APPLICATION OF CARBON QUANTUM DOTS FOR DYE-SENSITIZED SOLAR CELLS

Ivan Nikolov, Alexandre Loukanov, Anatoliy Angelov

Laboratory of Engineering NanoBiotechnology, Department of Eng. Geoecology, University of Mining and Geology "St. Ivan Rilski" – Sofia, Bulgaria

ABSTRACT. The emergence of quantum dot-sensitized solar cells (QDSSCs) has provided an alternative way to harvest sunlight for energy conversion. Efficiency of a QDSSC depends on the fabrication method of the quantum dots, morphology of the photoanode, type of electrolyte used and the choice of the counter electrode. It is therefore, imperative for engineering of materials and optimization of the fabrication method for the improvement of QDSSCs performance. As a new class of fluorescent carbon nanomaterials, carbon quantum dots(CQDs) possess the attractive properties of high stability, good conductivity, low toxicity, environmental friendliness, simple synthetic routes as well as comparable optical properties to quantum dots. CQDs can be used as photosensitizer in dye-sensitized solar cells and the photoelectric conversion efficiency is significantly enhanced. A novel synergistic photosensitized mechanism is proposed for the obtained hybrid CQDs /TiO_2 energy conversion system. It is based on a design of new generation C-dots with higher corrosion stability, charge transportation and controlled photocatalytic properties for oxygen reduction reaction, especially in terms of band gap energy, chemical composition and surface modification. The advantages of C-dots as a promising alternative of the expensive and unsustainable Ru-complex sensitizers are enhanced power conversion efficiency, good photoinduced electron transfer ability, environmental friendliness and lower cost of fabrication. This is a new direction for improving the efficiency of solar cells.

Keywords: quantum dots, carbon nanomaterials, photosensitizer, solar cells.

ПРИЛАГАНЕ НА ВЪГЛЕРОДНИ КВАНТОВИ ТОЧКИ В РАЗВИТИЕТО НА ОРГАНИЧНИТЕ ФОТОЧУВСТВИТЕЛНИ СЛЪНЧЕВИ КЛЕТКИ

Иван Николов, Александър Луканов, Анатолий Ангелов

Лаборатория инж. нанобиотехнология, Катедра „Инженерна геоекология", Минно-геоложки университет „Св. Иван Рилски" – София, България

РЕЗЮМЕ. Появата на квантова точка-чувствителни слънчеви клетки (QDSSCs) е осигурило алтернативен начин за улавяне на слънчевата светлина и преобразуването и в енергия. Ефективността на QDSSC зависи от метода на производство на квантови точки, морфология на фотоанода, типа на използвания електролит и изборът на обратния електрод.Това е наложило инженеринг на материали и оптимизация на метода на производство за подобряване на производителността на QDSSCs. Като нов клас от флуоресцентни въглеродни наноматериали, въглероден квантови точки (CQDs) притежават атрактивни свойства на висока стабилност, добра проводимост, ниска токсичност, грижата за околната среда, прости начини за синтез, както и съпоставими с оптичните свойства на квантовите точки. CQDs могат да бъдат използвани като фоточувствителени елементи в бои-чувствителни слънчеви клетки и фотоелектрическата им ефективност на преобразуване е значително подобрена. Фоточувствителен механизъм е предложен за получаване на хибридна CQDs / TiO2 система за преобразуване на енергия. Тя се основава на дизайна на новото поколение С-точки с по-висока стабилност на корозия, такса транспорт и контролирани фотокаталитичните за редукция на кислород, особено от гледна точка на лента празнина енергия, химичен състав и за промяна на повърхността. Предимствата на С-точки като обещаваща алтернатива на скъпите и неустойчиви Ru-сложни сенсибилизатори са подобрени енергийна ефективност преобразуване, добър електронен трансфер, грижата за околната среда и по-ниски разходи на производство. Това е нова посока за подобряване на ефективността на соларните клетки.

Ключови думи: квантови точки, въглеродни наноматериали, соларни клетки.

