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Assessment of the Potential of Polymer/HDI-GO Nanocomposites for Use in Organic Solar-Cells †

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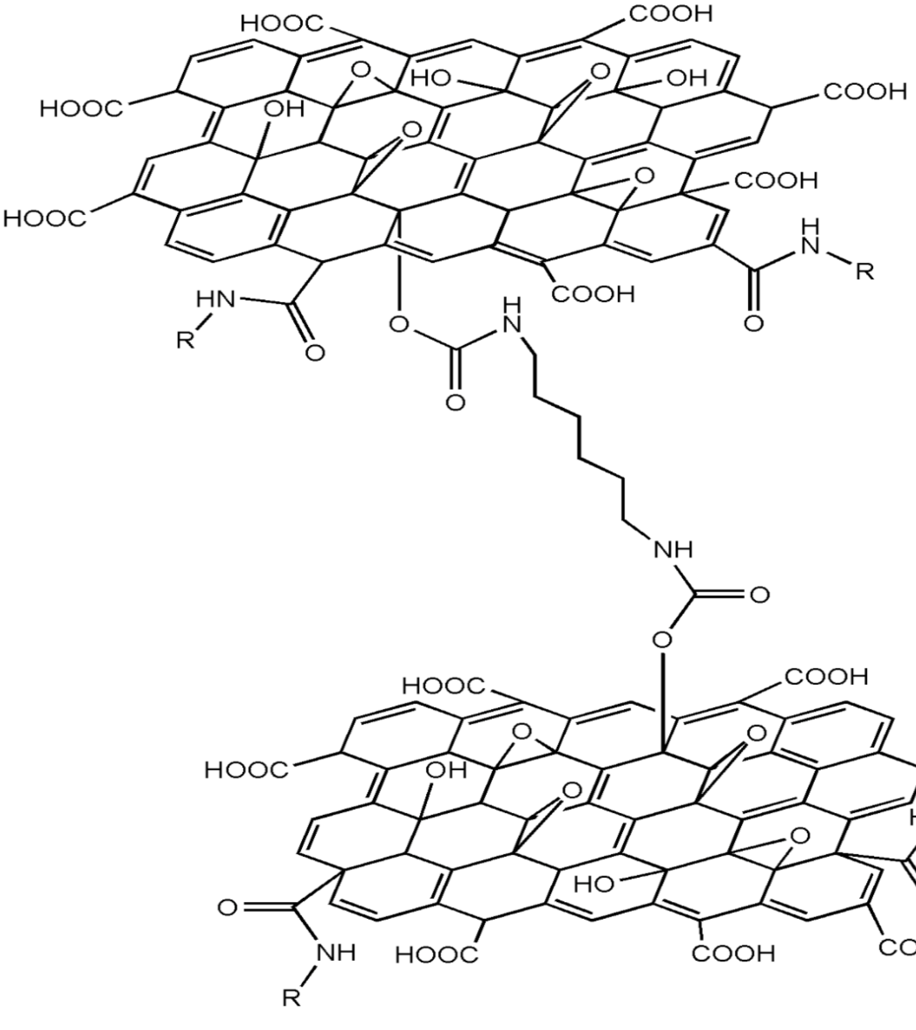
Abstract: Conducting films comprising conducting polymers and carbon nanomaterials have gained a lot of interest for applications in several fields, including transparent electrodes, supercapacitors, light-emitting diodes (LEDs), polymer solar cells (PSCs), and so forth. One of the main motivations is the replacement of costly oxides and degradable materials, like indium tin oxide (ITO). On the other hand, graphene oxide (GO) has emerged as an ideal filler to reinforce polymeric matrices owing to its large specific surface area, transparency, flexibility, and very high mechanical strength. Nonetheless, functionalization is required to improve its solubility in common solvents and expand its practical uses. In this work, the potential of polymer nanocomposites based on hexamethylene diisocyanate (HDI)-functionalized GO (HDI-GO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS) for use as active layers (ALs) or interfacial layers (IFLs) in PSCs has been assessed. Conventional deposition techniques applied to thin films were tested for the developed nanocomposites. Deposition methods included drop and spin casting, where different type of substrates, as clean glass and glass/ITO were tested. The results of deposition essays were analyzed by atomic force microscopy (AFM) and UV-vis spectroscopy. In addition, thermal evaporation was tried with the aim to obtain homogeneous layers. The layers obtained by drop casting showed poor film quality, with large aggregates. On the other hand, spin coating lead to layers not fully wetting the substrate. New synthesis procedures for the nanocomposites and/or alternative treatments of substrate surface will be investigated in the future to optimize their composition and properties (i.e., transparency) and improve their suitability for use in PSCs.

