Growth and characterization of hybrid (HoGO/P3HT) graphene-based nanostructures for photovoltaic (PV) applications.

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Abstract. Herein, we present a comparative study between nanostructures of poly(3-hexylthiophene) (P3HT), Holmium-Graphene Oxide (HoGO) nanocomposite and hybrid HoGO/P3HT thin-film nanostructures in terms of structural, morphological and spectroscopic properties. Specifically, the graphene based GO nanostructure was functionalized with rear earth ion Ho(III) to improve its mobility. Furthermore, semiconducting P3HT nanostructure was successfully grown with HoGO nanocomposite creating hybrid HoGO/P3HT nanostructure for energy materials. The nanostructures were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), (FTIR) and UV/VIS/NIR spectroscopy. The interaction between HoGO and HoGO/P3HT nanostructures is evidenced through substantial variations in nanoparticle morphologies. FTIR results provided the evidence of the presence of different types of carbon functionalities in the nanostructures. From the absorption spectra, growth of hybrid HoGO/P3HT nanostructure broadened the absorbance with a slight decrease in %. These nanostructures open a promising direction on growth of hybrids for photovoltaic applications because of their interesting optical properties.

Keywords: Hybrid, thin-film, nanocomposite, nanostructures, photovoltaics.

1. Introduction
For many years, intense scientific research has been performed on renewable energy materials that would replace conventional fossil fuels. The search for renewable and environmentally friendly energy sources is continuously increasing. As a result, many types of photovoltaic cells such as silicon, organic dyes, conducting polymers and graphene etc. as well as their combinations have been developed and tested [1]. Hybrid organic-inorganic thin-film nanostructures especially organic semiconductors come in as materials of interest for tackling energy challenges we facing globally. In the class of hybrid nanostructures one of materials of interest is organic conducting polymers because they possess various chemical structures.

Semiconducting polymers gained more interest because it is easy and cheap to process them at large scale from solution, provided they have impressive optoelectronic properties. Polythiophenes, in particular poly(3-hexylthiophene) (P3HT), are the most versatile representatives of polymer semiconductors investigated for various applications such as solar cells, supercapacitors and field-effect transistors [2,3]. It has been well established that tuning the surface morphology of this class of polymers with functional layer of nanomaterials has a significant impact on the performance of...
fabricated devices. However, it remains a challenge to determine charge transportation due to the complex semi-crystalline microstructure which consists of crystalline and amorphous domains. One way to improve charge transport is to make use of new materials with large surface area as active components. In this context, graphene is the most suitable candidate, the large surface area of which could be used to accept transported charges. In the previous research outputs, conducting polymers and graphene have been synthesized separately and mixed together in the solution to form composite structure [4, 5], but due to re-stacking property of graphene oxide layers the performance of photovoltaic devices was poor. Then we considered developing thin-film nanostructures where we’ve got GO mixed with Holmium (Ho) to create HoGO nanocomposite. Ho is a rare earth ion known to exhibit several interesting properties such as large magnetic moments and luminescence. The latter are shown in photostable upconversion nanoparticles, where energy transfer between two elements (e.g., ytterbium and erbium) give rise to multicolor luminescence [6]. Ho is within class of elements that possess unique optical, catalytic and magnetic properties due to the unique configuration of their 4f electrons. Ho (III) possess one of the highest magnetic moments of all elements, but of interest to our study is its spectroscopic characteristics. Introducing these atoms into a different matrix can lead to a material that shows multiple interesting effects. This means, its presence can greatly prevent the charge recombination of photo-induced electrons and holes in semiconductors and enhance photocatalytic activity and photosensitivity.

Our work paves the way to growth of hybrid HoGO/P3HT nanostructure leading to design of devices as potentially efficient for PV applications. Structural, morphological and optical properties were probed to clarify functionalization and interaction between the layers of nanostructures. The interaction between hybrid HoGO/P3HT nanostructures is important in the development and design of new solar cells devices.

