In situ decoration of gold nanoparticles on TiO_2/cellulose nanocomposites: An application toward dye-sensitized solar cells on paper substrates

Helena Aguilar Ribeiro, Christiane Santos, Ana Catarina Duarte

LEPAE, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
haguilar@fe.up.pt

Abstract

Dye-sensitized solar cells (DSCs) have long been envisaged as a cost-effective alternative to conventional inorganic solid state photovoltaic technologies (PV), but further optimization of the cells performance and manufacturing processes for large scale production is still underway. The major processes occurring in a DSC include photoexcitation of dye molecules, charge generation and electron percolation within a mesoporous metal oxide semiconductor, and electron scavenging by the electrolyte ionic species [1,2]. Recent studies suggest the use of one-dimensional morphologies such as nanotubes, nanowires and fibers in an attempt of improving electron transport in the semiconductor, also providing a larger surface area for dye adsorption and enhancement of the light harvesting efficiency. Among these alternatives, photoanodes made of cellulose fibers embedded with conductive nanoparticles and photosensitizers, and with a much lower tortuosity of the pores compared to mesoporous nanoparticulated films, apparently offers a decisive advantage. In fact, with the advent of printed electronics, paper has emerged as a focus area for researchers developing innovative paper-like substrates for lightweight, flexible, electronic devices such as DSCs [3,4]. The obvious motivation of this work was to demonstrate the potential of incorporating light-harvesting nanostructures and titania nanoparticles into cross-linked cellulose fibers, and use this new material architecture as a semiconductor for DSCs. Nanosized TiO_2 particles were deposited and grafted on cellulose fibers surface by using a sol-gel method at low temperature (<100 ºC) and titanium isopropoxide as the TiO_2 precursor. The as-prepared paper-like semiconductor was sintered at moderate temperatures (<200 ºC) and sensitized with N719 ethanol dye solution. Complete DSCs were characterized by means of electrochemical impedance spectroscopy to elucidate how composition and topography of the composite semiconductor impact on its global performance. Under one-third Sun - typical lower-light, real-world light conditions, tens of micro $A \cdot cm^{-2}$ were obtained with DSCs made of commercial bleached *Eucalyptus globulus* kraft paper. Although this was a very promising outcome, the low electric conductivity of the paper based substrates is still envisaged as one of the main bottlenecks toward PV and printed electronic applications. To further enhance the conductivity of paper, a sort of nanostructured carbon materials could be employed but that would limit the optical properties of the semiconductor [5]. Conjugation of gold nanoparticles (AuNP) with titania and cellulose fibers became the focus of this research, as these quantum sized particles may play two important roles: (i) preservation/enhancement of the semiconductor optical properties in the UV-visible light wavelength; for small monodispersed gold quantum dots the surface plasmon resonance phenomena causes an absorption of light similar to that of N719 ruthenium based dye, with a characteristic narrow absorption band observed at 530 nm [6]; (ii) promotion of electric contact among titania aggregates [7] and cellulose fiber cross-linking [8].

Electrodes made from commercial printing paper samples, in which titania nanoparticles had previously been grafted to cellulose fibers by the *in situ* precipitation method described above, were dipped into a solution of AuNPs stabilized with tannic acid and sodium citrate for 24h. After dipping, the electrodes were rinsed and dried at room temperature and used as photoelectrodes for DSCs. The performance of DSCs fabricated with AuNP@TiO_2 decorated commercial bleached kraft paper grafted on FTO (F:SnO_2) conductive glass was assessed by means of electrochemical impedance spectroscopy and photocurrent density vs. photovoltage characteristic data. Results are in line with previous studies reporting high adsorption of gold nanoparticles on paper, attributed to the interaction between the hydroxyl groups of the tannin acid-metal ion complex and cellulose through hydrogen bonding and minor Van-der-Wall interactions [8].

At the present time, research is being oriented to solve scaling-up issues related to substrate film adhesion and foster the development of stable, high-performance devices for energy conversion and smart packaging solutions.

Acknowledgements: The authors acknowledge the Portuguese National Science Foundation (FCT) for financial support under the contract PTDC/EQU-EQU/101397/2008 and Programa Ciência 2007. LEPAE, CEFT, LCM and DEMM at FEUP are greatly acknowledged for the much appreciated facilities.

References

[1] M. Shalom, J. Albero, Z. Tachan, E. Martinez-Ferrero, A. Zaban, E. Palomares, The Journal of Physical Chemical Letters, **1** (2010), 1134.

[2] K. Tvrdy, P.A. Frantsuzov, P.V. Kamat, PNAS, **108**, (2010), 29.

[3] B. Wang, L.L. Kerr, Solar Energy Materials & Solar Cells, **95** (2011), 2531.

[4] K. Fan, T. Peng, J. Chen, X. Zhang, R. Li, Journal of Materials Chemistry, **22** (2012), 16121.

[5] L. Hu, J.W. Choi, Y. Yang, S. Jeong, F. La Manti, L.-F. Cui, Y. Cui, PNAS, **51** (2009), 21490.

[6] S.A. Aromal, D. Philip, Physica E, **44** (2012), 1692.

[7] D. Tsukamoto,Y. Shiraishi, Y. Sugano, S. Ichikawa, S. Tanaka, T. Hirai, Journal of the American Chemical Society, **134** (2012), 6309.

[8] A. Higazy, M. Hashem, A. ElShafei, N. Shaker, M.A. Hady, Carbohydrate Polymers, **4** (2010), 890.

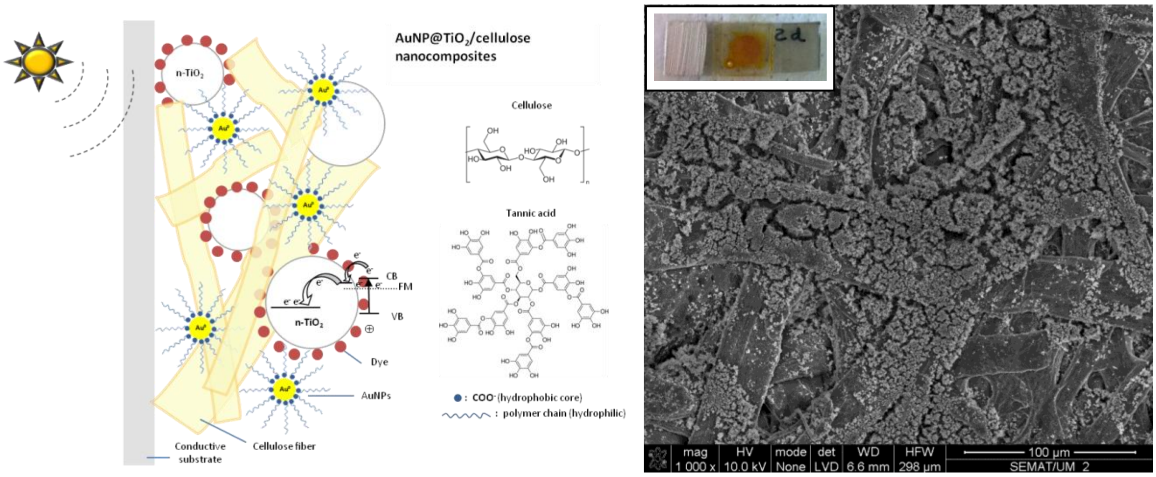

Figure 1. Schematic diagram of the paper-based semiconductor grafted on fluor-doped tin oxide transparent conductive glass (FTO); SEM image of titania surface coated cellulose fibers: the inset shows a dye-sensitized solar cell made with a AuNP@TiO_2/Cellulose nanocomposite electrode.