Keywords: graphene oxide; conducting polymers; nanocomposites; hexamethylene diisocyanate; organic solar-cells; deposition

1. Introduction

Conducting polymers are materials with a wide range of applications, such as light-emitting diodes (LEDs) [1], supercapacitors [2], transparent electrodes [3], polymer solar cells [4–10], and so forth. The combination of conducting polymers with graphene-based materials has also proved to be suitable for specific applications in some fields [11]. In polymer or organic solar cells, the typical structure involves costly oxides and degradable materials, like indium tin oxide (ITO) as a transparent electrode, but the recent tendency is to avoid ITO due to indium scarcity [12]. Graphene oxide (GO) has become an ideal filler to enhance the properties of polymeric matrices in different layers and different kind of cells [13,14], but its poor solubility in common solvents requires improvements using functionalization methods. Previous works presented different approaches for GO functionalization and its possible applications [15–22].

In this work, the potential of nanocomposites based on the mixtures of hexamethylene diisocyanate (HDI)-functionalized GO (HDI-GO)/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)(PEDOT:PSS) for use in organic solar cells, as an alternative to ITO or as an interfacial layer to assist on charge transport at the interface with ITO (as a secondary hole transport layer, HTL), has been assessed. The chemical structure of HDI-GO is shown in Scheme 1. The most typical deposition techniques employed in the preparation of organic solar cells, the characterization of the samples using UV-visible spectroscopy and AFM measurements, as well as the evaporation of samples to obtain homogeneous thin layers are described in this paper.



Scheme 1. Hexamethylene diiscocyanate-functionalized graphene oxide structure.

2. Materials and Methods

2.1. Reagents

PEDOT:PSS pellets (ratio of 1:2.5, $d_{25\,^{\circ}C} = 1.911$ g/cm^3), H_2SO_4, $KMnO_4$, P_2O_5, $K_2S_2O_8$, and H_2O_2 were acquired from Sigma-Aldrich. Graphite powder was obtained from Bay Carbon, Inc. For the synthesis of HDI-GO, triethylamine (TEA, >98%, $M_W = 101.193$ g/mol) and hexamethylene diisocyanate (HDI, >99%, $M_W = 168.196$ g/mol) were purchased from Acros Organics. The HPLC grade organic solvents used in the essays were acquired from Scharlau S.L. (Barcelona, Spain). The deionized water was produced with a Milli-Q-Water-Purification-System. All the chemicals were employed as received.

2.2. Synthesis of GO and HDI-GO

The preparation of GO was carried out using Hummers' method from graphite powder as reported in previous works [19]: firstly, graphite powder was heated with P_2O_5 and $K_2S_2O_8$, and later deionized water was added; the product was filtered and then mixed with $KMnO_4$, H_2O_2 and H_2SO_4. The final product was purified by centrifugation, followed by several cycles of purification with H_2O_2/H_2SO_4 washing, bath ultrasonication, and finally washed with deionized water followed by vacuum-drying.

The synthesis of HDI-GO was achieved by applying the procedure described in previous works [19], which can be summarized as: (1) GO functionalization step using HDI as reagent and TEA as catalyst, added dropwise at 60 °C under Ar atmosphere, followed by stirring overnight (12 h). (2) preparation of HDI-GO samples with different functionalization degree (FD) to study their effect on the deposition process: (a) 1:1:1 (FD of 3.12%, named as HDI-GO4), and (b) 1:1:1 with a previous ultrasonic tip treatment (5 min) (FD of 17.20%, named as HDI-GO5).

