Articles

A Route to Stable Nanostructures in Conjugated Polymers

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ABSTRACT: Copper nanoparticles with an average diameter of 32 nm were used as a template to nanostructure a conjugated polymer based on a soluble polythiophene. Mixtures of the polymer and the copper nanoparticles were processed into thin films and subjected to a thermal treatment whereby the solubilizing side chains of the polymer are eliminated, leaving an insoluble high-T_g conjugated polythiophene film with included copper nanoparticles. The copper nanoparticles were then removed using a copper-specific solubilizing agent, leaving voids in the polythiophene film that could be filled with small spherical molecules such as soluble fullerene derivatives, specifically 1-(3-(methoxycarbonyl)propyl)-1-phenyl[6,6]C_{61} (trivially named phenyl-C61-butyric acid methyl ester = PCBM). X-ray scattering techniques (grazing incidence wide-angle X-ray scattering (GIWAXS), grazing incidence small-angle X-ray scattering (GISAXS), reflectometry) and electron microscopy (SEM, TEM) were used for the characterization of the morphology and crystalline structure. A porosity of <20% could be achieved. In terms of application, the technique was applied to create nanostructures in a conjugated polymer based on the copper nanoparticle template. Bulk heterojunctions of the nanostructured polymer were studied.

Introduction

Many modern applications of conjugated materials rely on the nanoscale morphology.[1] A very successful example is the organic polymer and small molecule solar cells based on the concept of a bulk heterojunction where a donor and an acceptor component are mixed and processed into a thin film sandwiched between two electrodes.[2] The efficient function of the device relies on the phase segregation into an interpenetrating network of the two components that each allow for efficient transport of a carrier (a hole and an electron). The realization of the desired morphology and nanostructure has so far been through empirical experiments and fortuitous observation of the particular properties of a given material. The control that one has over the nanostructure and morphology is often through indirect means, as for instance thermal and/or solvent annealing.[3] Deliberate and direct means for controlling the morphology are needed for instance if one wishes to tune the size of the domains in the nanostructure such that all domain boundaries are within the exciton diffusion range in the material[4] (i.e., ∼10 nm scale). Also, the required segregated nanostructure of the two desired components of the binary mixture may not be accessible by thermodynamic equilibrium processes. Although a particular system may be optimized and made to work well, a clear drawback is that the results are not generic in the sense that the system changes if one of the components is replaced. Simple replacement of one polymer material with another polymer material is a new situation that again requires detailed study, and there is no guarantee that the formation of the right morphology and nanostructure is possible. A further complication is that the morphology must, once formed, be stable thermally[5] and in time, and one may argue that a morphology that is reached through thermal annealing at only slightly elevated temperatures will never be stable in time. Methods for the deliberate control and shaping of the morphology and nanostructure of conjugated materials are thus urgently needed.

Some of the most successful methods that offer a good control of the morphology and nanostructure that have been explored so far rely on the ability of certain classes of materials to crystallize on the desired nanoscale[6] (i.e., as spheres or rods) or organize on the desired nanoscale through thermodynamic equilibrium by phase segregation in block copolymers in their pure state[7] or in emulsions with a solvent such as water where the composition rules the predominant phase in a predictable manner.[8] Whereas a material may have the ability to form the correct morphology and nanostructure, it may not have the desired optical and electronic properties. One challenge that has to be overcome is thus to combine the structure generating property of a particular material with the desired optical and electronic properties, and this is by no means straightforward. An example where the structure, the morphological stability, and the optical and electronic properties are in place is that of the hybrid solar cells employing conducting oxides such as ZnO that can be processed into nanorods that are transparent and good electronic conductors.[9] Although appealing, the approach has only been partially successful because intimate mixing of the two phases is required, and it has been problematic to efficiently fill the voids in the nanostructure with polymer molecules that are too large to enter the structure. The approach of creating a nanostructure based on one component followed by filling with another component has thus only been successful when the filling is made with small molecules that can enter the structure as exemplified by the Grätzel cell[6a] or with small

