Quantum dot solar cell utilizing optical properties of carbon nanotubes

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高知工科大学 博士論文

2017-03

http://hdl.handle.net/10173/1507
This dissertation focuses on an application of CNTs to improve an efficiency of quantum dot solar cells (QDSSCs) utilizing optical reflectance carbon nanotubes. The originality ideas were provided firstly to utilize the reflected light, total, diffuse, and specular optical reflectance of carbon nanotube (CNT) honeycomb structures. Secondly, the novel study is to investigate efficiencies improvement by the utilization of optical reflectance to improve the quantum dot sensitized solar cell (QDSSCs) efficiency, and to investigate CNT forests grown on stainless steel serving as a photoanode for CdSe/ZnS core/shell QDSSCs as a means of reducing the resistivity to improve photovoltaic efficiency.

The unique morphologies and structures of carbon nanotubes (CNTs) have received much attention for optical and electronic applications because CNTs have extraordinary photonic properties, high electrical current endurance, and mechanical stiffness. In addition, the morphologies of CNT forests can be modified to enhance charge generation, separation, and transport in optical-electronic applications. For modifying CNT forest morphologies, liquid or vapor treatment is a simple, economic method that provides a high yield. The liquid treatment of CNTs exhibits self-assembly, where one-dimensional material forms into three-dimensional micro or macro structures with various morphologies. The liquid and vapor treatment onto multi-walled CNTs (MWCNTs) exhibits the self-assembly of hierarchical networks to form honeycomb structures due to capillary forces arising during solution evaporation. The larger surface area of such honeycomb structures is expected to allow the efficient assembly of sensitized nanoparticles of quantum dots (QDs), which can serve as an electrode scaffold to capture and transport photo-generated electrons in solar cells. Additionally, the spacing in the structure of silicon solar cells with CNT honeycomb top electrodes allows higher transmission of light to photo-active parts of solar cells when light irradiation is perpendicular to the substrate. Moreover, wall-shaped condensed CNT films can serve as an “electron-carrying highway”, enhancing high conductivity to an electrode of solar cells. The total reflectance of randomly oriented CNT-compressed sheets is more than 80% for a CNT film thicknesses of 0.3–1 μm, while for high nanotube forests (300–500 μm in height) it is 1%-2% across a range from UV to mid IR (200–2000 nm). Yang et al. reported an extraordinarily low total reflectance of 0.045% for a mat of vertically aligned multi-walled carbon nanotubes (VA-MWCNTs) forests in a visible region at wavelengths of 457–633 nm. Theoretically, the reflectance of CNT forests can be explained by the fact that, for light incidence on a forest top surface of CNTs of small angle with respect to the CNT axis, electrons on the CNT body cannot couple with the electric fields, which provides a weak optical interaction between the CNT forests and normally incident light resulting in a lower total reflectance.

For photovoltaic applications, the optical properties of the materials are one of the most important parameters for achieving light enhancement. Recently, the reuse of the optical reflectance of existing light to significantly increase the efficiency in dye sensitized solar cells (DSSC) has been reported. It is expected that solar cells using CNTs can be designed so that the highly reflected light from the CNTs is absorbed by sensitizers, generating a larger number of electron-hole pairs.

In the first part, the aims are to study the relationship between the physical structure of CNT honeycomb structures and the total, diffuse, and specular reflectance of the CNT honeycomb structures. It can be summarized that this study investigated the controlling of cell area in a CNT honeycomb structure by a simple method of ethanol.
In the second part, the aims are to study the utilization of optical reflectance to improve the quantum dot sensitized solar cell (QDSSCs) efficiency, and to investigate CNT forests grown on stainless steel serving as a photoanode for CdSe/ZnS core/shell QDSSCs as a means of also improving photovoltaic efficiency. As mentioned in the first part, the extraordinary mechanical, chemical, and electronic properties of carbon nanotubes (CNTs) make them outstanding materials for energy applications. The modified CNT structure is expected to be a good material for use as a counter electrode or photomode with semiconducting quantum dots (QDs) in order to harvest a broader range of light from the ultraviolet (UV) to the infrared (IR). A significant increase in optical total reflectance using a structural modification of CNT honeycombs, which will increase the utility of CNT honeycomb structures in high-efficiency solar cells. QD-decorated CNTs exhibit efficient charge transfer from photoexcited QDs to the CNTs. QD sensitized solar cells (QDSSCs) have attracted considerable interest from researchers because their power conversion efficiency (PCE) may exceed the Shockley and Queisser limits. In particular, QDs can harvest a broad range of optical wavelengths by multiple exciton generation (MEG), thus improving the photovoltaic efficiency. Optical absorption by QDs fabricated from materials such as CdS, CdSe, and CdSe/ZnS is intrinsically tunable from the UV to the near-IR due to the particle-size dependence of the bandgap. A major advantage of QDs as light sensitizers compared with conventional dyes is that electron recombination is suppressed, thereby improving the efficiency of QDSSCs. One dimensional (1D) wires, of e.g., TiO$_2$, ZnO, and Si have been extensively used for electron transfer from QDs to electrodes. In particular, CNTs have arisen as a superior candidate 1D wire electrode material for QDSSC because of their large surface area, high conductivity, high aspect ratio, and chemical stability. Due to their excellent electrical and thermal conductivity, flexible metal substrates serving as a counter-electrode of DSSCs can reduce both the sheet resistance and production cost of solar cells. It was reported the PCE of QDs/Si coaxial nanowires on the gold (Au) sputtering metal electrode in QDSSCs shows 0.253%.

From the study, it was found that Multi-walled carbon nanotube (MWCNT) forests grown on a stainless steel substrate were used as a photoanode in CdSe/ZnS (core/shell) quantum dot (QD) sensitized solar cells (QDSSCs). QD-treated MWCNTs on the conductive metal stainless substrate showed a higher power conversion efficiency (PCE) of 0.015% than those grown on a doped silicon substrate with a PCE of 0.005% under AM 1.5 sunlight intensity (100 mW/cm$^2$). This higher efficiency can be attributed to the lower sheet resistance of 0.0045 $\Omega$/sq for the metal substrate than the value of 259 $\Omega$/sq for doped silicon. The relationship between the total reflectance of the as-prepared CNT photoanode and the PCE was investigated for CNTs of various heights and amounts of QDs. A QDSSC fabricated
using a CNT photo anode with a height of 25 μm showed the highest efficiency of 0.014% with the lowest total reflectance of 1.9%, which indicates a higher surface area of CNTs and a larger amount of QDs. The as-grown 25-μm CNTs combined with 25 mL of QDs in toluene solutions exhibited the highest PCE of 0.015%, due to the larger surface area of the CNTs and the higher light absorption from the large amount of QDs on the CNTs.

In conclusion, firstly the relationship between CNT honeycomb structures and the total, specular, and diffuse reflectance was investigated. CNT honeycomb structures with average cell areas of smaller than 30 μm² show a higher total reflectance. Secondly, the first QDSSCs with photoanodes of MWCNTs on a metal substrate, and found that the PCE for such QDSSCs on stainless steel substrates was three times higher than those on a low-resistivity (0.15 Ω·cm), doped silicon substrate. Also, the lower total reflectance QD-treated CNT forest of 25-μm height achieved a higher PCE. The as-grown 25-μm CNTs combined with 25 mL of QDs solutions exhibited the better PCE.