2.3. Deposition of HDI-GO and HDI-GO/PEDOT:PSS Films

HDI-GO samples were dispersed in different solvents (NMP, 2-propanol and DMSO) at a concentration of 5 wt% and the dispersions were stirred to achieve a good dispersion; this fact is very important since photovoltaic device preparation requires very homogeneous dispersions to avoid imperfections in the layer surface. Then, the dispersions were deposited by two different methods: drop casting and spin coating. The samples were deposited onto glass substrates, except some spin coating essays that employed glass/ITO substrates.

Drop casting method consists in the dropwise addition onto the substrate surface until the whole surface is covered. In our samples, a thermal annealing step was applied to dry the samples.

Spin coating deposition involves the use of a speed-regulated rotative support where the substrate to be covered is placed. The substrate is hold using a vacuum pump, and subsequently, the solution is added and the rotation of the substrate is started.

2.4. Instrumentation

The thermal annealing of drop casted and spin coated layers was carried out with a conventional heating plate. The spin coating was performed using a spin coater. UV-visible spectra were recorded using a Cecil 2700 spectrophotometer. The AFM measurements were obtained using a Nano-Observer–Model 5100 microscope.

3. Results

3.1. Layer Deposition

The dispersions obtained presented the tendency to get aggregated after a small time of no use, so a previous sonication cycle is recommended before the employment of solution if they are not prepared at the moment of the essay.

The HDI-GO/PEDOT:PSS samples obtained by drop casting onto glass resulted on little transparent layers to be employed either as HTL before ITO layer or in between ITO and the photoactive layer [23,24], considering DMSO and NMP solvents. Furthermore, a clear phase separation between HDI-GO and PEDOT:PSS was observed, which suggests a very heterogeneous layer deposition. These two facts, opacity and heterogeneity, are not compatible with the requirements for HTL layers, i.e., transparency in the visible spectral region and homogeneous deposition. Regarding HDI-GO4 and HDI-GO5, the samples showed higher transparency in the visible than the samples with PEDOT:PSS, although some agglomerates were present; further, the substrates surfaces were not covered in all their extension. The results of drop casting deposition (Figure 1) show that the high hydrophobic nature of the nanomaterials, and the strong Van der Wall forces between flakes, hinders a homogeneous deposition and forms agglomerates.

The second approach was the spin coating deposition of HDI-GO5 in DMSO onto glass. The deposition of each sample follows different preparation conditions; the values of each deposition variable considered are collected in Table 1.

