Synthetic Metals 215 (2016) 14–20

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Preparation of pyridinium iodide-grafted nano-silica and its application to nano-gel systems for dye sensitized solar cells

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ARTICLE INFO

Article history:
Received 8 October 2015
Received in revised form 29 January 2016
Accepted 30 January 2016
Available online 15 February 2016

Keywords:
Dye-sensitized solar cells
Quasi-solid electrolyte
Pyridinium iodide
Nano-silica
Long-term stability

ABSTRACT

Dye sensitized solar cells (DSSCs) have emerged as promising candidates for replacing silicon-based photovoltaics in the renewable energy field as it has advantages such as low-cost and simple preparation procedures. However, conventional DSSCs have shown a critical limitation for practical use because of durability problems arising from the liquid solvent used in devices. Therefore, it is still necessary to develop a technology that is stable in the long term. This study demonstrates a system of nano-gel silica electrolyte with pyridinium iodide grafts (PISi) and its application to DSSCs. The PISi has been synthesized by a two-step process starting from nano-silica, 2-(4-pyridylethyl)triethoxysilane, and iodoalkane. The prepared PISi was analyzed using thermogravimetric analysis and scanning electron microscopy. The performance of DSSCs with the PISi electrolyte was optimized by changing the iodoalkane chain length, electrolyte solvent, and iodide concentration in the electrolyte. We have compared the performance of DSSCs employing two different electrolytes: a typical liquid electrolyte cell and the PISi electrolyte. Power conversion efficiency of DSSCs with the liquid electrolyte was retained around half of the initial value after 100 h. In contrast, PISi electrolyte-based devices have shown a consistent efficiency. From this result, we conclude that the PISi electrolyte helped to improve the long-term stability in DSSCs.

1. Introduction

Solar energy, being renewable and abundant, has attracted many researchers seeking alternatives to fossil energy. For the past few decades, dye-sensitized solar cells (DSSCs), a promising type of solar cells, have received considerable attention because of their possibility of low-cost fabrication compared to conventional silicon solar cells as well as potential applications to various fields because they are colorful and semitransparent [1–5]. The general structure of DSSCs consists of a transparent conductive oxide (TCO), a dye-coated nanocrystalline metal oxide film, an electrolyte for the redox reaction of I^-/I_3^-, and a platinum-based counter electrode [6,7]. A power conversion efficiency (PCE) of up to 13% has been achieved for a conventional liquid electrolyte-based DSSC [8]. However, the problem of stability, induced because of solvent leakage and volatility, remains [9]. Several attempts have been made in order to address the stability issue [10,11]. One of the solutions, ionic liquids (ILs) such as alkylimidazolium iodide and alkylpyridinium iodide salts have been employed in DSSCs because of their superior properties in terms of stability and ion conductivity [12–14]. Although IL compensates for volatile acetonitrile electrolytes, the sealing on the sandwiched configuration of the device needs to be resolved. In this regard, inorganic nanoparticles, especially nanocomposite silica, is one of the suitable candidates for the fabrication of quasi solid-state DSSCs (QSSDSSCs) by solidifying the electrolyte [15,16]. Berginc et al. have demonstrated 20% enhancement in the PCE for QSSDSSCs by using imidazolium iodide-based electrolyte with an optimized amount of silica nanoparticles [17]. Upon addition of silica nanoparticles into an electrolyte containing imidazolium iodide, imidazolium can be adsorbed on the surface of the silica nanoparticles, and can improve the charge transport of the I^-/I_3^- redox couple by the

Abbreviations: BMII, 1-butyl-3-methylimidazolium iodide; BPI, butylpyridinium iodide; DMAc, dimethyl acetamide; DMF, dimethyl formamide; DMSO, dimethyl sulfon; DSSC, dye sensitized solar cell; EiPS, ethyl isopropyl sulfone; EMII, 1-ethyl-3-methylimidazolium iodide; GBL, γ-butyrolacton; IL, ionic liquid; NMP, N-methylpyrrolidone; PC, propylene carbonate; PCE, power conversion efficiency; PISi, pyridinium iodide graft; QSSDSSC, quasi solid-state DSSC; SEM, scanning electron microscopy; TCO, transparent conductive oxide; TGA, thermogravimetric analysis; VN, valeronitrile.

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http://dx.doi.org/10.1016/j.synthmet.2016.01.023

