226029

1. FINAL PUBLISHABLE SUMMARY REPORT

This section normally should not exceed 2 pages.

This is a comprehensive summary overview of results, conclusions and the socio-economic impacts of the project. The publishable report shall be formatted to be printed as a stand alone paper document. This report should address a wide audience, including the general public.

Please ensure that it:

- *Is of suitable quality to enable direct publication by the REA or the Commission.*
- *Is comprehensive, and describes the work carried out to achieve the project's objectives; the main results, conclusions and their potential impact and use and any socio-economic impact of the project. Please mention any target groups such as policy makers or civil society for whom the research could be relevant.*
- *Includes where appropriate, diagrams or photographs and the project logo, illustrating and promoting the work of the project.*
- *Provides the address of the project Website (if applicable) as well as relevant contact details.*

Attached documents: Include where appropriate, diagrams or photographs and the project logo, illustrating and promoting the work of the project.

The objectives of the project for the first half term of its duration (from 28-11-2008 until 28-05-2010) were, to produce NPs by laser ablation of bulk target materials in liquids, characterize the NPs and the colloidal solutions, introduce the NPs into polymers for the fabrication of polymer-NPs nanocomposites and characterize the resulting nanocomposites. The materials out of which NPs were produced as well as the polymers for the formation of nanocomposites were chosen among the materials which are of current interest for the fabrication of hybrid organic solar cell devices.
As has already been pointed out in the original grant proposal, the method of NPs synthesis by laser ablation in liquids was chosen in this work due to the fact that it allows a direct, one-step functionalization of the produced NPs by choosing appropriately the liquid in which ablation takes place in combination with the laser ablation parameters. Other advantages of the method include the possibility of tuning the NPs sizes and size distribution by adjusting appropriately the ablation time duration (in combination again with the laser ablation parameters) due to the effect of the interaction of the ablating laser beam with the produced NPs, the avoidance of the use of toxic and pyrophoric chemical precursors for the synthesis of nanomaterials (environmentally friendly “green” method) and thus the possibility of synthesizing surface-ligand free NPs and the easiness of the method, overall.
For the synthesis of NPs by laser ablation of bulk target materials in liquids an experimental set-up was used consisting of a quartz cuvette inside of which the target material was fixed. The cuvette was filled with liquid and sealed. The laser beam was focused onto the target surface and the material was ablated forming NPs within the liquid which was surrounding the target. The cuvette was fixed onto a translational stage and either the sample was moved under a stationary

beam or the beam (using a scanning galvanometer) was moved onto the surface of a stationary sample following a certain pattern. Using this system NPs out of Si and II-VI semiconducting materials such as CdTe and ZnO were produced.

The produced NPs colloidal solutions were first characterized by UV-vis spectrophotometry in order to obtain information about the average size of the produced NPs. From the absorption spectrum for Si NPs the band gap of Si NPs was calculated equal to 1.2 eV which corresponds to a blue shift of 0.08 eV from the band gap of 1.12 eV of bulk Si due to the effect of quantum confinement. From relations which describe the theoretical dependence of the band gap of Si NPs versus their diameter, the above blue shift implied NPs with diameter of d≈15.8 nm. The onset of absorption at ~800 nm in the absorption spectrum from CdTe NPs was consistent with absorption from an ensemble of NPs which have a maximum diameter of ~20 nm while a broad band centered at ~345 nm in the spectrum from ZnO NPs implied an ensemble of NPs with an average diameter of ~6 nm.

From Transmission Electron Microscopy (TEM) images of NPs ensembles from droplets of the colloidal solutions dried out onto carbon coated grids it was confirmed that the NPs for all materials were spherical. From the TEM images the size distributions of the produced NPs were determined and they were found to follow log-normal functions with median diameters d and geometrical standard deviations σ of: 20 nm, 0.81, 7.1 nm, 1.5 and 5.4 nm, 0.5 for Si, CdTe and ZnO NPs respectively. Under the present conditions of laser ablation, a rather wide Si NPs size distribution is obtained including particles with diameters from ~5 up to ~200 nm. The larger median diameter (of d≈20 nm) which is deduced from the TEM images as compared to the diameter (d≈15.8 nm) estimated from the spectrophotometry data, might be due to the fact that very small particles are not easily distinguished in the TEM images because they do not appear with high enough contrast and thus they are not included in the statistical distribution. This results in an overestimation of the average NP diameter from histograms calculated from TEM images. A quite narrow size distribution is obtained for CdTe NPs while the percentage of ZnO NPs with diameters above ~20 nm is estimated to be less than 10 % of the total number of the produced NPs in the solution. The Si NPs produced in DIW were partially amorphous. X-Ray Diffraction (XRD) patterns confirmed the crystal structure of cubic (zincblende) for CdTe NPs and Wurtzite for ZnO NPs. Having fully characterized the produced NPs, a precise control of their properties in relation to the conditions for their synthesis had been achieved.