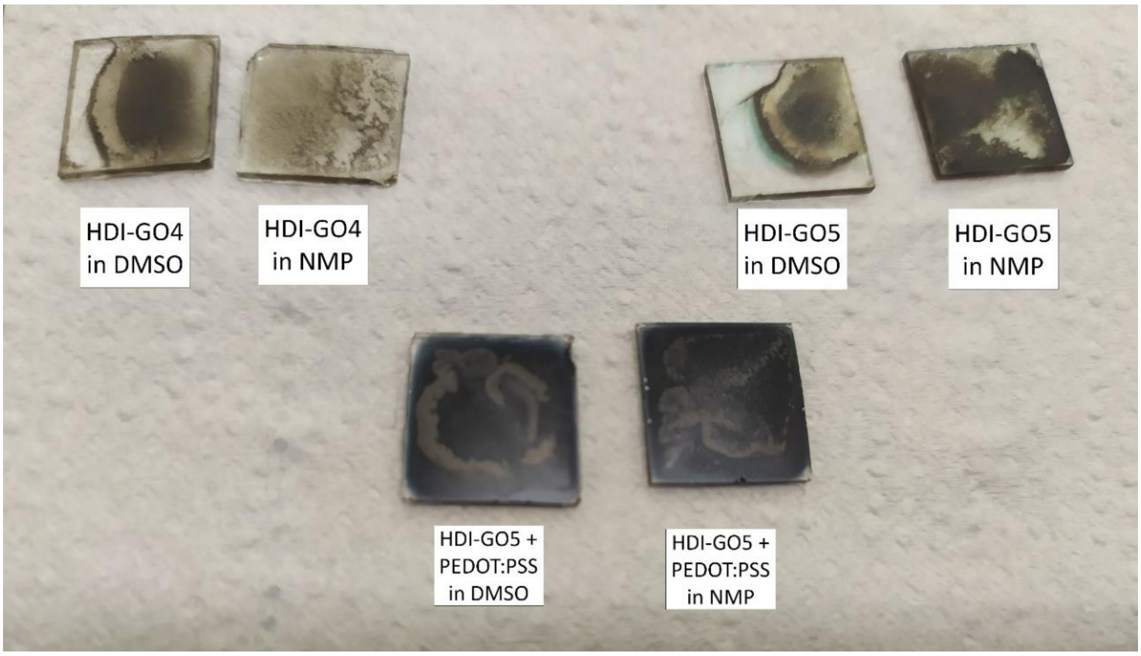


Figure 1. Typical images of drop-casted (DC) samples (caption inside the figure).

Table 1. Experimental conditions for spin coating essays.

Sample	**With Plasma Treatment**	**No Plasma Treatment**	**Coating Speed (rpm)**	**Drying Speed (rpm)**	**Annealing Time (min)**	**Annealing Temperature (°C)**
PEDOT:PSS	Deposition of sample	Clean the substrate surface with N_2	1800	1800	10	125
HDI-GO5 + DMSO			1800/1000	1800/1000	30	165
HDI-GO + 2-propanol			1800/1000	1800/1000	10–15	150

The comparison with drop casting reference is clear: spin coating method produces thinner and more transparent layers than drop casting. However, the samples do not show a clear layer deposition onto the surface, and small aggregates can be observed in all samples; the size of these aggregates seems to be reduced with increasing coating speed, which can be explained considering that it provides less time to the samples to get attached to the surface. Furthermore, it was found that surface plasma treatment had not effect on the morphology of samples deposited with the same speed.

3.2. UV-Visible Spectra Analysis

The UV-visible spectra were recorded for the spin coated samples and the drop casting reference; the other drop casted layers were not considered due to their opacity. The spectra of the samples studied are shown in Figure 2.

There is a clear difference between the transmittance of the drop casting sample (GO-dro) and the spin coating samples; this fact is consistent with the visual observations. The spin coated samples do not show significant changes in their transmittance values, neither comparing the treatment with plasma (cp vs. sp) or the coating speed (1000 rpm vs. 1800 rpm). These results point that the coating speed or plasma treatment have no direct correlation with the transmittance values, and the differences found among them could be due to scattering or experimental errors in the measurements.