Introduction

Carbon quantum dots (C-dots) have recently emerged as viable alternatives to traditional semiconductor quantum dots because of their facile and low cost synthesis, long term colloidal stability, and low environmental and biological toxicity (Li et al., 2012). The compatible surface chemistry, good solubility in polar solvents and extensive optical absorption throughout the visible and near-infrared wavelength regions render C-dots as potentially useful sensitizers for photovoltaic applications (Mirtchev et al., 2012). N-doped C-dots have attracted much attention because the doping can induce new unique physical and chemical properties of carbon. In this study, we report that N-doped C-dots can combine with rutile TiO_2 and form hybrid nanocomposites with enhanced photocatalytic activities under visible light irradiation (Zhang et al., 2013). We propose a new synergetic photosensitized mechanism for operation of the dye-sensitized solar cell. A preliminary study shows that under sun illumination (AM 1.5), the open circuit voltage and fill factor values reach 0.44 V and 42 %, respectively, achieving a power conversation efficiency of 0.11 % in the proof-of-concept TiO_2 based solar cell device. N-doping lowered the work function of carbon nanodots, which was responsible for enhanced photocatalytic activity of C-dots/TiO_2 and better quantum dot-sensitized solar cell (QDSSCs) performance.

Experimental Procedures

Preparation of hybrid nanomaterials as energy conversion systems

Carbon nanodots were prepared according to our previous report (Loukanov et al., 2016).Citric acid (1 g) was diluted with 10 ml distilled water and ethylenediamine (0.2 ml, 0.18 g) was injected to the solution under vigorous stirring. The clear transperant solution mixture became a yellowish brown gum after microwave irradiation for 3 minutes at microwave oven (750 W). The obtained yellowish brown solid was dissolved in Milli-Q and dialyzed against pure water through a dialysis membrane. The diazotization reaction was performed in ice bath at temperature between 0 and 5 °C. While 20 mL of concentrated hydrochloric acid was diluted with about 60 g of crushed ice to which 2.5 g sodium nitrite dissolved in 10 mL of water was added. 5 – 7 mL of such prepared nitrous acid (blue color) was added to 20 mL solution of 5-amino–fluorescein with concentration 5 mg/mL (the color of precursor solution was changed to orange – yellow). The prepared diazonium ion was slowly added dropwise to 20 mL solution of naked CDs (with concentration 20 mg/mL) at alkaline pH (pH ~ 9). The color mixture was changing from light yellow to dark red. The obtained Fluorescein–N=N–CDs were purified from the reaction mixture by centrifugation and washed with acetone (as described above). 200 mg carbon nanodots modified with diazofluorescein (or Fluorescein–N=N–CDs) were dissolved in 2 mL MilliQ water. The prepared aqueous solution was injected in a triple flask, which contains 1 mmol metal chloride (iron or copper) in 50 mL solution of ethylene glycol under Ar atmosphere. The reaction mixture was refluxed for 4 hours at ~ 180 – 190 °C. The color changed from a dark black to a bright yellow in approximately two hours. The resulting solution was then cooled down to room temperature and analyzed. The obtained [Fluorescein–N=N–CDs]Me^{2+} nanoparticles were purified from the reaction mixture by centrifugation and washing with acetone.

