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SPR effect of AgNPs decorated TiO_2 in DSSC using TPMPI in the electrolyte: Approach towards low light trapping

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ABSTRACT

Nano-porous titania matrices were doped with AgNPs by UV assisted reduction of $AgNO_3$ solution to fabricate the photo-anode in dye sensitized solar cell using N3 as the absorber dye. The composite matrices were subjected to physicochemical characterization using XRD, TEM, XPS, EDAX, FESEM, spectral and micro Raman techniques. Electrochemical characterizations of the Ag-TiO_2 matrices were carried out to evaluate the photoresponse, current-voltage output, interfacial charge transfer and stability of the DSSC under illumination of 10–100 mW/cm^2 using white LED light source. The dye-electrode embedded with an optimal level of Ag, produced solar conversion efficiency of 11.17% and IPCE 73%. Attempt was taken to make the plasmon based DSSC more low light sensitive by using triphenylmethylphosphonim iodide (TPMPI) as the electrolyte component.

1. Introduction

Introduction of surface plasmon onto photosensitizer electrodes has been one of the recent trends for achieving improved functional properties of dye sensitized solar cells (DSSC) [1–6]. The surface plasmon resonance (SPR) phenomenon induces an electronic dipole on the metal nano particles (NPs) resulting in an enhancement of the electric field in and around the active sites. This in turn intensifies the light scattering and absorption, elongates the optical pathway and in effect, enhances light harvesting in the DSSC system. Several approaches of introducing SPR in the photosensitive matrices include addition of Ag, Au, Cu nanospheres, nanowires etc on to the base matrix [3–5]. Further reports are also available for plasmon application in optical devices [6–8], study of photoluminescence [9], chemical sensing [10] and Raman spectroscopy [11,12] and so on. Jeong et al. [6] reported the overall power conversion efficiency of 8.9% in DSSC using plasmonic AgNPs and Ru based dye as the sensitizer. Standridge et al. [13] investigated the effect of distance between AgNPs and the dye in DSSC systems and observed that the photocurrent decreases with increasing thickness of the spacer. One of the contemporary trends in DSSC includes the use of white LED as the radiating source [14–18]. FD Rossi [14], D. Bari et al. [17] and F. Malara et al. [18] investigated the DSSC performances using N719 dye under white LED light source. A recent work has been reported by one of our groups on a novel terpyridine Ru dye used in DSSC operating under white LED light source [19].

Infact the low intensity light has several advantages related to the sustainability of the DSSC system during operation [17]. In low light the dispersed metals NPs can retain their fine grain structure and effectively contribute to the plasmonic behaviour. On the other hand high intensity light exposure may lead to conglomeration of nano particles which becomes a detrimental factor in achieving high performance efficiency in the plasmonic DSSC. Tanaka et al. [20] have shown the increment in SERS intensity as a result of coalescing AgNPs under high electromagnetic radiation. Similarly, Kevin et al. [21] have shown that exposure of the Ag nano seeds to high intensity light, leads to the growth of larger spheres, platelets and rods which however can be avoided in low light exposure. Further, non linear aggregation of AgNPs is also caused by the ambient thermal energy under high intensity light. It therefore implies that the narrow distribution of metal NPs is readily sustained in low intensity light source while there is fair possibility of conglomeration of metallites on high intensity light exposure, leading to changes in the shapes and the sizes of the nano particles. In this investigation nano porous titania matrices with multiple phase composition were activated through the SPR effect by introduction of various levels of AgNPs for optimizing the functional properties of N3 dye based DSSC system under white LED light irradiation.

Regarding the choice of electrolytes in DSSC systems, sulfonium and imidazolium salts have been successfully applied [20,22].

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However, the phosphonium salts have received limited attention for DSSC, even though they have been extensively used in supercapacitors [23]. A maximum of 5.7% conversion efficiency has been reported in DSSC system under light intensity of 8.9 mW cm^{-2} using phosphonium salts, as the electrolyte [24]. Further using triphenylmethylphosphonium iodide (TPMPI), in particular, an overall increase in the conversion efficiency from 5.34% to 7.10% has been reported with a fall of radiant power from 100 to 10 mW/cm^2 [25]. The present choice of electrolyte for the DSSC is TPMPI, along with NaI in the solution and it is expected that addition of organic electrolyte in the medium can improve the stability of the Ag-TiO_2 matrix rather than using only NaI in the medium. Moreover since the conductivity of the electrolyte affects the kinetics of ionic and electronic processes during photovoltaic performances, [26,27] tuning of the electrolyte composition is also essential for obtaining enhanced open-circuit voltage in DSSC.

The composite Ag-TiO_2 and the bare TiO_2 films were subjected to physico-chemical characterizations through X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), UV–vis and Micro Raman techniques. The matrix was subsequently sensitized with N3 dye. The electrochemical parameters, electrode-electrolyte interfacial properties and the power output characteristics of the cell were evaluated using a series of electrochemical techniques. The SPR modified DSSC is found to exhibit high level power conversion efficiency and advocated for efficient energy harvesting, particularly in low-light interior environments under fluorescent or LED light sources.