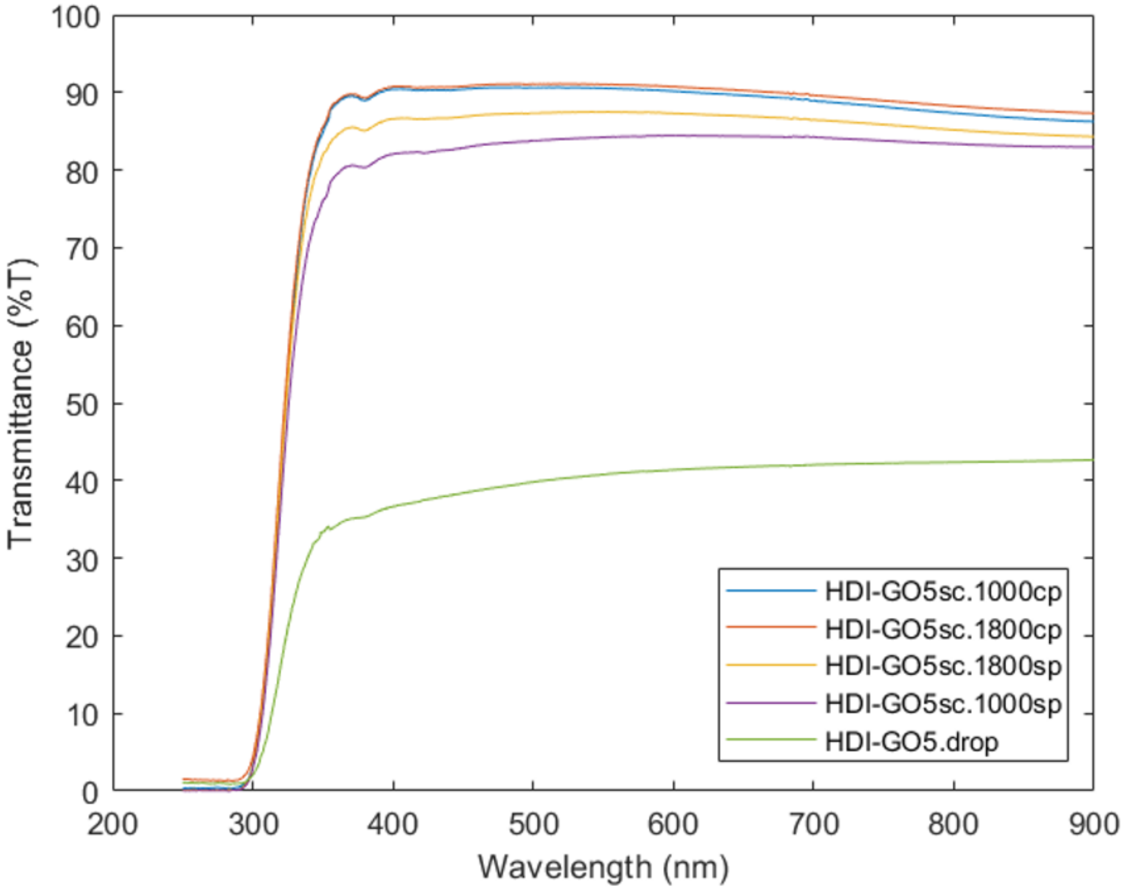


Figure 2. UV-visible spectra of samples: the abbreviation “sc” means spin coating sample; the abbreviation “drop” denotes drop casting sample; the numbers indicate the coating speed; the abbreviation “cp” denotes surface plasma treatment, and “sc” no surface plasma treatment.

The effect of different solvents was also studied. Three samples using DMSO without plasma treatment, 2-propanol with plasma treatment, and 2-propanol without plasma treatment were prepared. The substrate in this case was ITO onto glass. The results reveal no noticeable changes between DMSO and 2-propanol transmittance, and neither for both 2-propanol samples, hence it was concluded that solvent effect was negligible with these nanocomposites.

The ultrasonication effect on HDI-GO deposition was also investigated by UV-Vis spectra. A set of samples were prepared according to two different sonication cycles: (a) 1 h of sonication, followed by a rest of 12 h and another 2 h of sonication; and (b) 2 h of sonication. Both sonication cycles were applied for HDI-GO4 and HDI-GO5 nanocomposites, with and without plasma treatment. In the case of HDI-GO4, no changes between samples with different sonication cycle or plasma treatment were found. However, in the case of HDI-GO5, the sample without plasma treatment presents a slightly better transmittance in the range 300-570 nm, but also shows less scattering when the sonication cycle was a). This result can be related with the higher FD value of the sample comparing with HDI-GO4: the higher FD, the higher the HDI-GO remnant at the hydrophobic surface.

3.3. AFM Results

The AFM technique was applied to study HDI-GO5 samples, since UV-visible spectra results showed a slightly better deposition than HDI-GO4. DMSO and 2-propanol were selected as solvents, and typical results are shown in Figures 3 and 4.

