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Carbonaceous allotropes modified ionic liquid electrolytes for efficient quasi-solid-state dye-sensitized solar cells

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ABSTRACT

Quasi-solid-state dye-sensitized solar cell (qss-DSSC) is a promising photovoltaic system, intended to solve the problem of electrolyte leakage and enhance the stability of this type of cell. The most challenging issue for thus type of cell is its relatively low power conversion efficiency (η), compared with that of its counter-part cell with a liquid electrolyte. In this study, various geometric structures of carbon, *i.e.*, graphite, carbon nanotubes (CNT) and carbon spheres (CS) are added in an ionic liquid (IL) electrolyte to fabricate qss-DSSCs. Compare to the qss-DSSC with pristine IL electrolyte, the cells with graphite, CNT, and CS modified IL electrolyte show higher conversion efficiency. The highest photovoltaic performance of the cell with CS-modified IL electrolyte is explained on the basis of enhanced conductivity, increased diffusion coefficients of I^- and $I_3{}^-$ ions, and reduced charge transfer resistances, with reference to these parameters in the cases of pristine IL or ILs with graphite or CNT. Further comparative study is made among the performances of the qss-DSSCs using the CYC-B6S dye, reported by us previously, and the conventional N3 dye, both in the presence and absence of CS in the respective IL electrolytes. Finally, stability studies are made for these qss-DSSCs under continuous light soaking at 55 °C for 1,000 hours. All these studies demonstrate that the best performance ($\eta = 6.16\%$) and stability (< 95%) are exhibited by the qss-DSSC with CS-modified IL electrolyte and CYC-B6S dye.

1. Introduction

It is well known that performances of dye-sensitized solar cells (DSSCs) reach their best only when the cells have liquid electrolytes [1–3]. However, commercialization of these cells has been impeded owing to the technological problems related to hermitic sealing, precipitation of salts at low temperature, evaporation of liquids at high temperature, corrosion, and lack of long-term stability.

Replacing liquid electrolytes in DSSCs with solid or quasi-solid electrolytes is expected to make the cells viable. Some of the materials to replace the liquid electrolytes are non-volatile ionic liquids, organic or inorganic hole-transport materials, and solid or quasi-solid-state polymers [4–11]. In most solid or semi-solid DSSCs, only low overall energy conversion efficiencies were achieved, essentially due to low conductivity of the electrolytes. Thus, ionic conductivity of a quasi-solid-state electrolyte is the dominating factor to determine the photovoltaic performance of the DSSC. In this direction of research, polymer electrolytes were blended with conductive fillers, such as carbon black and carbon fiber [12–14] to make them pseudo-solid state electrolytes. Zhang *et al.* have demonstrated that a fraction of carbon nanoparticles in a polymer electrolyte of PEO/P(VDF-HFP)/SiO_2 has significantly increased its ionic conductivity [14]. Appetecchi *et al.* have introduced a small volume fraction of carbon powder into a PEO type lithium polymer electrolyte, and thereby achieved an improved ionic conductivity and interfacial stability [15], with reference to these parameters of the electrolyte without the carbon powder. Ikeda *et al.* reported a simple preparation of a solid-state conductive material, containing polyaniline (hole transport material), carbon black, and ionic liquid as an incombustible paste. This material has enabled solidification of the electrolyte in the DSSC, and the pertinent cell rendered a conversion efficiency of more

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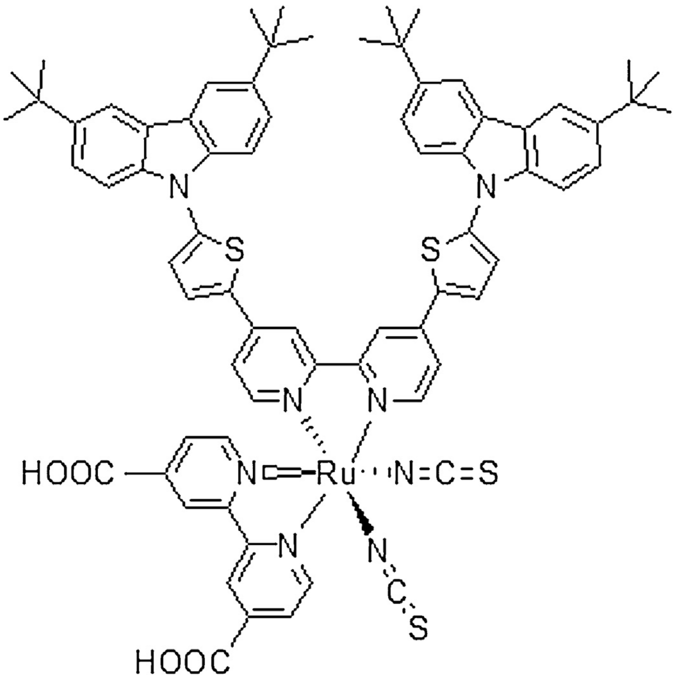


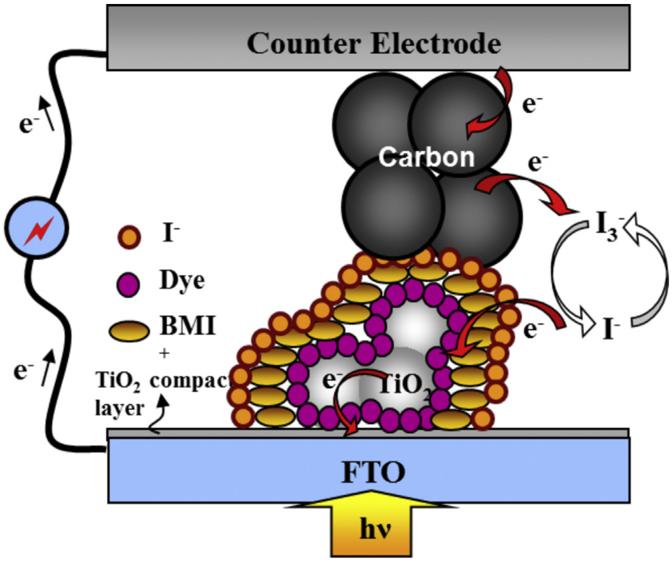
Scheme 1. Molecular structure of CYC-B6S dye.

