Preparation of a Nanostructured Composite of Titanium Dioxide and Polythiophene: New Routes Towards 3D Heterojunction Solar Cells

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Design of a 3 dimensional hybrid solar cell

In 1991 Prof. Grätzel and his coworkers have shown that a solar cell, consisting of nanoporous titanium dioxide and covalently attached ruthenium complexes, exhibits an efficiency of around 10%. This is a large step forward in the utilisation of organic dyes in combination with wide-bandgap semiconductors photovoltaic devices. Since that time much effort has been directed towards development of the similar nanostructured heterojunctions that can function without liquid electrolyte. One of the possible solutions is the use of dyes that are not only the lightabsorbing and electron-injecting species, but also can transport holes. Electrons diffuse through the n-type semiconductor to the front electrode and the remaining holes migrate through the p-type organic layer to the back electrode. Although organic substances have in general much lower hole mobilities than inorganic



compounds, semiconducting polymers, like polythiophenes and polyphenylene vinylenes, have been used successfully in combination with C_{60} molecules. Designing a solid-state heterojunction is a tedious task, as intimate, nanorange contact is required as well as control over morphology, structure, and layer thickness. A one-step process, in which both the n-type metal oxide and the p-type semiconducting polymer are deposited on the substrate in the form of a nanostructured network, is an elegant method to achieve the desired 3-dimensional heterojunction.

Technique

Nebulized Vapour Deposition (NVD) is a novel technique, which enables the formation of nano-sized particles of metal oxides (like TiO₂) and the simultaneous built-up of a polymer network. Titanium isopropoxide (TTIP) is ultrasonically agitated in a flask and an aerosol of small droplets is formed above the surface.



Fig. 1: a) Schematic representation of a nanostructured heterojunction. b) Set-up of Nebulized Vapour Deposition.

Using an inert carrier gas, these droplets are led through a glass tube where they are heated to form TiO₂ particles. The decomposition reaction to TiO_2 is spontaneous at temperatures above 100°C, but to ensure that stoichiometric anatase TiO₂ is formed, oxygen is added. The TiO₂ particles are deposited on a substrate, which is placed on a spin coater at the end of the tube. At the same time drops of a polythiophene (PT)solution are applied onto the substrate. The substrate is rotating at high speed, making sure that both TiO₂ particles and polymer drops are equally spread and form an interpenetrating network. By variation of parameters like gas flow, furnace temperature, precursor concentration, and polymer addition interval, the crystal structure, particle size, and percolation of the deposited blend can be influenced.



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В

Fig. 2. a) Top view of deposited TiO_2 particles. Small particles with diameters of ~50 nm form agglomerates of several µm. b) Crosssection of the same sample. The film thickness is about 4 µm.

Synthesized solar cells

To investigate whether or not the TiO_2 particles, produced with NVD, are suitable to use in a solar cell, first a conventional dye sensitized cell has been constructed using a Ru-complex iodine/iodide (Ru353) and an electrolyte. This cell shows a clear photovoltaic effect and a photocurrent action spectrum, which indicates that the Ru-dye injects in the TiO₂. Also a polymer-based cell is produced by spincoating PT on top of a film of TiO₂ particles. The current-voltage characteristics of this cell are compared to a cell constructed from a flat-film TiO₂, with a spincoated PT layer with similar optical density. The nanostructured cell shows a higher photocurrent, but a fairly low fill factor. The next step in the process is to simultaneously deposit TiO₂ and PT on a sample. Experiments are currently directed towards this objective.



Fig.3. a) Photocurrent action spectrum of a $\sim 4 \,\mu m$ thick dye sensitized TiO₂ layer immersed in I_2/I^- electrolyte. b) Current-Voltage characteristics of: (\blacksquare) a ~100 nm thick spincoated layer of PT on flat TiO_2 (~100 nm thick, deposited using Chemical Vapour Deposition) and (o) spincoated PT on a $\sim 3 \mu m$ layer of nanoparticles TiO₂, deposited using NVD. In both cases the illumination direction is through the conducting oxide using white light and a 360 nm high-pass filter.