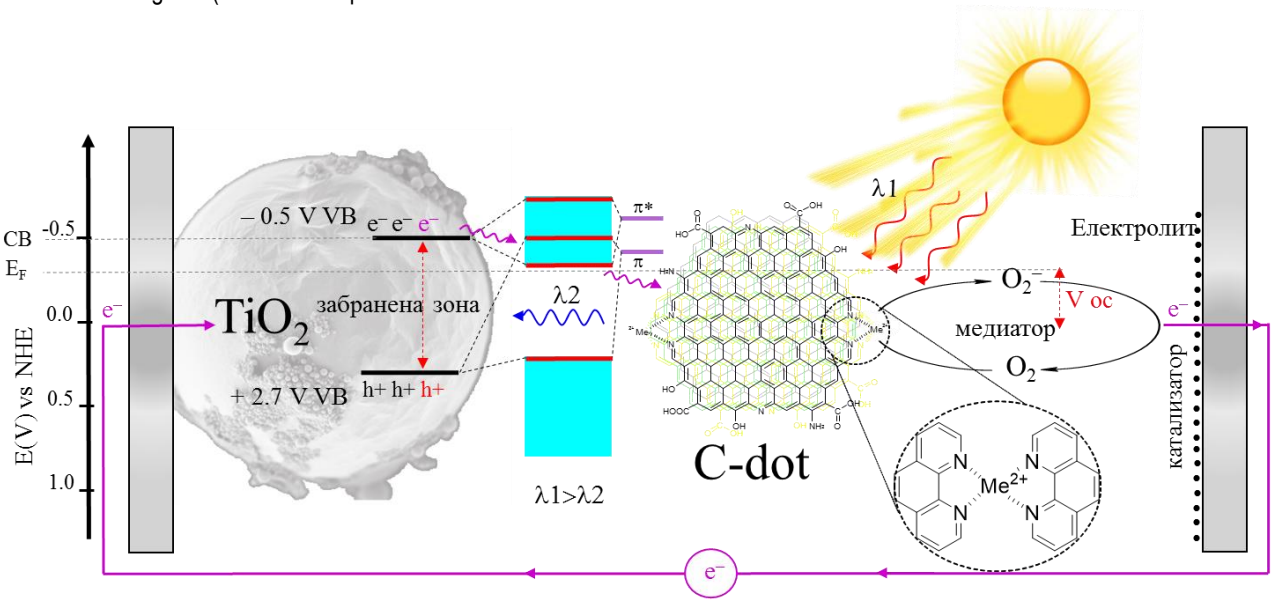

Fig. 1. Schematic drawing of the designed quantum dot-sensitized solar cells showing the principles of operation

Fabrication of quantum dot-sensitized solar cells

The as-prepared TiO_2 electrode and 22 mg of C-dots were put into 50 ml of distilled water. Then they were hydrothermally treated at 100 °C for 4 h. After that, the C-dots sensitized TiO2 electrodes were rinsed with absolute ethanol for several times and dried under vacuum. The liquid electrolyte contained: (i) 0.6 M of tetrapropylammonium iodide, 0.1 M of I_2, 0.1 M of KI, 0.5 M of 4-tert-butylpyridine in acetonitrile, or (ii) aqueous buffer solution saturated with oxygen at alkaline pH. QDSSCs were assembled by dropping a drop of liquid electrolyte above the C-dots sensitized TiO_2 porous film electrode. A graphite counter electrode was placed above it. The two electrodes were clipped together and an adhesive was used as sealant to prevent the electrolyte solution from leaking. The device structure of QDSSCs is shown on Fig. 2. *I-V* measurements were obtained by using a solar simulator (Newport) with an AM 1.5 G filter under an irradiation intensity of 100 mW cm^{-2}. The light intensity was calibrated using a standard silicon photovoltaic solar cell. The active cell area was 0.15 cm^2.

Result and discussion

Principles of operation of the classical dye-sensitized solar cell

The luminescence studies on dyes adsorbed onto semiconductor electrodes have shown that the excited states could be efficiently quenched on these surfaces. With semiconductors, oxidation of the dye takes place through transfer of an electron from a molecule's excited energy level to the conduction band of the semiconductor. In an electrochemical cell using semiconductor as bulk electrodes, the excited-state charge injection manifests itself as photocurrents, measurable quantitatively under anodic polarization. Exposure of the classic dye-sensitized solar cell assembly to visible light lead to a sequence of reactions. Figure 2 shows schematically these processes. We first consider the reactions that take place at the anode, where the absorption of the light by the dye S leads to formation of its electronically excited state S*:

$$S + h\nu \rightarrow S^* \text{ (photoexcitation)}$$

The molecule in the excited state can decay back to the ground state or undergo oxidative quenching, injecting electrons into the conduction band of TiO_2.