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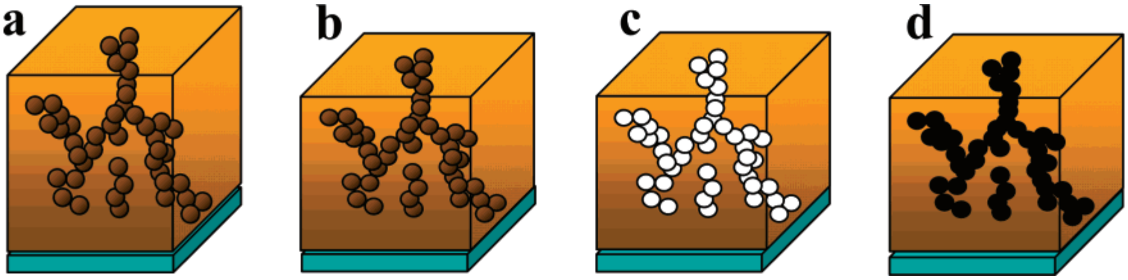

Figure 1. Illustration of different steps of the process. The soluble film containing copper nanoparticles (a) is thermocleaved whereby the thickness changes because of the loss of the solubilizing side chains (b). The copper nanoparticles are removed (c), and the voids are filled with PCBM (d). The change in volume from step (a) to step (b) is not to drawn to scale.