2. Experimental

2.1. Materials Preparation

Preparation of P3HT is similar to the one we stated in our previous report [7]. For the preparation of GO, we have adopted the modified Hummers method presented by Khenfouch et. al. [8]. Upon preparation of Holmium (Ho) solution in 50 ml of distilled water we added 0.1g NaOH, the solution was stirred for 10 min until NaOH was completely dissolved. After that, a solution of 0.5g of Holmium (III) Nitrate Ho(NO$_3$)$_3$ in 40 ml of distilled water was prepared and stirred using a magnetic stirrer for 30min. Later, a volume of 10 ml from the NaOH solution, was mixed with 40 ml from the Ho(NO$_3$)$_3$ solution followed by heat treatment in an oven at 90 °C for 24 hours. The inclusion complex for making HoGO nanocomposite was prepared by mixing the solutions in the molar ratio 1:1 Ho:GO and stirred for 30 min by ultrasonication. For all samples under investigation, 1.2 x 1.2 cm$^2$ glass substrates were cleaned successively in deionized water, ethanol and acetone for 15 min prior coating. The P3HT solution was preheated to 50 °C for 15 min prior coating, in order to prevent polymer pre-aggregation and gelation in solution [9]. Hybrid thin-film nanostructures were prepared by drop casting solutions on glass slide substrates. Right after deposition, thin-film nanostructures were dried in an oven at 50 °C for period of 2hrs to remove residues.

2.2. Materials Characterization

The phase and purity of thin-film nanostructures were examined by X-ray diffraction in Reflection (Bragg-Brentano geometry) by a Rigaku Smart Lab diffractometer with CuKa (1.5418Å) radiation. Morphological study was done using the Field Emission Scanning electron microscope (FE-SEM) (Shimadzu model ZE-SSX-550 Superscan). FTIR PerkinElmer spectrometer in the scan range 400 to 4000 cm$^{-1}$ was used to probe chemical bonding. The optical absorbance of the thin-films in the UV to visible region (250-800 nm) were performed with (PerkinElmer Lambda 1050 UV/VIS/NIR Lambda) spectrometer equipped with an integrating sphere.
3. Results and discussion

3.1. XRD analysis

Figure 1 presents the XRD patterns of nanostructures, P3HT, HoGO and HoGO/P3HT. The XRD diffraction pattern of P3HT reveals an amorphous basis dominated by (100) peak at ~5.7 ° corresponding to its well-known diffractions from literature [7]. Additionally, there are other diffraction peaks represented with asterisk (‘’) that can be attributed to the glass substrate. The HoGO nanocomposite presented glass substrate peak at ~8.7 ° which is also observed in P3HT and at ~10.3 ° there is an emerging diffraction indicating the existence of GO with couple of small development of Ho phase. In the case of hybrid HoGO/P3HT nanostructure, the diffraction patterns become broader suggestive of decrease in crystallinity. Zhao et. al. [10] indicated that crystallization of P3HT is hampered by the crystalline entities when interacting with other nanostructures leading to less ordering of the semiconducting moieties.

![XRD spectra of P3HT, HoGO and HoGO/P3HT nanostructures.](image)

3.2. SEM analysis

In Figure 2(a) we have SEM image of pristine P3HT nanostructures showing clusters of small spherical particles. It can be seen that the distribution of particles with respect to the substrate is not uniform throughout the film. This is caused by the substrate being highly sensitive to the polymer film thickness [11]. The clustering symbolizes that π-stacked aggregates are oriented and distributed in an amorphous matrix. It is well explained in literature that surface morphology of regioregular P3HT is highly affected by its parameters such as molecular weight, regioregularity and polydispersity [12, 13]. Figure 2(b) presents morphology for HoGO nanocomposite wherein we observed some wrinkles from GO sheets and rod-like structures representing the inclusion of Ho³⁺ ions. The SEM image in Figure 2(c) for hybrid HoGO/P3HT nanostructure indicated a relatively smooth surface and small islands. This shows that diffusion was undertaken between P3HT and HoGO leading to internal and surface interaction. Our results agree with statement by Tian et. al. [14] that organic compounds including both polymers and small molecules have more compatibility and have been widely used as components to tune the morphology.
3.3. FTIR analysis

