



## Short communication

Surface NH<sub>2</sub>-rich nanoparticles: Solidifying ionic-liquid electrolytes and improving the performance of dye-sensitized solar cells

Yanyan Fang<sup>a, b, 1</sup>, Pin Ma<sup>a, b, 1</sup>, Nianqing Fu<sup>c, d</sup>, Xiaowen Zhou<sup>a, b</sup>, Shibi Fang<sup>a, b</sup>, Yuan Lin<sup>a, b, \*</sup>

<sup>a</sup> Beijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, China

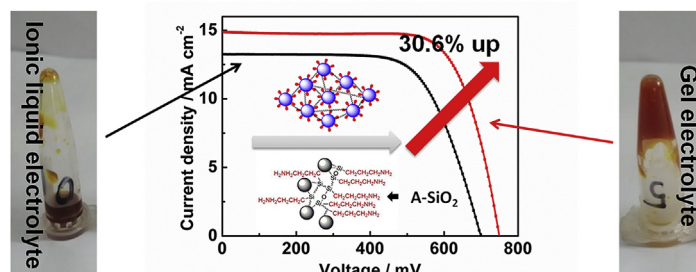
<sup>c</sup> School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

<sup>d</sup> Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong, China

## HIGHLIGHTS

- Surface NH<sub>2</sub>-rich nanoparticle (A-SiO<sub>2</sub>) with a tightening network is synthesized.
- A-SiO<sub>2</sub> could solidify ionic-liquid electrolyte in much less amount (5 wt%).
- The best efficiency of DSCs based on ionic-liquid gel electrolyte is up to 8.1%.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 4 July 2017

Received in revised form

12 September 2017

Accepted 2 October 2017

## Keywords:

Ionic-liquid

Nanoparticle

Gel electrolyte

Dye-sensitized solar cell

## ABSTRACT

The surface properties of nanoparticles have a significant influence on the properties of the gel electrolytes. Herein, the surface NH<sub>2</sub>-rich nanoparticle (A-SiO<sub>2</sub>), with a tightening network, is synthesized by silanizing SiO<sub>2</sub> nanoparticles with pre-polymerized aminopropyltriethoxysilane, which is further employed to prepare ionic-liquid gel electrolytes for dye-sensitized solar cells. The addition of a small amount of A-SiO<sub>2</sub> can effectively solidify the ionic-liquid, whereas a large number of NH<sub>2</sub> groups on the SiO<sub>2</sub> surface leads to a large negative shift of the TiO<sub>2</sub> conduction band edge, and can react with I<sub>3</sub><sup>-</sup> in the form of a Lewis complex, resulting in an increase in the concentration of I<sup>-</sup> and a decrease in the concentration of I<sub>3</sub><sup>-</sup> in the electrolyte. In addition, the ionic-liquid gel electrolyte possesses thixotropic behavior, which allows it to easily penetrate into the inner part of the TiO<sub>2</sub> mesoporous film. As a result, large improvements of the photovoltage from 695 mV to 785 mV and of the photocurrent from 13.3 mA cm<sup>-2</sup> to 14.9 mA cm<sup>-2</sup> are achieved. This leads to significant enhancement of the power conversion efficiency, from 6.2% to 8.1%, for the cell with A-SiO<sub>2</sub> compared to that of the pristine ionic-liquid electrolyte.

© 2017 Published by Elsevier B.V.

\* Corresponding author. Beijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

E-mail address: [linyuan@iccas.ac.cn](mailto:linyuan@iccas.ac.cn) (Y. Lin).

<sup>1</sup> These authors contributed equally to this work.

## 1. Introduction

Dye-sensitized solar cells (DSCs) have aroused intense interest due to their potential application in the fabrication of cost-effective

renewable energy devices [1–3]. To further improve the power conversion efficiency (PCE) of DSCs, many efforts have been exerted, including the synthesis of more efficient sensitizers, preparation of alternative working and counter electrodes and optimization of electrolytes [4–7]. Recently, the addition of nanoparticles to ionic-liquids has been shown to be an effective way to optimize the performance of electrolytes, with the resulting gel electrolytes having high conductivity, solid-like mechanical strength and excellent interfacial contact [7–13]. Various nanoparticles such as SiO<sub>2</sub>, TiO<sub>2</sub> or carbon-based materials have been investigated. In addition, modified nanoparticles, such as ZnO capped with long alkyl chains and SiO<sub>2</sub> modified with 3-aminopropyltriethoxysilane [8,11,12], were also used to obtain gel electrolytes. The performance of DSCs can be improved by adding various nanoparticles in ionic-liquid electrolytes, whereas efficiencies of 5%–7% were achieved for ionic-liquid-based quasi-solid-state DSCs without any additional organic solvents.