$$S^* \rightarrow S + h\nu' \text{ (emission)}$$

$$S^* \rightarrow S^+ + e\text{-cb } (TiO_2 \text{ charge injection})$$

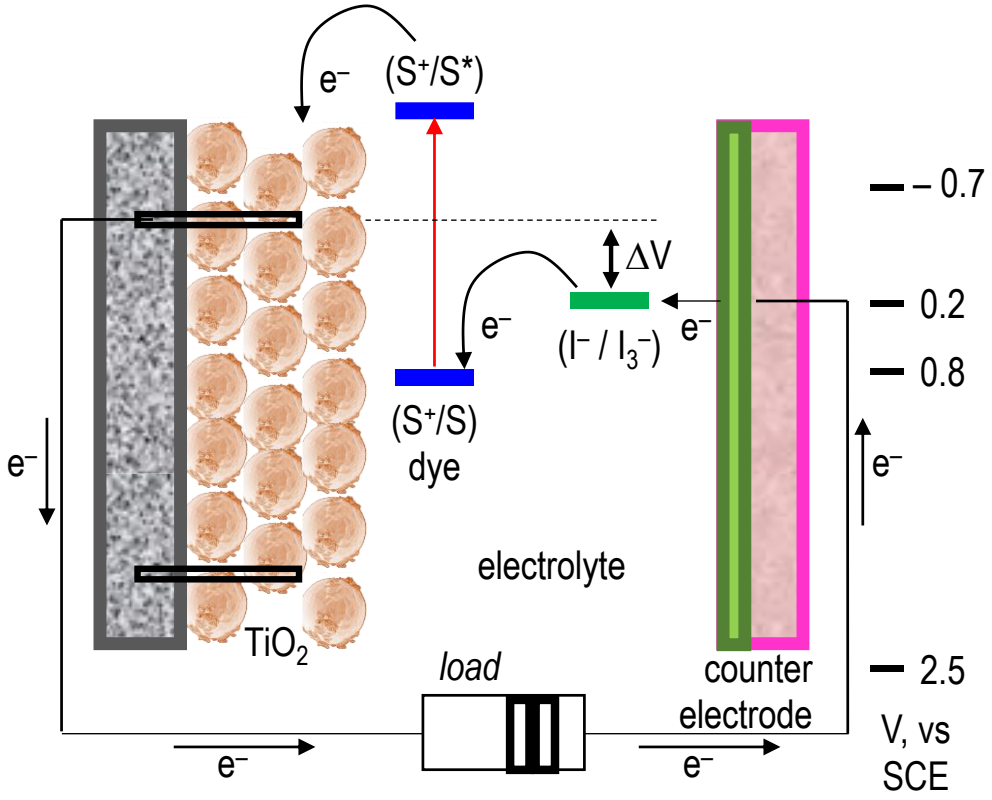

Fig. 2. Schematic drawing of a dye-sensitized solar cell showing the principles of operation

The injected electrons travel through the mesoporous network of particles to reach the back-collector electrode to pass through the external circuit. The oxidized dye is reduced rapidly to the ground state by the donor (iodide) present in the electrolyte:

$$2S^+ + 3I^- \rightarrow 2S + I_3^- \text{ (regeneration of S)}$$

In the absence of a redox mediator to intercept and rapidly reduce the oxidized dye (S^+), recombination with the electrons of the titania layer takes place, without any measurable photocurrent:

$$S^+ + e^- (TiO_2) \rightarrow S \text{ (recombination)}$$

The electrons reaching the counter-electrode through the external circuit reduce in turn the oxidized iodide (I^-) so that the entire sequence of electron transfer reactions involving the dye and the redox mediator (I_2-I^-) is rendered cyclic:

$$I_3^- + 2e^- \rightarrow 3\ I^- \text{ (regeneration of } I^-)$$

If cited reactions alone take place, the overall effect of irradiation with sunlight is to drive the electrons through the external circuit, i.e. direct conversation of sunlight to electricity.

Key efficiency parameters of a dye-sensitized solar cell

The spectral response of the dye-sensitized solar cell depends on the absorption properties of the dye. Characterization of the cell depends on a number of experimentally accessible parameters, including the photocurrent and photopotentials measured under different conditions (open and closed circuit, under monochromatic light or sunlight illumination): I_{oc}, V_{oc}, I_{sc} and V_{sc}. The term *incident photon-to-electrical conversion efficiency* is a quantum-yield term for the overall charge-injection collection process measured using monochromatic light (single wavelength source).

Exploiting the excellent optical properties of C-dots, we demonstrated the design of hybrid TiO_2/C-dots complex to harness the use of the full spectrum of sunlight (based on the upconversion luminescence properties of C-dots). Upon illumination of TiO_2/C-dots the hybrid nanocomposite absorb visible light, and then emit shorter wavelength light (325 to 425 nm) via upconversion, which in turn excites TiO_2 to form electron/hole (e^- / h^+) pairs as shown on Fig. 3. Consequently, N doping is responsible for enhanced photocatalytic acitivity of C-dots/TiO_2. The reason is that N doping can lower the work function of carbon nanomaterials.