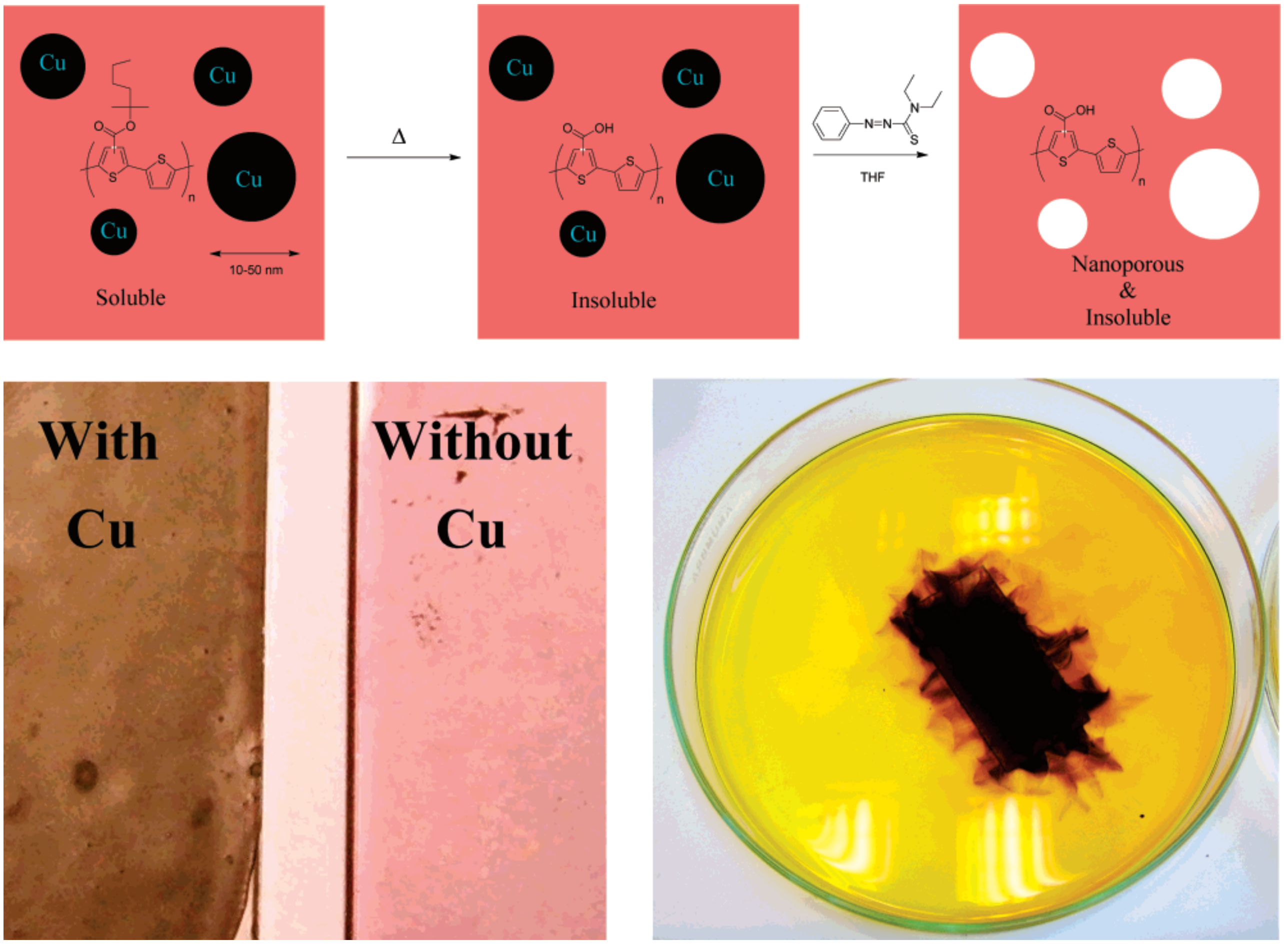

Figure 2. Reaction scheme for the process (above) and pictures of the films before and after removal of the copper nanoparticles. The film loaded with copper nanoparticles has a black appearance whereas the film where the copper nanoparticles have been removed has a red color (lower left). The dissolution step is also shown where a device slide (50 mm × 25 mm) is covered with a THF solution of azothioformamide. The dark color is due to the formation of the copper complex of azothioformamide (lower right).

ZnO nanoparticles mixed with a conjugated polymer.[6c] Finally, the use of templates has been explored whereby the nanostructure is generated by a material that is then sacrificed at a later stage in the process. This latter approach is also subject to the constraints imposed by the molecular size of the filling component.[10] The requirements and challenges for a generic and successful template approach to the formation of a nanostructure where one has a choice in the composition of the two phases are thus as follows: (1) The template must be structurally stable while the first component of the desired nanostructure is formed. (2) The first component must in its final form be structurally stable without the template. (3) The removal of the template must be mild and chemically nonintrusive. (4) The filling of the nanostructure with the second component must be efficient, and preferably the second component is a small molecule.

In turn, these criteria can be met in several ways although they are interdependent, and some caution has to be excercised when deciding on the strategy. The first criterion is traditionally hard to achieve with polymer materials because they are soft materials that do not easily support a nanoporous structure without collapsing. It is also desirable that solution processing can be used for the formation of, for instance, a nanostructured film of the material.

An appealing strategy is one where the side chains that are added to the conjugated polymer to allow for solution processing are removed after the film with the template has been formed.[11] In effect, this conveys stability at many levels. Most notably,

