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# An efficient electron storage photovoltaic cell based on $TiO_2$/carbon aerogel composite prepared by in-situ method

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ABSTRACT

An encouraging electron storage photovoltaic cell (ESPC) based on $TiO_2$/carbon aerogel (TCA) composite prepared by in-situ method has been developed to simultaneously achieve solar energy conversion and electron storage. The structures, morphologies, and electrochemical performances of the TCAs are investigated by X-ray diffractometry, scanning and transmission electron microscopy, UV-vis absorption, charge-discharge test and electrochemical impedance spectroscopy. The uniformly dispersed TCA at 550 °C shows typical porous spherical structure with the large BET area of 556.1 $m^2\,g^{-1}$. The ESPC exhibits excellent electrochemical properties with the highest open-circuit photovoltage of 750 mV, the maximum short-circuit current density of 15.3 mA $cm^{-2}$ and the capacity retention rate of 88% after 50 cycles. And the ESPC formed by two electrodes provides a successful solution of energy conversion and electron storage simultaneously for the direct photovoltaic cells.



## 1. Introduction

Solar cells have attracted extensive researches as a promising solution to the continuously growing energy problem by providing a sustainable clean source of energy and obtained remarkable achievements in scientific research and practical application [1]. As promising photovoltaic devices, dye-sensitized solar cells (DSSCs) based on nanocrystalline porous $TiO_2$ have received much attention in recent years, due to their high efficiency, low production cost and simple fabrication process [2,3]. The studies of DSSCs focus on improving the conversion efficiency ($\eta$) by changing preparation methods [4–6], adding a scattering layer outside the $TiO_2$ film [7–9], developing many kinds of sensitizers [10–12], or using various ionic liquid electrolytes [13–16]. However, the conventional solar cells merely act as energy converters [17,18] and a complete solar cell also needs an electrical energy storage device. In order to realize energy storage, several relevant tentative explorations have been worked out, such as stacking directly photovoltaic cells and supercapacitors into one device [19–22], connecting with external rechargeable batteries [23,24] or attaching a third electrode between the positive and negative electrodes [25,26]. Nevertheless, how to achieve the integration by a single component including solar energy conversion and electron storage needs to be solved urgently.

From these points of views, we have developed an efficient electron storage photovoltaic cell (ESPC) based on $TiO_2$/carbon aerogel (TCA) prepared by in-situ method, within superior solar-to-electric conversion efficiency and energy-storage ability relative to common DSSCs. The integrated ESPC is a simple sandwich-type electrochemical cell, where the light-absorbing electrode and the counter-electrode consists of a film of dye-sensitized TCA and a thin carbon aerogel film, respectively. And the two films are deposited on the surface of a conductive transparent glass. The internal space between the two electrodes is filled with ionic liquid electrolyte, which is often an organic solvent containing the redox couple of $I_3^-/I^-$. The made ESPC shows encouraging performances with the efficient solar energy storage and the conversion efficiency of 6.94%. This new configuration of the ESPC demonstrates feasible solar conversion and electric storage and offers an efficient way to promote broader applications for solar cells. A relevant patent has been applied in 2012 [27].

## 2. Experimental

### 2.1. Preparation of TCAs

The TCA composite was prepared by in-situ method typically as follows: firstly, resorcinol (5.5 g) was dissolved in a solution of

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tetrabutyl titanate (TBT, 98%, 8 mL) and ethanol (10 mL) in a beaker, the formaldehyde solution (35%, 20 mL), succinic acid (0.5 g) and cetyl trimethyl ammonium bromide (CTAB, 0.1 g) were slowly and successively added into the above solution under constant stirring. Following this, an appropriate quantity of 18.4 M $H_2SO_4$ acid was added dropwise to this turbid solution under stirring until the solution didn't become further expanding. Finally, the mixture was transferred into crucibles and maintained at 150 °C for 24 h, followed by given temperature (450~750 °C) for 6 h in liquid seal vacuum atmosphere. A rigid and well-distributed TCA composite was obtained with the carbon aerogel content of ~60%. These various powders were named as TCA450, TCA550, TCA650 and TCA750 for calcination temperature at 450, 550, 650 and 750 °C, respectively.

### 2.2. Cell assembly

To make a photoanode with square working area of ~1 cm$^2$, the mixed slurry of 80 wt.% TCA powder, 16 wt.% acetylene black (AB) and 4 wt.% polyvinylidene fluoride (PVDF) in N-methylpyrrolidinone (NMP) was spread uniformly on a fluorine-doped tin oxide (FTO) conductive glass using doctor-blade method. The resulting photoanode film was sensitized in an ethanoic solution of 0.5 mM C106 (NaRu(4,4′-bis(5-(hexylthio)thiophen-2-yl)-2,2′-bipyridine)(4-carboxylicacid-4′-carboxylate-2,2′-bi-pyridine)(NCS)2) for 12 h in the dark. Another FTO conductive glass covered with a layer of the carbon aerogel was then used as the counter electrode. The ESPC was fabricated by injecting a drop of ionic liquid electrolyte into the aperture between the TCA film electrode and the counter electrode separated by membrane, where the electrolyte is contained 0.05 M $I_2$, 0.5 M LiI, 0.4 M 1,2-dimethyl-3-propylimidazolium iodide and 0.5 M 4-tert-butylpyridine in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF4) solvent referred in literature [26] and the membrane is 0.2 μm made in Nylon [28].