Figure 3 shows the FTIR spectra helpful for determining various vibrational frequencies of P3HT, HoGO and HoGO/P3HT nanostructures in the range 4500-500 cm\(^{-1}\). In all nanostructures we observed carbon peak at \(~2364\) cm\(^{-1}\) coming from environmental CO\(_2\) because it is hygroscopic. The spectrum for regioregular P3HT exhibits principal vibration bands at \(~671\), \(~819\), \(~1035\) and \(~1307\) cm\(^{-1}\) indicating aromatic out of plane C-H vibration band, which is the characteristic of 2,5-disubstituted-3hexylthiophene for rr-P3HT chain conformation \([15]\). Other C-H vibration band is seen at \(~1460\) cm\(^{-1}\) which is associated with symmetric stretching vibration as well as aliphatic C-H stretching bands at \(~2856\) and \(~2924\). Furthermore, there’s a weak band associated with C=O stretching vibration at \(~1750\) cm\(^{-1}\) verifying the presence of ester group and it appears to be the most pronounced for hybrid HoGO/P3HT nanostructures. HoGO nanocomposite only revealed weak bands located at \(~2000\) and \(~2171\) cm\(^{-1}\) corresponding to the oxygen containing groups on the surface. Main changes were observed at lower side of FTIR spectra for hybrid HoGO/P3HT nanostructure where four strong characteristic adsorption peaks appear at around \(~1241\), \(~1362\), \(~1436\) and \(~1750\) cm\(^{-1}\), respectively. These peaks correspond to C-H vibration band which indicates partial decomposition of the thiophene \([16]\). We observed \(~3267\) cm\(^{-1}\) peak indicating water absorbed on the surface of P3HT and this vibration band is not applicable in HoGO and HoGO/P3HT. The significant reduction in vibrational frequencies observed in hybrid HoGO/P3HT nanostructure may be due to oxygenation at the interface.
3.4. UV/Vis/NIR analysis

Figure 4 represents absorption spectroscopy measurements, which is helpful for determination of degree of intra and interchain order within thin-film nanostructures containing P3HT. Firstly, pristine P3HT have slightly better absorption in the region 300-600 nm. The UV-vis spectrum of HoGO nanocomposite has a lower absorption compared with P3HT with well-defined shoulders except the 574 nm. The growth of hybrid HoGO/P3HT nanostructure enhances the absorption and there is better enhancement in the 600-800 nm region. Furthermore, the absorption spectrum of HoGO and HoGO/P3HT took the same shape as evidence of interaction with the rebuilt 574 nm absorption band of pristine P3HT on hybrid HoGO/P3HT nanostructure. This is because when the thin-film is completely dried, the arrangement of organic materials does not change. Some researchers indicated that absorption peaks tends to shift to the blue or red region when the interchain interaction between organic materials is changed [15, 17]. However, we observed no wavelength shift in the absorption spectra indicating that the interchain interaction is not responsible for improved absorption. We assign the absorption enhancement to the increase in internal reflection caused by modified arrangement of organic materials in thin-films. The improved absorption in 600 - 800 nm for hybrid HoGO/P3HT nanostructures may be due to highly delocalized electron rich and few charges formed along the \( \pi \)-conjugated thiophene backbone upon growth of nanostructure [18].
4. Conclusion

It was feasible to grow thin-film nanostructures of hybrid HoGO/P3HT. Through the XRD results we can declare that the synthesized nanostructures revealed phases of P3HT, HoGO and HoGO/P3HT. The surface morphology of hybrid HoGO/P3HT nanostructure became very smooth with some tiny islands and there was no indication of spherical, rodlike and nanosheets observed in P3HT and HoGO before growing film onto another. The evidence of chemical interaction between thin-film nanostructures is seen from changes observed in FTIR stretching/vibrational modes. From optical study the nanostructures present a broader absorption for the hybrid over a larger spectral range towards IR region which will enhance the performance of devices. These finding are useful in the fabrication of graphene based hybrid nanostructures for PV applications.

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