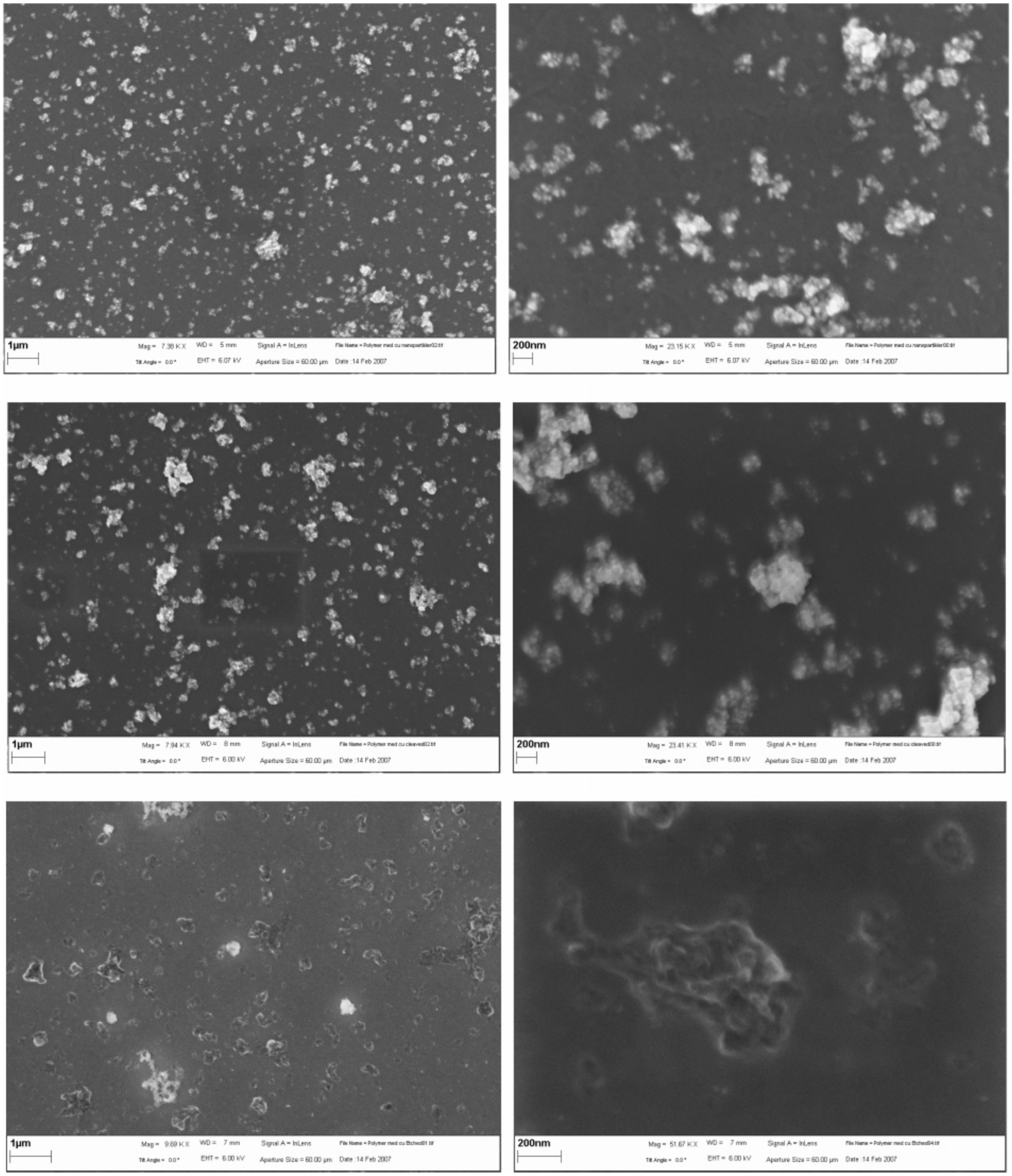

Figure 3. SEM images at different magnifications (1 μm scale bar in the left column and 200 nm scale bar in the right column). The raw (soluble) film loaded with nanoparticles (top), the thermocleaved film loaded with nanoparticles (middle), and the nanoporous film where the copper nanoparticles have been removed (bottom).

the polymer material becomes structurally stable, insoluble, and less likely to collapse once the template is removed. The material also acquires a better operational stability in a solar cell context.[5a] The film is thus formed simply by mixing the template with a solution of the polymer material. A subsequent thermal treatment hardens the polymer and makes it structurally stable. The removal of the template must be chemically mild, and transitional methods such as heating to very high temperatures or the use of very strong acids are not compatible with organic materials. A very efficient and mild method employs the use of azothioformamides that efficienctly dissolve metals such as copper, palladium, platinum, and nickel under very mild and neutral conditions (nonacidic) in organic solvents and avoids chemical interaction with the polymer material and doping.[12] The filling of the voids in the nanostructure can efficiently be achieved with small molecules such as PCBM[13] whereby a bulk heterojunction has been created ex situ as compared to the traditional in situ formation by mixing the components when creating the film (as shown schematically in Figure 1).

In this work we demonstrate how copper nanoparticles can be used as the template by mixing them with a soluble thermocleavable polymer material. Solution processing into a thin film followed by a thermal treatment that eliminates the solubilizing side chains on the conjugated polymer chain renders the film insoluble. Subsequently, the copper nanoparticles are removed by treating the films with a THF solution of phenylazodiethylthioformamide. This yields a polymer film with voids in place of the copper nanoparticles. These voids are finally filled with the small soluble molecule, PCBM. Electron microscopy was employed in combination with X-ray scattering techniques to ensure that our interpretation reflected the general state of the film and not just a local representation.

Results and Discussion

Our method makes use of a polymer based on polythiophene as shown in Figure 1. As one of the crucial steps in the process is the removal of the nanoparticle template we chose to employ copper nanoparticles as the azothioformamides dissolve copper nanoparticles most rapidly.[12b] Cu nanoparticles, wires, and clusters[14] are however not very stable in time, sensitive to oxygen, quite difficult to prepare in a controlled manner, and difficult to prepare in large quantities (i.e., on a gram scale). We attempted many methods and finally settled on the method developed by Wu and Chen.[15] Following this method, the Cu nanoparticles were prepared from an aqueous ammonious cupric chloride solution by reduction using hydrazine.