### 2.3. Characterization

Crystal structure of all the samples were examined by X-ray diffractometer (XRD, Rigaku D/max-rB) using Cu-Ka radiation source between 10° and 70° with a step size of 0.02°. Field emission scanning electron microscopy (FESEM, SU8020) and high resolution transmission electron microscope (HRTEM, JEM-2100F) were examined to view and analyze TCA550 morphology. An Agilent UV-CARY 5000 spectrophotometer was used to record the absorbance spectra of all the samples. Brunauer-Emmett-Teller (BET) surface area and pore size analysis were performed using a surface area analyzer (Micromeritics American Inc. ASAP 2020 M + C). The electrochemical impedance spectrometry (EIS), and chronopotentiometry experiments were investigated by using CHI 660B in a four-electrode mode.

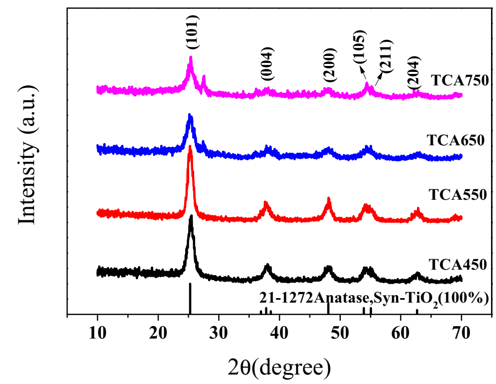


**Fig. 1.** Powder XRD patterns for TCA materials.

## 3. Results and discussion

### 3.1. Structure and morphology of TCAs

The XRD patterns of the as-prepared TCA samples are shown in Fig. 1. Six Bragg diffraction peaks (2θ = 25.3°, 37.8°, 48.0°, 53.9°, 55.1° and 62.7°) being in good agreement with a typical anatase phase pattern, can be clearly viewed (JCPDS no. 21-1272), which are indexed as the (101), (004), (200), (105), (211) and (204) planes, respectively. The anatase $TiO_2$ structure demonstrates a higher open-circuit photovoltage ($V_{oc}$) in ESPCs for its higher conduction band edge energy and larger bandgap compared with rutile structure [29]. Generally speaking, rutile remicrosphes will be formed when the calcination temperature is over 550 °C [30,31], but only the strongest characteristic peak (2θ = 27.4°) of rutile phase pattern appears in the XRD patterns of TCA650 and TCA750. To that wonder, we have conducted experiments repetitiously and draw the same conclusion finally, so we consider the carbon aerogel plays a vital part in draging the formation of rutile remicrosphes. And the diffraction peaks of the TCA550 become sharper compared with TCA450, suggesting the improved crystallinity. However, the characteristic peaks of carbon aerogel (2θ = 43.9° and 51.3°) are not clearly resolved, which indicates that the carbon aerogel is amorphous.

From the FESEM image of the TCA550 sample, it can be seen that the obtained TCA550 microspheres have uniform spherical porous structure (Fig. 2b), while the pure $TiO_2$ is composed of smooth and irregular particles in Fig. 2a. The typical spherical porous structure in Fig. 2b implies the TCA550 material will has a large surface area. Additionally, the HRTEM image in Fig. 2c indicates clearly that $TiO_2$ and carbon aerogel distribute uniformly with the $TiO_2$ average crystals diameter of ~7 nm. The result is consistent with the XRD and FESEM data. The high content (~60%) of carbon aerogel in TCAs makes it reasonable to improve the conductivity of the FTO substrate, and more electrons would be stored to achieve the function of efficient electron storage. The Fig. 2c displays a lattice fringe

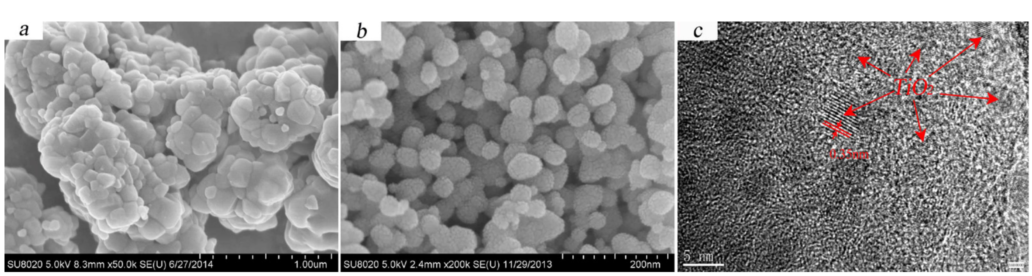


**Fig. 2.** FESEM images of (a) pure $TiO_2$ (b) TCA550, and HRTEM image (c) of TCA550.