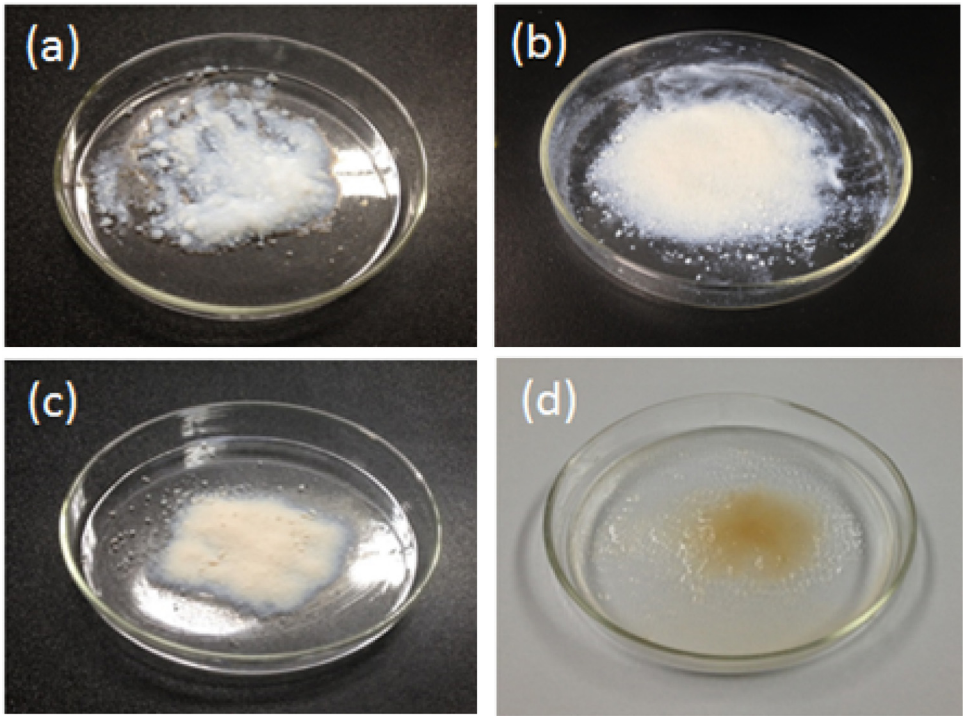

Fig. 1. Optical images of pyridinium iodide-grafted nano-silica. (a) Bare nano-silica, (b) pyridinium-grafted nano-silica, (c) dried, and (d) wet pyridinium iodide-grafted nano-silica.

ordering of a specific structure in the electrolyte, which is favorable for electron hopping. Meanwhile, pyridinium iodide can be easily prepared at a lower cost than imidazolium iodide and this has been successfully demonstrated in DSSCs [14]. Herein, we have prepared pyridinium iodide-grafted nano-silica (PISi) to construct QSSDSSCs. The photovoltaic performances were studied by varying the length of the alkyl chain and optimized conditions and PCEs up to 5.85% have been obtained under illumination intensities of 100 cm^{-2}. In addition, the effect of several solvents and iodide concentration in the electrolyte were investigated for determining the optimum conditions in QSSDSSCs. Furthermore, the stability test for conventional liquid electrolyte and PISi electrolyte-based devices was conducted for 100 h. Photovoltaic devices with the PISi electrolyte have shown a consistent efficiency compared to that shown by liquid electrolyte-based devices. Consequently, PISi electrolyte-based devices could be a solution for the lack of stability in DSSCs.

2. Experimental

2.1. Synthesis of pyridinium-grafted nano-silica (PSi)

Silica powder (Arosil hydrophilic fumed silica 12 nm, Evonik) was dissolved in toluene and stirred at 110 °C for 30 min under nitrogen atmosphere. Subsequently, 4-(2-pyridylethyl) triethoxy silane was added and the mixture was continuously stirred under the same conditions for 18 h. The resultant product was filtered and washed with methanol and acetone 3 times and dried at 200 °C overnight.

2.2. Modification of nano-silica with pyridiniumiodide (PISi)

The synthesized PSi was modified with 6 forms of iodoalkane; iodomethane, iodopropane, iodobutane, iodopentane, iodohexane, and iodododecane, which differ in the number of carbons in the alkyl chain. Each iodoalkane was reacted with PSi in acetonitrile for 1 h, filtered, and washed with diethyl ether and ethanol 3 times. The final product (PISi) was obtained after drying it in an oven for 24 h [18,19].

2.3. Device fabrication

Fluorine-doped SnO_2 conducting glass (FTO) glass was washed with DI water, ethanol, and acetone in sequence. An 18–21-μm-

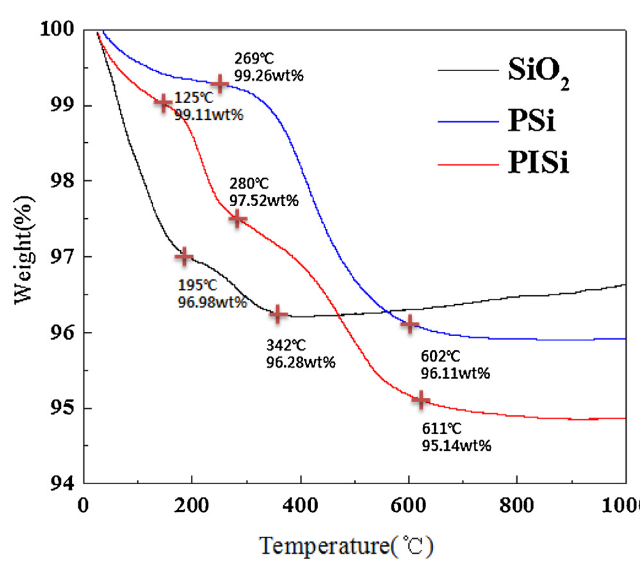

Fig. 2. TGA analysis of bare SiO_2, synthesized PSi, and PISi.