The Cu nanoparticles were stabilized with the detergent cetyltrimethylammonium bromide (CTAB) and harvested by centrifugation and sequential resuspension in CTAB saturated ethanol, ethanol/toluene, and toluene. The nanoparticles were finally resuspended in a toluene solution of the polymer. All processing steps were performed under argon and as quickly as possible to avoid oxidation and aggregation of the copper nanoparticles. The nanoparticles were stable for several hours under argon in the aqueous solution where they are stabilized by both the CTAB and the reducing environment provided by hydrazine. The moment they are extracted into ethanol, ethanol/toluene, and pure toluene they were stable for a total of around half an hour, and the transfer to the glovebox and preparation of the films were swift and typically completed in less than 30 min. Once prepared, the films were stable, although the copper in the films gradually oxidizes to Cu_2O. Fortunately, azothioformamide also dissolves Cu_2O, albeit at a slower rate than the near-instantaneous dissolution of freshly prepared metallic copper nanoparticles.

The dissolution of the copper nanoparticles was achieved by covering the sample with a 10 mg mL^{-1} THF solution of phenylazodiethylthioformamide. The solution of phenylazodiethylthioformamide is light yellow whereas the copper complex is dark colored.[12] Black crystals of the copper complex readily form in the solution upon standing.

Because of this large change in color, it is very easy to follow the reaction which is virtually instantaneous when the Cu nanoparticles are fresh. The picture shown in Figure 2 was taken 5 min after addition of the THF solution. If the volume of the THF solution is known, simple UV−vis spectroscopy can be used afterward to determine the exact amount of copper that has been dissolved as the azothioformamides have been explored as very sensitive analytic tools for the quantitative determination of transition metals at the ppb level.[12]

SEM showed that the films contained mostly clusters and aggregates of nanoparticles with a typical size of around 100−500 nm (Figure 3). The individual nanoparticle diameter was estimated to 30 ± 10 nm. The films before and after thermocleavage of the polymer were identical in terms of morphology, spread of particles, and aggregates. The film however shrinks upon thermocleavage[11] (see also Supporting Information), and there was some oxidation of the copper in the thermocleaved samples as evidenced by the GIWAXS experiments (see below). After removal of the copper there were voids where the Cu particles had been, and the morphology had not changed, indicating that the structure did not collapse. It should however at this point be emphasized that the porosity of the films was fairly low, <20% (see Supporting Information).