than 4%, though the iodine content was very small in the device [12]. Proper amount of a conductive filler is required to enable continuous conducting paths and increased electrical conductivity in a polymer matrix. Electrical conductivity of a carbon filled polymer composite depends on the conductivity-related properties of the carbon material, *i.e.*, particle size, shape, porosity and surface chemistry of the material, in addition to the characteristics of the polymer (chemical structure and crystallinity).

The present work reports enhanced performance of three quasi-solid-state DSSCs (qss-DSSCs) owing to the incorporation of carbon derivatives, *i.e.*, graphite, carbon nanotubes (CNTs) and carbon spheres (CS) in their electrolytes. The purpose of addition of one of these carbonaceous allotropes to the electrolyte is not only to increase the mechanical strength of the electrolyte, thereby achieving its solidification, but also to enhance its ionic conductivity. Addition of a carbon material to an electrolyte is expected to enable continuous conducting paths for ions in the electrolyte and to impart electronic conductivity to the electrolyte [12–14]. It is to be emphasized here that hole-transport polymers were not incorporated in this near-solid state electrolyte; this non-incorporation is aimed at reducing the associated electrochemical complexity. Further, a home-made ruthenium sensitizer, coded CYC-B6S, synthesized and reported by us previously (molecular structure in Scheme 1)[16], was used in this study. This is a ruthenium sensitizer having a bipyridine ligand functionalized with thienyl-carbon moiety. The novel aspects of this report include comparative study on the performances of the qss-DSSCs, using three types of carbon derivatives and such study on the DSSCs with the CYC-B6S dye and the regular N3 dye in the presence and absence of CS in the electrolytes.

2. Experimental Section

TiO_2 paste was prepared by a sol-gel method according to the procedure reported in the literature [17]. A paste of titanium isopropoxide (TTIP) in 2-methoxyethanol was spin-coated on a cleaned conducting fluorine-doped tin oxide (FTO) glass (sheet resistance = 8 Ω sq.$^{-1}$, Solaronix S. A., Aubonne, Switzerland) for the preparation of a thin buffer layer of non-porous TiO_2. The FTO glass was dried and annealed at 500 °C for 30 min. The above mentioned pre-prepared TiO_2 paste was thrice coated on the buffer-TiO_2/FTO surface by a doctor blade method to obtain a TiO_2 transparent layer with an optimum thickness [18]. For the first coating, the TiO_2 paste was incorporated with polyethylene glycol (PEG) having a molecular weight of 200,000. The TiO_2 paste for the second coating contained PEG with the molecular weight of 20,000. A mixed paste, containing light scattering particles of TiO_2 (particle size: 300 nm) and usual nanocrystalline TiO_2 particles (particle size: 20 nm) in the ratio of 3:7 by weight, was used for the final coating, for reducing light loss by back scattering. An active surface area of 0.16 cm^2 from the coated surface was then selected by scrapping the remaining coating. The TiO_2-coated FTO glass was then sintered and immersed overnight in 2×10^{-4} M acetonitrile solution, containing the CYC-B6S dye and tert-butylpyridine (tBP) in the volume ratio of 1:1. Thus the photoanode was prepared.



Scheme 2. Schematic representation of incorporation of a carbon derivative in the qss-DSSC.

A platinum-sputtered FTO conducting glass plate (Pt thickness = 100 nm) was used as the counter electrode. The quasi-solid-state ionic liquid based electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide (BMImI), 0.1 M I_2, 0.5 M TBP, 0.1 M guanidinium thiocyanate (GuSCN), 10 ml of 1-ethyl-3-methylimidazolium thiocyanate (EMISCN), and one of the carbon derivatives, *i.e.*, graphite, CNTs, and CS. Graphite (>99.0%) and CNTs (>7.5%, MWCNT basis, O.D.×L = 6–20 nm × 1–5 μm) were acquired from Fluka and Aldrich, respectively. CS was prepared as follows. Glucose (0.04 mole) was dissolved in 60 ml of distilled water, and then placed in a 600 ml stainless steel autoclave. The autoclave was heated to 180 °C for 12 h. After the heating, the product was filtered off, washed several times with distilled water and then ethanol, and was finally dried in a vacuum oven at 60 °C for 5 h. After the synthesis, the black carbon powder was calcined in an argon atmosphere at 600 °C (at the heating rate of 1 °C min^{-1}) for 1 h to obtain the carbon spheres.

A photograph of the quasi-solid-state ionic liquid based electrolyte, consisting of 0.3 g of carbon spheres, 0.6 M BMImI, 0.1 M I_2, 0.5 M TBP, 0.1 M GuSCN and 10 ml EMISCN, is shown in Scheme 2. In the fabrication process of the quasi-solid-state DSSC, the electrolyte was pasted between the dye anchored photoanode and the Pt sputtered FTO glass, which physically sandwiched the two electrodes together, assisted by a cell holder.

The cell was illuminated by an Oriel solar simulator (#6266), equipped with a water-based IR filter, under AM 1.5G filter