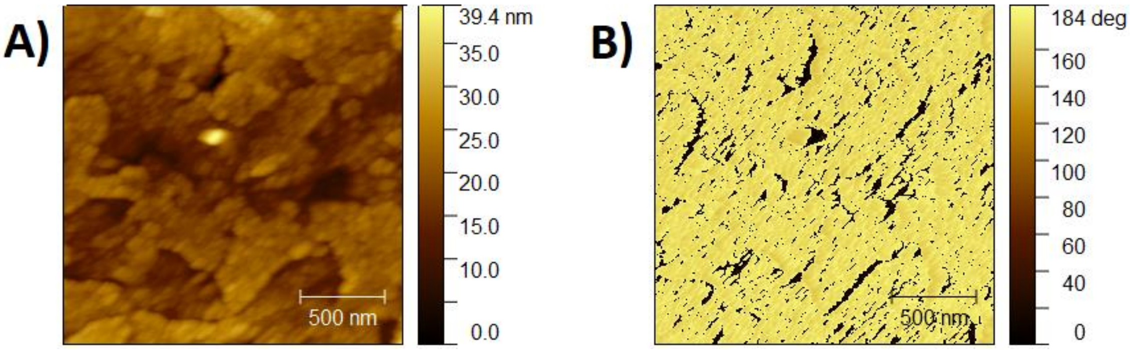


Figure 3. AFM measurement of HDI-GO5 in ITO using 2-propanol as solvent: (**A**) topography; (**B**) phase diagram.

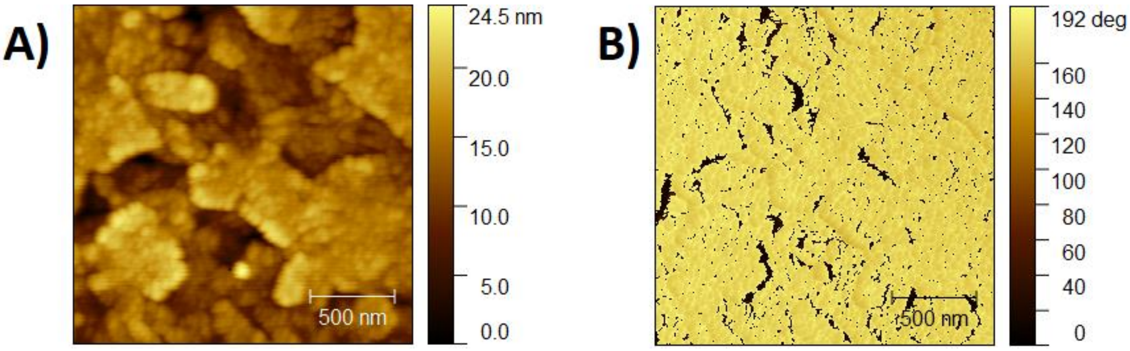


Figure 4. AFM measurement of HDI-GO5 in ITO using DMSO as solvent: (**A**) topography; (**B**) phase diagram.

In both figures, no differences of phases are found, which means that HDI-GO5 was poorly or not even deposited onto the ITO surface. No conclusive results could be obtained from the AFM images, given that the layers were too heterogeneous to be properly characterized.

3.4. Thermal Evaporation

The thermal evaporation was applied to obtain a homogeneous thin film of HDI-GO5, with the aim of avoiding the problem of processing it as a dispersion. The evaporation was carried out under high vacuum-atmosphere (2×10^{-6} mbar). However, the sample could not evaporated, and this fact could be related with the high thermal stability of HDI-GO5 (higher than 600 °C under air [25]).

4. Conclusions

In this work, the potential of HDI-GO based nanomaterials to form transparent and homogeneous layers on top of glass and glass/ITO substrates was studied considering the most typical deposition techniques employed for organic photovoltaic solar-cells. Samples prepared via spin coating technique also showed heterogeneities, but only small irregular depositions were detected; however, the loading of HDI-GO on the surface was very low; these visual observations were corroborated by UV-visible spectra. A plausible solution for these issues could be to modify the synthesis procedure of the nanocomposites in order to achieve transparent and homogeneous layers. The effect of solvents, surface plasma treatment and ultrasonication cycle were also studied, and the results were almost the same considering the different conditions investigated. Overall, it can be concluded that the synthesis procedure of these promising nanomaterials should be tailored and optimized, which will be the task of future works.

Author Contributions: J.A.L.-S. performed the experiments and wrote the draft of the article; A.C. and A.M.D.P. performed the formal analysis and reviewed the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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