2. Experimental

2.1. Synthesis of TiO_2 NPs

TiO_2 NPs were prepared by heating titanium (IV) chloride precursor solution (0.5 M) containing 1.0 M ammonium sulfate at 75 °C for 1.5 hrs followed by addition of ammonium hydroxide solution and maintaining the pH at 7.0. The precipitated titanium hydroxide was washed in aqueous ethanol and dried at 50–55 °C. Finally the samples were calcined at 500 °C for 1hr.

2.2. Fabrication of AgNPs doped TiO_2 matrix

The laboratory prepared (LP) anatase TiO_2 were mixed with commercially available Degussa P25 (TiO_2) (Sigma Aldrich, Size 21 nm) in 2:3 proportion and ethanolic solution containing acetic acid and ethyl cellulose and terpineol (Fluka) was added to the mixture. The TiO_2 paste was ultrasonicated to maintain the homogeneity of the solution and further concentrated by evaporation. In course of fabrication of the DSSC anode, TiO_2 paste was uniformly coated on FTO glass substrate (Dyesol, Australia) by the help of doctor's blade technique and sintered at 500 °C for 1 hour. Finally, the AgNPs were synthesized directly onto the mesoporous TiO_2 network by photoreduction of $AgNO_3$ solution at different concentrations by using UV radiation with the help of UWave-100, Sineo (China).

2.3. Electrolyte preparation

The working electrolyte for the DSSC configuration consisted of 0.05 M TPMPI, 0.5 M NaI, 0.05 M I_2 and 0.5 M 4-tertbutylpyridine (TBP) in acetonitrile where TBP acted as a binder molecule for anchoring dye to the nano-porous titania surface. Triphenylmethylphosphonium iodide (TPMPI) was synthesized by mixing an equimolar solution of triphenylphosphine (Ph_3P) and methyl iodide (CH_3I) in dry tetrahydrofuran (THF) under stirring condition till a white solid TPMPI separates out which was thoroughly washed with THF.

2.4. Dye Sensitized Solar Cell Assembly

In course of preparing the photo-anode the FTO coated TiO_2 and Ag-TiO_2 thin films were sensitized overnight with 1 mM ethanolic solution of N3 ($[RuL_2(NCS)_2].2H_2O$; L = 2,2′-bipyridine-4,4′-dicarboxylic acid) dye. The cathode was fabricated by electroplating PtNPs onto FTO glass from 1 mM H_2PtCl_6 (Arora Matthey, India) in H_2SO_4 solution under current density of 5 mA cm^{-2} using AUTOLAB 302N PG-stat, Eco–Chemie BV (The Netherlands). The anode and cathode were assembled together using Bynel (SX1170-60, 50 μm thick, Solaronix) as the sealant and heating at ~80 °C, followed by injecting the working electrolyte into the cell. The active area of the electrode was limited to 0.5 cm^2 by the sealing frame.

2.5. X-Ray diffraction and surface morphology

The morphology of the films was studied through SEM and TEM analysis deploying the respective instruments JEOL JSM-6700F FESEM and HRTEM, JEOL 2010F, Japan, with an accelerating voltage of 200 kV. The crystallinity of the surface was studied by employing Philips PW 1710, X-ray diffractometer using CuKα radiation of wavelength 1.542 Å. The X-ray machine was operated on 25 kV, 20 mA within the 2θ ranging between 20° and 80° with increment of 0.02°. The film thickness was determined gravimetrically using Metler-Toleodo digital micro-balance, [Model No.AB265-S], Switzerland and subsequently verified with Mitutoyo ABSOLUTE (No. 547-301) thickness meter. The measured thickness was of the order of 14.5 ± 0.5 μm.

2.6. UV-Vis, FT-Raman and XPS studies

Transmittance spectra for each of the TiO_2 and Ag-TiO_2 composite films were recorded within the range of 300–1100 nm using JASCO V-530 UV-Vis-NIR Spectrophotometer, Japan. The ceramic oxide films were further analyzed through FT-Raman spectroscopy within the Raman shift range 100–750 cm^{-1} using Spex double monochromator (model 1403) fitted with a holo graphic grating with 1800 grooves/mm and a cooled photo-multiplier tube (model R928/115) from Hamamatsu Photonics, Japan. Spectra Physics Ar^+ ion laser (model 2020-05) of 200 mW power was used to obtain excited radiation (514.5 nm) for acquisition time 0.5 sec. XPS studies were performed with the help of Omicron Multiprobe (Omicron Nano Technology, UK) spectrometer fitted with an EA 125 (Omicron) hemi-spherical analyzer, using a conventional Al-Kα radiation source operated at 150 W where pass energy of the analyzer was 50 eV for the survey scans and 40 eV for the individual line scans, in ultra high vacuum system maintaining base pressure at 1×10^{-10} mbar.

2.7. Electrochemical characterization and Photovoltaic performance of DSSCs

Electrochemical impedance spectroscopy (EIS) was carried out with the DSSC configuration, FTO (Ag-TiO_2)/Dye/I_3^-–I^- (NaI + TPMPI)/Pt–FTO, at room temperature under background white LED light source (simulated LED light soaker, Dyesol, Australia) assembled with electrochemistry workstation, AUTOLAB 302N PG-stat, Eco–Chemie BV (The Netherlands) and using NOVA-v1.10 software package. Nyquist plots were derived from the frequency dispersion impedance spectra by applying sinusoidal perturbation of 5 mV amplitude in the cell system over a frequency range of 100