



Combining Energy Conversion and Storage: A Solar Powered Supercapacitor



Remya Narayanan^a, P. Naresh Kumar^a, Melepurath Deepa^{a,*}, Avanish Kumar Srivastava^b

^a Department of Chemistry, Indian Institute of Technology Hyderabad, Ordnance Factory Estate, Yeddumailaram-502205, Telangana (India)

^b CSIR-National Physical Laboratory, Dr. K.S. Krishnan road, New Delhi-110012 (India)

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ABSTRACT

A solar powered supercapacitor wherein a plasmonic quantum dot solar cell (QDSC) sources the photocurrent for charging/discharging a conjoined supercapacitor based on multiwalled carbon nanotubes (MWCNTs) is demonstrated. Gold or Au fibers are integrated into a titanium dioxide/cadmium sulfide (TiO₂/CdS) electrode to yield a TiO₂/CdS/Au photoanode. The plasmonic effect of Au fibers is reflected in the higher incident photon to current conversion efficiency (IPCE = 55%) and an improved overall power conversion efficiency (3.45%) produced by the TiO₂/CdS/Au photoanode relative to the non-plasmonic TiO₂/CdS photoanode. A Janus type bi-functional electrode composed of MWCNTs on either face separated by glass is prepared and it is coupled with the TiO₂/CdS/Au electrode and another MWCNT electrode to yield the tandem solar powered supercapacitor. By channelling the photocurrent produced by the QDSC part, under 0.1 sun illumination, the capacitance of the symmetric supercapacitor, without the application of any external bias is 150 F g⁻¹ which compares well with reported values of electrically powered MWCNT supercapacitors. Our innovative design for a photo-supercapacitor offers a new paradigm for combining low cost photovoltaics with energy storage to yield a technologically useful device that needs nothing else other than solar energy to run.

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1. Introduction

Growing demands of cheap and effective methods for (i) converting solar energy to electricity and (ii) for electrochemical energy storage (for mobile devices and electric vehicles) are two linked requirements which have seldom been fulfilled by a single device. While for energy conversion, quantum dot solar cells have aroused significant research interest due to several attributes such as size dependent electronic structure, good environmental stability, low cost and solution processability [1–11], for energy storage, supercapacitors which require shorter charging times and deliver higher power densities compared to Li ion batteries, are useful for applications wherein a large spurt of power is required for a short span. Carbon based materials like mesoporous carbon, activated carbon, carbon fibers, multi-walled nanotubes and reduced graphene oxide nanosheets have been examined extensively as electrodes in electrical double layer

capacitors (EDLCs) owing to high surface area, excellent electrical conduction properties, good mechanical strength and chemical inertness [12–19]. Previously, the twain have met in a cell configuration employing a combination of a dye sensitized solar cell (DSSC) and a conducting polymer based supercapacitor [20,21]. Poly(alkyldioxythiophene) derivatives were used by the authors as charge storage materials [20,21]. In another report of note, a DSSC was combined with two different charge storage materials: (a) poly(3,4-ethylenedioxythiophene)/carbon nanotubes and (b) hydrated ruthenium oxide, and photocapacitors were successfully demonstrated [22]. In yet another study, a photocapacitor with a dye sensitized TiO₂ electrode was coupled with two activated carbon based charge storage electrodes, and a light driven self-charging process was shown [23]. A high-voltage photocapacitor with a three-electrode configuration, encompassing a dye-sensitized mesoporous TiO₂ electrode, two carbon coated electrodes, and two liquid electrolytes, acquired a charged-state voltage of 0.8 V and a high energy density as well [24]. In another study, a DSSC was combined with an electrochemical capacitor of hydrous ruthenium oxide electrodes and excellent performance characteristics were shown [25]. However, to the best of our knowledge, to

* Corresponding author.

E-mail address: mdeepa@iith.ac.in (M. Deepa).

date, an amalgamation of a quantum dot solar cell (QDSC) and a carbon based supercapacitor has hardly been reported. In such a configuration, the QDSC converts solar energy into current and this current is utilized for charging the supercapacitor. It is obvious that the solar cell should produce high photocurrents to induce charge separation in the supercapacitor. In the realm of photovoltaics, an effective strategy to increase efficiencies of DSSCs or hybrid solar cells involves the incorporation of metal nanoparticles (NPs).

Integration of plasmonic nanostructures with semiconductors increases the solar conversion efficiency [26]. Localized surface plasmon resonance (LSPR) are the coherent oscillations of charge density and electric field in metal NPs created by an incident field. At resonance, the charge oscillations generate a local electric field with a strength up to ~ 10 times the incident field and increase near-field scattering [27–29]. Small metal NPs (< 50 nm) primarily localize the electromagnetic field and large particles (> 100 nm) predominantly scatter the incident field in all directions [29]. In a plasmon/semiconductor assembly, solar energy conversion efficiency is improved via the following mechanisms: (a) enhancing the light absorption in the semiconductor by near-field and far-field scattering effects and (b) directly transferring the plasmonic energy from the metal to the semiconductor to induce the charge separation in the semiconductor, or by plasmon induced resonant energy transfer (PRET) via an insulating shell [29,30].

