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Abstract of PhD thesis:

Development and characterization of dye- and semiconductor sensitized solar cells based on structurally organized titanium dioxide

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The main scientific goal of the project was to proof a feasibility of creation of a working TiO_2 nanotube-based solid state photovoltaic device and this is the first attempt of such kind. The work deals with development and fundamental studies of physical and chemical properties of metal oxide-based solar cells relying on a combination of nanostructured working electrode (WE) material, organic light harvesting dye and organic solid state hole transport material (HTM). This system is based on already existing principle implemented in a “classical” dye sensitized solar cells (DSSC), i.e. separation of light harvesting process from charge transport in selected materials due to a difference in electrochemical potentials. However, a new strategy with an emphasis on selection of component materials based on their chemical stability, architecture on a nanometric scale and unique electronic properties of TiO_2 nanotubes allowed to partially overcome the existing limitations of established approach (e.g. exclusive use of mesoporous TiO_2 electrodes) and showed a promising research direction.

The first stage of my work was focused on a development of TiO_2 nanotube working electrode (WE) suitable for the use in a photovoltaic device. A TiO_2 WE with a nanotubular morphology (TNT) was grown by anodic oxidation of Ti thin film deposited on a transparent conducting substrate (TCO), in a viscous fluoride ion-containing electrolyte. Ti thin films of thickness from 1 to 3 μm were sputtered at a high temperature (550°C) in high vacuum conditions on FTO glass substrate. It was established that a high temperature of FTO($\text{SnO}_2 \cdot \text{F}$)

substrate during Ti plasma deposition is a crucial condition for successful growth of TiO₂ nanotube array via anodic oxidation and adhesion of TNT to the substrate.

Homogenous TNT films with desired single tube dimensions (90 nm internal, 110 nm external diameters) and anatase crystal phase were prepared by a combination of anodization parameters tuning and high temperature post treatment. Ti thin film anodic oxidation is a complex process involving three distinguished stages. The current density – time dependences at constant potential were used for monitoring of anodic oxidation process in fluoride-containing ethylene glycol solution. Changes in such curves depending on voltage, temperature, concentration etc. gave important information about mechanism of titanium dioxide nanotube growth and allowed establishing optimum preparation conditions for synthesis of free standing TiO₂ nanotubes on transparent conducting glass substrate. It was found that decrease of anodization temperature to 5°C was essential to minimize thermal damage to the growing TNT array caused by a passing current. The process with a rate of TNT growth of ~20 nm/min was performed until a formation of optically transparent highly homogenous TNT layers of a thickness from 2 to 6 μm was complete.

The third step of TNT preparation was a high temperature annealing of the film to enhance desired crystallinity of anatase and remove impurities. A new method of removal of irregular top porous layer on TNT array, with the help of directed Ar ion beam was demonstrated. At the completion of this stage of the work it was, hence, possible to prepare defect-free homogenous TiO₂ arrays on a transparent conducting substrate with a choice of several discrete array thicknesses.

The second stage of the work was focused on creating a complete TNT-based liquid electrolyte and solid state photovoltaic devices and their characterization. An organic high extinction coefficient dye (D35) was chosen as a primary light harvesting material for the photovoltaic cell. 0.1 mM ethanol solution of such a dye was normally used as a deposition bath to cover the TNT substrate. The choice of this particular dye was justified by its well-established performance in liquid electrolyte mesoporous TiO₂ DSSCs, reported stability against aggregation on a substrate surface as well as strong covalent bond attachment to TiO₂ via deprotonation of –COOH functional group. It was also important to estimate the relative D35 loading capabilities of mesoporous and TNT films of the same thickness and electrode working area (1 cm²) for several discrete electrode thicknesses. For adsorption of D35 onto TiO₂ substrate the times of submersion and rinsing (to remove an excess of dye) were 20 h and 30 min, respectively. To remove the dye molecules from the TiO₂ surface, a substrate with

adsorbed dye was placed in the solution of 0.01 M TBAOH in DMF for 40 min. Spectroscopic absorbance measurement of the desorbed dye solution showed that in spite of much more developed surface areas of meso- vs TNT electrode judging from surface roughness consideration, the TNT electrode had smaller, but comparable amount of D35 and even surpassed a mesoporous substrate at 6 μm film thickness.

To assemble a working solid state DSSC, an organic solid state hole transport material such as Spiro-MeOTAD (2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spiro-bifluorene) was brought in contact with TNT/dye interface by deposition from a saturated chlorobenzene solution by spin-coating. 100-200 nm thick Ag contact was evaporated to finish the device assembly.

Optical properties of the materials and their morphology in the bulk and interface were characterized by UV-VIS spectroscopy, scanning and transmission electron microcopies and X-ray diffraction. A complete solar cells power conversion efficiency and incident-photon-to-electron conversion efficiency (IPCE) were measured with a set-up consisting of solar spectrum simulating light source, a monochromator and computer-controlled sensitive source meter. A power conversion efficiency of prepared sDSSC devices was compared to that with a classical Co – bipyridyl complex. A system was also probed by a photo induced spectroscopy (PIA) to estimate the quality of HTM infiltration into the TNT array. This was done by comparing a steady-state concentration of charged species (D35 cation, oxidized Spiro-MeOTAD) in a photoactive medium by their characteristic absorption on the opposite sides of the WE. The results demonstrated lower power conversion efficiency and IPCE of a solid state 4 μm TNT based device in comparison with a Co – bipyridyl complex liquid electrolyte device (0.6 % vs 2% for power conversion and 20% vs 60% at 550 nm for IPCE, respectively) which can be explained by none-complete infiltration of Spiro-MeOTAD material through the TNT array and a large over-standing HTM thickness which increased a series resistance of the cell. The results demonstrated that HTM infiltration and pore-wetting remain crucial parameters in improvement of solid state DSSC performance. The obtained I-V curves were used to calculate fill factor, open circuit voltage and short circuit current for each system.

In a third stage of the project an alternative light harvesting material (inorganic quantum dot nanocrystals (NCs) such as PbS) was prepared and characterized by a femtosecond laser transient absorption (TA) studies. PbS NCs were prepared from a solution containing synthesis precursors and polar organic ligands (oleic acid), to obtain a stable suspension of charged colloid particles in toluene. Resultant PbS NCs were shown to have a

narrow size distribution (about 4 nm) using laser scattering experiment. Electrophoretic deposition of nanoparticles onto the surface of TNT WE created an attached nanoparticle layer along the length of single TNT. A femtosecond TA spectrometer was used to characterize a charge injection from excited state of PbS NC into conduction band of TiO₂. A sample was excited by a laser at 420 nm and probed at 600 nm. Two components in the kinetics of decay of main excited state were distinguished for PbS/TNT system: fast τ_2 and slow τ_1 , whereas only one component was observed for pure PbS NPs in toluene solution. This suggested that a fast electron injection (charge transfer) from a dominant excited state of PbS NP is occurring on tens of ps timescale. This direction of the studies will be pursued further.

To summarize, it was demonstrated that it is feasible to create a working solid state TNT array-based photovoltaic cell, but such a cell clearly needs further optimization in such parameters as HTM infiltration, overstanding layer thickness and post-preparation treatment. The project improved scientific understanding of physical and chemical processes at the interfaces between components of geometrically organized metal oxide-based solid state solar cells.