimadzu UV3101PC. SEM observation was performed on a Hitachi S4800.



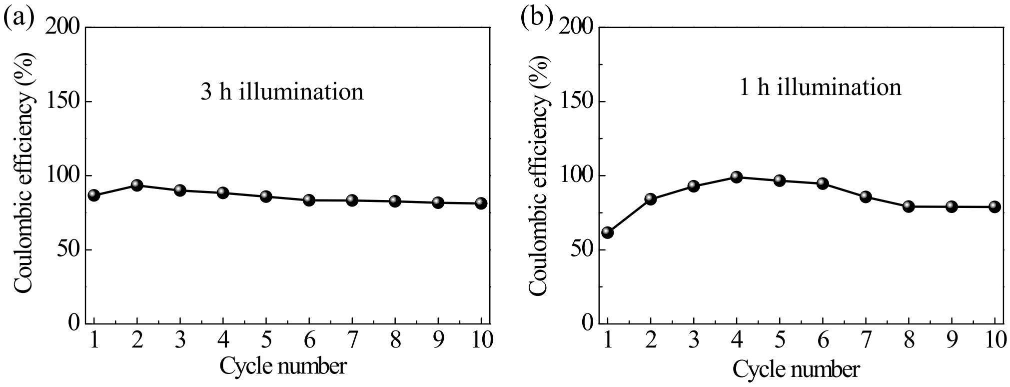
Supplementary Figure S1 CV curve of Li-ion battery with the 1 M Li_2SO_4 and 0.01 M LiI as electrolyte at a scan rate of 0.01 mV s^{-1}.



Supplementary Figure S2 The charge/discharge curve of a simple Li-$LiFePO_4$ battery at a current density of 0.01 mA cm^{-2}.



Supplementary Figure S3 The cycling performances of the photoassisted chargeable LIB under the illumination for 3h (a) and 1h (b).



Supplementary Figure S4 The Coulombic efficiencies of the photoassisted chargeable LIB under the illumination for 3 h (a) and 1 h (b).

In this work, upon charging, Li anode and the TiO_2 photoelctrode are connected to the outside circuit, while upon discharging, Li anode and $LiFePO_4$ electrode are connected to the outside circuit as shown in Fig. 1a. Therefore, different from conventional two-electrode system, the proposed Coulombic efficiency was calculated using the equation

$$CE= \frac{I_{photoelectrode} \cdot t_c}{I_{LiFePO4} \cdot t_d} \times 100$$

Where CE is the Coulombic efficiency (%), $I_{photoelectrode}$ (mA) is the charging current on TiO_2 photoelectrode and $I_{LiFePO4}$ (mA) is the discharging current on $LiFePO_4$ electrode. t_c and t_d (h) is the charge and discharge time, respectively.

1. A. Kumar, A. R. Madaria and C. W. Zhou, *J. Phys. Chem. C* 2010, **114**, 7787.