Metal NPs can also promote charge transfer by accepting electrons from the conduction band (CB) of the photoactive semiconductor, via Fermi level equilibration upon illumination. In the latter scenario, the open circuit voltage (V_{oc}) increases as the Fermi level of the wide gap semiconductor is pushed to more negative potentials (with respect to normal hydrogen electrode or NHE) and as a consequence the zero current potential increases. The roles of charge transfer and plasmonic effects in enhancing the power conversion efficiency of an $Au@TiO_2$ and an $Au@SiO_2$ assembly have been distinguished in an earlier report by Choi et al. [31]. In another study, for a solar cell with a photoanode composed of PbS QDs and Au plasmons, both short circuit current density (J_{sc}) and V_{oc} were higher than that of solar cells without Au plasmons; J_{sc} increased by 13% and the overall power conversion efficiency (PCE) amplified by 11% in the plasmonic device [32]. A cell with Ag plasmons surrounded by a TiO_2 shell and a N3 dye as the photosensitizer delivered a larger incident photon to current conversion efficiency (IPCE) compared to the dye only cell [33]. For a cell based on a $TiO_2/N719$ electrode enriched with $Au@SiO_2$ core/shell plasmons, a PCE of $1.65 \pm 0.32\%$ was achieved which was significantly higher than a PCE of $1.08 \pm 0.1\%$ attained for a cell without the plasmons [34]. The above survey illustrates that plasmonic solar cells can help realize substantial enhancements in photovoltaic performance.

Supercapacitors are typically low voltage devices, and the current produced by the plasmonic quantum dot solar cell herein is adequate for charging a supercapacitor (~ 0.5 V). Among supercapacitors, electrical double layer capacitors (EDLCs) undergo a non-Faradaic charge separation at the electrolyte/electrode interface wherein the electrode is typically a high specific surface area carbonaceous material like carbon nanotubes (CNTs) or activated carbon or graphene or carbon aerogels. However, the capacitance of activated carbons, despite a high surface area (usually ranging between 1000 to 2000 $m^2 g^{-1}$) is limited by the low mesoporosity and poor electrolyte accessibility. Similarly, although graphene based EDLCs yield high capacitances, but chemical reduction of graphene oxide to yield high quality non-aggregated reduced graphene oxide nanosheets involves repetitive washing/centrifugation steps, which is cumbersome. Multiwalled carbon nanotubes (MWCNTs) are therefore attractive for not only are they endowed with a large specific surface area and high electrical conductivity, but their hollow one-dimensional cores

provide a greater number of electroactive sites for ions to bind to, thus increasing the capacitance of the EDLC [35]. Carboxylate functionalization of MWCNTs is facile and the functionalized product can be easily deposited in the form of a film on conducting electrodes by electrophoresis. We chose MWCNTs as supercapacitor electrodes owing to a high electrical conductivity, which will allow rapid propagation of electrons and transfer especially at the $SnO_2:F/MWCNTs$ interface. MWCNTs also provide a large surface area which facilitates greater adsorption of ions from the electrolyte during charging, effectively leading to high capacitances. Furthermore, MWCNTs serve as a cheap alternate to the traditional but expensive Pt, as the counter electrode in a QDSC. MWCNTs have a favorable work function of 4.5 eV, and due to their intrinsic conductivity, can catalyze the electrolyte reduction at the FTO/MWCNT interface in the QDSC.

In the present report, a yet unreported photoanode architecture of $TiO_2/CdS/Au$ (fibers) was employed as the exciton generator. Acid functionalized MWCNTs (in the form of a Janus type electrode) were employed as the counter electrode for the QDSC and also as one of the electrodes for a symmetrical supercapacitor, thus yielding a three electrode integrated photovoltaic supercapacitor. The photocurrent produced by the plasmonic QDSC, upon irradiation, is channeled to the symmetrical MWCNT supercapacitor. The role of Au plasmons in improving the solar cell performance of the TiO_2/CdS photoanode was determined by absorbance, fluorescence quenching, lifetime analysis, Kelvin probe force microscopy (KPFM) and solar cell parameters. The supercapacitor performance was evaluated from photo-charging-discharging behavior, cycling stability and cyclic voltammetry. The ease and economy of fabrication coupled with the dual functions of energy conversion and storage opens up opportunities to combine different photoactive and ion storage materials for creating solar-powered supercapacitors, as they rely only on the sun's munificence and literally do away with the need for any other external electrical stimulus.

2. Experimental section

2.1. Preparation of Au fibers

The list of chemicals used and their sources are provided in supporting information. Au fibers were prepared using a previously reported method [36]. A solution of 20 mL of sodium citrate (0.025 M) and 0.2 mL of $HAuCl_4$ (0.00025 M) in deionized water was prepared. A mixture of two reducing agents was used: sodium citrate and sodium borohydride (the latter is introduced in the next step). Citrate is a non-toxic, milder reducing agent compared to the borohydride, and therefore better control over the Au nanostructures could be achieved by using a combination of two reducing agents. An ice cold aqueous solution containing $NaBH_4$ (0.01 M) and sodium citrate (0.025 M) was prepared in another beaker. 0.6 mL of the $NaBH_4$ /sodium citrate solution was added to the Au salt/sodium citrate solution while stirring. An orange red colored seed solution was formed and this "initial gold seed solution" was stored in a fridge for further use. The seed particles of gold are formed at this stage by the rapid reduction of the Au^{3+} salt into Au^0 by the stronger reducing agent, $NaBH_4$. To convert the nanoparticles into elongated structures, ascorbic acid and cetyl trimethylammonium bromide (CTAB) were used. Growth solution was prepared by mixing 15 mL of CTAB (0.2 M) and 15 mL of $HAuCl_4$ (0.0005 M) in deionized water. It was then distributed in two vials labeled as A, B and in a beaker labeled as C. The growth solution was distributed in such a way that A, B and C contained 2.25 mL each. Aliquots of 12.5 μL of an aqueous solution of ascorbic acid (0.1 M) were added to A and B, whereas to C, 125 μL of ascorbic acid (0.1 M) solution and 100 μL of concentrated nitric acid was also added. Ascorbic acid reduces the

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