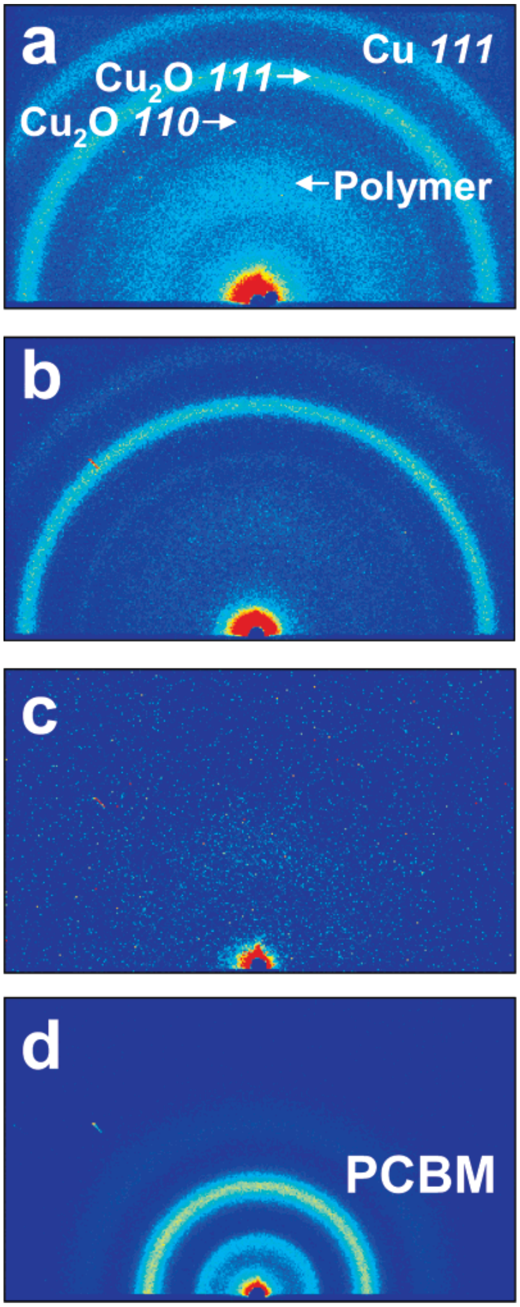

Figure 4. Grazing incidence X-ray scattering (GIWAXS) as recorded on the area detector. (a) Blend of the thermocleavable polymer and Cu nanoparticles, as prepared. Reflections from metallic Cu and Cu_2O are indicated as well as the broad scattering contribution from the polymer, presumably caused by side-chain packing and the stacking of conjugated planes. (b) After cleaving at 200 °C, a larger fraction of the copper is present as Cu_2O relative to metallic Cu, as indicated by the relatively stronger Cu_2O 111 peak. The scattering from the polymer is much reduced after the removal of side chains. (c) The film after dissolution of Cu revealing no trace of crystalline Cu, neither metallic nor oxidized. (d) The diffraction from crystalline PCBM completely dominates the pattern after filling.

Having established that the films could be prepared and that the copper nanoparticles could efficiently be removed, it was of interest to see whether the voids left after the copper nanoparticles could be filled with a small organic molecule such as PCBM. The films were finally studied by X-ray scattering methods as these techniques offer certain advantages over SEM in terms of contrast, and they represent averages over large parts of the film ensuring that the observation is general and not accidentally biased by the experimenter's choice of view. GIWAXS first confirmed the presence of copper nanoparticles in both the spin-coated film and in the thermocleaved film. The GIWAXS also showed the presence of some Cu_2O, especially in the cleaved sample. This is ascribed to oxidation of the reactive copper nanoparticles during thermocleavage at 200 °C. In the samples where the copper nanoparticles had been removed there were in most cases neither diffraction from metallic copper nor from Cu_2O, thus confirming complete removal. GISAXS confirmed the presence of a nanostructure with good contrast in the presence of nanoparticles with an average size of 32 nm, consistent with the SEM observations.

The nanostructure is virtually unaffected by the thermocleaving process. The small-angle scattering intensity when the copper nanoparticles are removed is much weaker consistent with the smaller difference in electron density between polymer and air as compared to the difference in electron densities of the polymer and Cu (or Cu_2O). When the voids are filled with PCBM, the scattering is almost eliminated because of the similar electron densities of the two polymers, thus confirming the near complete filling of the nanostructured void space by PCBM.

X-ray reflectometry showed that the film thickness did not change significantly upon removal of the nanoparticles, thus also confirming that the porosity of the film is present after removal of the copper nanoparticles and that the morphology induced by this method is stable.

Photovoltaic devices prepared for films based on the nanostructured films where the porosity had been filled with PCBM showed diode behavior in the dark and under illumination. A dark rectification ratio of 15 was obtained. Under illumination with a sun simulator (1000 W m^{-2}, AM1.5G) an open-circuit voltage of 0.43 V, a short-circuit current of 0.19 mA cm^{-2}, a fill factor of 27.4%, and a power conversion efficiency of 0.02% were obtained for a device with an active area of 3 cm^2. These data are much lower than the state of the art where power conversion efficiencies of several percent are easily obtained. We ascribe the poor photovoltaic behavior obtained here to the low porosity and the large size of the PCBM domains that in principle is given by the size of the copper nanoparticles. The ideal size of the PCBM domains (particles) should be of the order of 5−10 nm, and the porosity should be closer to 50% or more.

Conclusion

We have described how to nanostructure a conjugated polythiophene film using a metal nanoparticle template approach whereby the template is removed after the film is converted into an insoluble form, leaving voids in the stable nanostructured film. The voids could successfully be filled with a small soluble molecule relevant to solar cell research. Although the photovoltaic response was not improved significantly by the nanostructure, it does show that it is possible to design a nanostructure and obtain a stable morphology. A limitation of the technique is currently the low porosity (<20%) and the large size of the voids that could be obtained. We ascribe these two factors as the main reasons for the little effect the nanostructure had on the photovoltaic response. The challenges for future development are methods that allow for incorporation of larger amounts of well-dispersed smaller nanoparticles into the polymer film.

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Supporting Information Available: Preparation of nanoparticles, films and etching procedures, experimental descriptions, and data for SEM/TEM, GIWAXS, GISAXS, X-ray reflectometry, solar cell preparation, and photovoltaic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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