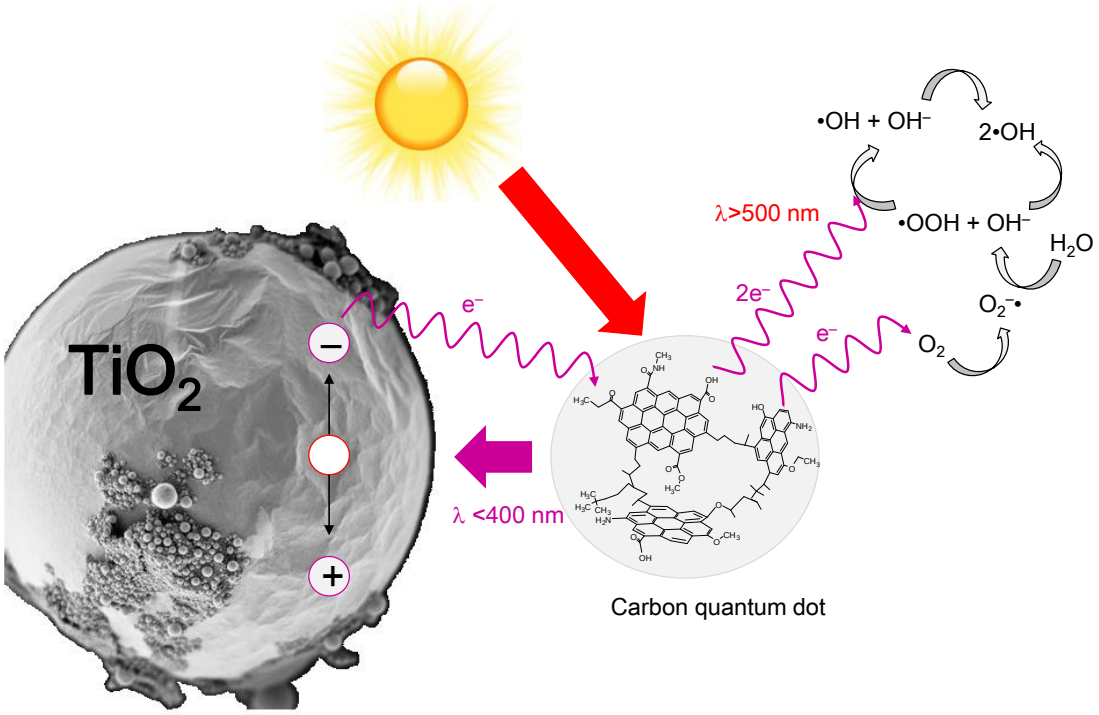

Fig. 3. Proposed photooxidation mechanism of C-dots/TiO_2 hybrid nanocomposite as energy conversion system

The lower work function of N-doped C-dots will produce much barrier between C-dots and TiO_2. When excited by visible light, photogenerated electrons more efficiently transfer to CB of TiO_2 and subsequently convert into other reactive oxidative species. As a result, C-dots/TiO_2 displays higher photocatalytic activity than the control experiment. Therefore, N doping lowers the work function of C-dots, which is probably main reason for enhanced activity.

The solar-cell current voltage and associated parameters show that all hybrid nanocomposite improve the efficiency compared to the uncoated (TiO_2) devices. QDSSCs device has the highest efficiency owing to a combination of relatively high open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}) associated with relatively low series resistance (R_s) and high shunt resistance (R_{sh}), as it is shown in Table 1:

Table 1.
Solar-cell parameters of C-dots sensitized TiO2 solar cells derived from J-V characteristics

Sample	J_{sc} [mAcm^{-2}]	V_{oc} [mV]	FF	PCE [%]	Rs [kΩ]	Rsh [kΩ]
Uncoated	0.083	15	0.34	0.0004	0.27	0.30
C-dots	0.690	440	0.42	0.1120	0.85	9.18

The power conversion efficiency of 0.112 % for the QDSSCs device is the best one obtained in our experiments.

Conclusion

We have developed C-dots/TiO_2 quantum dot-sensitized solar cells, which showed a synergetic power conversion activity, due the doping of nitrogen in the nanoparticles. This is attributed to the lower work function, induced by N doping. So, the performance of the device is depended on the absorbance and functional groups on the carbon nanodot surface.

References

Li, H., Kang, Z., Liu, Y., Lee, S-T., (2012) Carbon nanodots: synthesis, properties and applications. J. Mater. Chem. 46, 24230-24253.

Loukanov, A., Sekiya, R., Yoshikawa, M., Moriyasu, Y., Nakabayashi, S., (2016) Photosensitizer-conjugated ultrasmall nanodots as multifunctional fluorescent probes for bioimaging. Journal of Phys. Chem.

Mirtchev, P., Henderson, E., Soheilnia, N., Yip, C., Ozin, G., (2012) Solution phase synthesis of carbon quantum dots as sensitizers for nanocrystalline TiO_2 solar cells. J. Mater. Chem. 22, 1265-1269.

Zhang, Y. et al., (2013) N-doped carbon quantum dots for TiO_2-based DSSC, Nano Energy, 5, 545-552.

The article has been recommended for publication by department “Engineering geoecology”.