Research has shown that the surface properties of nanoparticles have a significant influence on the properties of the gel electrolytes. Additionally, it was found [11,12] that increasing the amount of nanoparticles modified with 3-aminopropyltriethoxysilane continuously enhanced the photovoltage ( $V_{oc}$ ), which is ascribable to the increased concentration of NH<sub>2</sub> groups on the nanoparticles. However, in this system, a large amount of nanoparticles ( $\geq 15$  wt%) is usually required to achieve a desired gel. Since SiO<sub>2</sub> is non-conductive, the larger amount of SiO<sub>2</sub> in the electrolyte will lower the photocurrent ( $J_{sc}$ ) of the DSC. As a result, the improvement in photovoltaic performance is rather limited. To solve this problem, we modified the surface of SiO<sub>2</sub> nanoparticles by increasing the amount of NH<sub>2</sub> groups attached on the SiO<sub>2</sub> nanoparticle to produce an NH<sub>2</sub>-rich nanoparticle (A-SiO<sub>2</sub>). The surface NH<sub>2</sub>-rich nanoparticle, with a tightening network (Scheme 1), is synthesized by introducing a pre-polymerized coupling agent with abundant NH<sub>2</sub> groups and inorganic-philic groups onto the SiO<sub>2</sub> nanoparticle. As a consequence, the gelation is improved, and only a small quantity of A-SiO<sub>2</sub> (5 wt%) is required to solidify the ionic-liquid. More importantly, we note that the use of an A-SiO<sub>2</sub> solidified electrolyte to fabricate DSCs leads to a large enhancement of all the photovoltaic parameters, achieving a PCE of 8.1% under the illumination of 100 mW cm<sup>-2</sup> (AM 1.5) (increased by 30.6% compared to ionic-liquid based DSCs). To the best of our knowledge, this is the first time that such a high efficiency is achieved for ionic-liquid based quasi-solid-state DSCs without a volatile component.

## 2. Experimental

### 2.1. Synthesis of A-SiO<sub>2</sub>

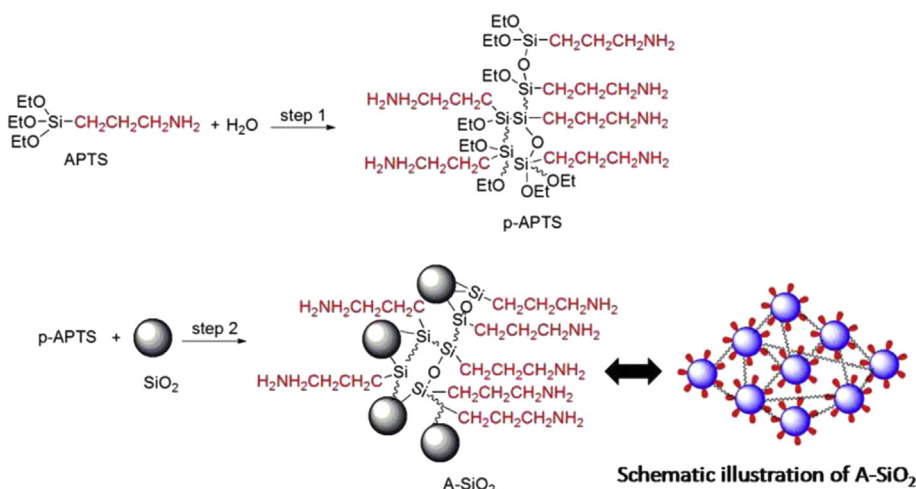
A-SiO<sub>2</sub> was prepared as shown in Scheme 1. The pre-polymerized (3-aminopropyl)triethoxysilane (*p*-APTS) was synthesized as follows: 0.36 g of H<sub>2</sub>O was mixed with 6.63 g of APTS (Alfa) by stirring for 24 h, 0.04 g of Ca(OH)<sub>2</sub> was added, and the mixture was kept under 300 Pa at 80 °C for 1 h. The <sup>1</sup>H NMR signals for the *p*-APTS protons were shifted upfield and broadened compared to those of APTS. This confirmed the formation of the APTS pre-polymerization [14]. A-SiO<sub>2</sub> was obtained by refluxing SiO<sub>2</sub> with *p*-APTS in toluene for 48 h. The solid product was filtered, washed with chloroform and dried at 90 °C. The final product was designated A-SiO<sub>2</sub>. Characterization data: FTIR  $\nu$  (*p*-APTS, cm<sup>-1</sup>): 960, s, SiOEt; FTIR  $\nu$  (A-SiO<sub>2</sub>, cm<sup>-1</sup>): 3391 and 2933, s, NH<sub>2</sub>; 1300, vb, SiOSi and SiOC; 795, s, SiC.

### 2.2. Preparation of electrolytes and assembling of DSCs

The ionic-liquid electrolyte (denoted as HA) is composed of guanidinium thiocyanate (GuNCS) (Acros), N-methylbenzimidazole (NMBI) (Alfa), I<sub>2</sub> (Acros), 1-hexyl-3-methylimidazolium iodide (HMII) and 1-allyl-3-methylimidazolium iodide (AMII) (prepared according to the literature [11]) with a molar ratio of 1.2:1.2:1:8:8. The gel electrolytes were prepared by grinding an appropriate amount of A-SiO<sub>2</sub> with HA. The fabrication procedure for DSCs followed previous reports [15–17]. The cells were fabricated by spreading the aforementioned electrolytes on the dye-sensitized TiO<sub>2</sub> electrode, and then pressing the Pt counter electrode on that. The cell was 0.20 cm<sup>2</sup> in active area. The thicknesses of the TiO<sub>2</sub> electrodes before and after penetration of the electrolyte calculated from SEM images (Fig. S1) are about 6.53  $\mu$ m and 7.33  $\mu$ m respectively. Therefore, the thickness of gel electrolyte layer is approximately 0.8  $\mu$ m.

### 2.3. Measurements and instruments

The *I*-*V* measurements were performed as previously reported [17]. The nanoparticles were characterized by FTIR (Tensor 27 spectrometer) and transmission electron microscopy (TEM) (Tecnai T20). Thixotropic behavior measurements were performed on a programmable cone/plate-type viscometer (spindle CPE-41, HBDV-



**Scheme 1.** Schematic representation of the A-SiO<sub>2</sub> synthesis routine.

Download English Version:

<https://daneshyari.com/en/article/5148577>

Download Persian Version:

<https://daneshyari.com/article/5148577>

[Daneshyari.com](https://daneshyari.com)