The NPs colloidal solutions after formation were directly mixed with the polymers and the solutions were stirred using a magnetic stirrer for a few hours and also ultrasonicated at specific times. This simple method for the fabrication of polymer-NPs nanocomposites seemed to work very well for the production of nanocomposites characterized by a uniform dispersion of the NPs within the polymer matrix as it was confirmed by images of the finally produced composite thin films. To this contributed to a large extend, also the fact, that because the NPs are surface ligand free and with the minimum amount of surface defects as they are synthesized (due to the unique characteristics of the method of synthesis of NPs by laser ablation in DIW that no chemical precursors are needed for nanomaterials synthesis as it was emphasized previously), the NPs formed chemical bonds directly with the polymer which resulted to the polymer acting as a surfactant to the NPs.

The nanocomposites were deposited by spin coating as thin films onto suitable substrates (glass or polyethylene terepthalate (PET) which is commonly used as a substrate in flexible organic electronic devices (OEDs)). We had considered so far the polymer PEDOT:PSS (poly(3,4-ethylenedioxythiophene) oxidized with poly(4-styrenesulfonate)) which is commonly used as the anode electrode (hole injection/transport layer) in OEDs. We had incorporated into the polymer matrix ZnO NPs synthesized by laser ablation whose properties were already been characterized and achieved a tuning of the electrical properties of the polymer and in particular an increase of its electrical conductivity by almost twice. The surface morphology of the resulting composite thin films was characterized by Atomic Force Microscopy (AFM) imaging. Films spin-coated from the polymer exhibited the characteristic surface morphology of PEDOT:PSS films consisting of grains (PEDOT-rich regions) and large areas among them which appear almost featureless (PSS-rich regions). A distinctly different surface morphology was observed for the film spin-coated from the nanocomposite. Its surface was characterized by larger size grains. The AFM images of the nanocomposite films can provide information about the changes of the microscopic structure of the polymer which are induced by the incorporation into it of the NPs. The change of the surface morphology of the PEDOT:PSS film is due to conformational changes of the macromolecular polymer chains from a coil conformation to a linear or expanded-coil conformation induced by the ZnO NPs. The optical properties of the nanocomposite thin films were characterized by Spectroscopic Ellipsometry (SE) in the UV-vis and with Raman spectroscopy. Theoretical relations based on the Bruggemann Effective Medium Approximation (BEMA) were fitted to the experimentally measured ellipsometry spectra. For the case of the film spin-coated from the nanocomposite, the optical response of the organic and inorganic parts have been modeled by the use of the Tauc-Lorenz oscillator model. From the SE spectra the thicknesses of the films were determined. By using the four probe Van der Pauw method the electrical conductivities of the nanocomposite films were measured equal to ~300 S/cm as compared to ~168 S/cm for the pure polymer without any NPs. In the Raman spectra taken from nanocomposite film a band at 1128 cm^{-1} was detected which is due to the 2LO phonon mode from the ZnO NPs and confirmed the presence of NPs within the polymer matrix. Further analysis of the Raman spectra in the region around the band corresponding to the symmetric $C_\alpha=C_\beta$ (-O) stretching mode of the PEDOT thiophene ring (around 1446 cm^{-1}) confirmd that the observed increase of the conductivity of the polymer was due to the transformation of the resonant structure of the polymer upon incorporation of the ZnO NPs, from a mixture of benzoid and quinoid in the polymer to a mostly quinoid in the nanocomposite.

The work carried out for the project had significant and important societal impacts. In particular the method of synthesizing NPs by laser ablation avoids the use of toxic, pyrophoric and hazardous chemical precursors which are traditionally used for the synthesis of NPs by chemical methods. This establishes the method as an environmentally friendly method thus making a significant contribution towards the adoption of a “green” technology for nanomaterials synthesis which is one of the most desirable objectives of any newly incoming technology. Also the method of the synthesis of NPs by laser ablation is an easy, fast and straightforward method for NPs synthesis which also allows the direct, one-step functionalization of the produced NPs and these features are meant to indicate reduction of labour time, equipment operational costs, energy saving and solvent waste, characteristics which have important economic impact especially in the potential utilization of the technology in an industrial environment.
The web site of the project is: http://omalanp.webs.com/