

MYOSOTIS: Matériaux hYbrides Orientés et nanoStructurés: élabOration, sStructure et proprIétés (ANR-08-NANO-012-01)

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Abstract: Nanostructured organic-inorganic hybrid materials combining semiconducting polymers such as regio-regular poly(3-hexylthiophene) (P3HT) and quantum dots are promising systems for the fabrication of solution-processed photovoltaic devices [1]. This application requires: (i) an appropriate phase separation between the nanoparticles and the polymer host matrix on a 10 nm length scale and (ii) a strict control of the interface between the polymer (electron donor) and the nanoparticles (acceptor) to optimize the charge transfer. We present the elaboration of oriented and nanostructured thin films of hybrid materials by directional epitaxial crystallization of P3HT in 1,3,5-trichlorobenzene, in the presence of inorganic nanoparticles (CdSe). The resulting structure is described by the periodic alternation (period ca. 30 nm) of crystalline P3HT lamellae separated by amorphous interlamellar zones sequestering the inorganic nanoparticles (Fig.1). Transmission electron microscopy tomography shows that the nanoparticles are embedded in the bulk of the P3HT matrix. In an attempt to improve the charge transfer between the polymer and the nanoparticles, we performed ligand exchange, substituting the insulating layers of tri-n-octyl phosphine oxide (TOPO) and stearate by small conjugated molecules, e.g. Alkylthiophenes and polypyridines.

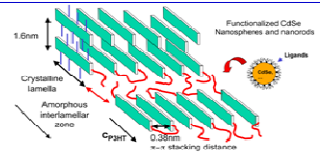


Figure 1: Schematic representation of the semi-crystalline structure of P3HT showing the alternating crystalline lamellae and amorphous interlamellar zones.

I. Functionalization of Nanoparticles

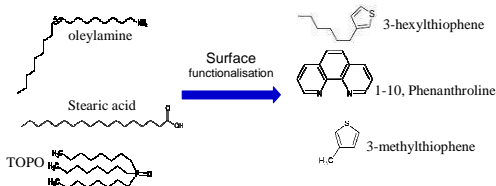


Figure 2: The ligands on the NC must ensure a good interparticle charge transport as well as good dispersion of the NCs in the polymer matrix. Long alkyl chains are therefore substituted by conjugated molecules e.g. 1-10, Phenanthroline, alkylthiophenes and polypyridines.

Process of ligand exchange: Ligand exchange is performed by adding a large excess (more than 10 times) of the new ligand to the NCs colloidal solution. The solution is heated at 70-80° C for 6-7 hours under Argon atmosphere and refluxing. The amount of ligand exchange increases with increasing reaction time. Once the exchange is performed, NCs are washed in order to remove the excess (the unbound part) of the new ligand.

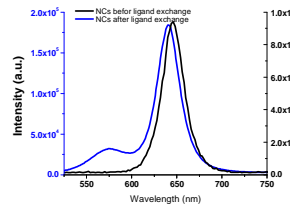


Figure 3: PL before and after exchange of the NCs with 1-10, Phenanthroline. Note the apparition of an additional peak after exchange. The origin of this peak is presumably due to surface states involving the Phenanthroline ligands on the CdSe NCs.

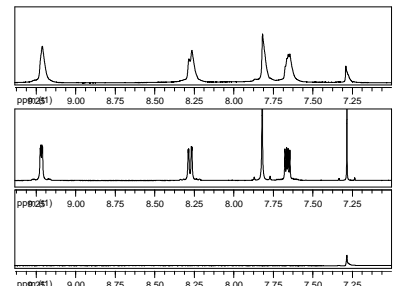


Figure 4: Kinetics of ligand exchange followed by H¹-NMR spectroscopy. After ligand exchange the characteristic peaks of 1-10, phenanthroline appear. The longer the exchange reaction, the broader the peaks. This broadening is typical for the binding of the ligands to the NC's surface.

II. Fabrication of highly oriented and nanostructured P3HT thin films by epitaxial growth

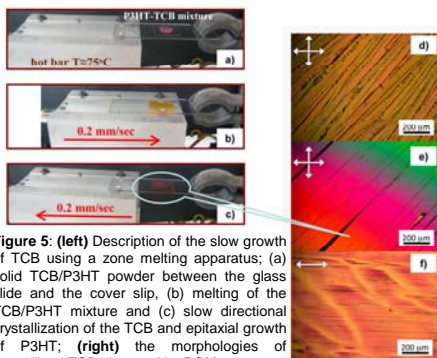


Figure 5: (left) Description of the slow growth of TCB using a zone melting apparatus; (a) solid TCB/P3HT powder between the glass slide and the cover slip, (b) melting of the TCB/P3HT mixture and (c) slow directional crystallization of the TCB and epitaxial growth of P3HT; (right) the morphologies of crystallized TCB observed by POM; (d) without slow growth (on Koeffler bench), (e) using the zone melting method and (f) the highly oriented P3HT film after removal of the TCB.

The crystallization front of TCB (1,3,5 trichlorobenzene) is slowly moving at 0.2 mm/sec which allows to grow highly uniform crystals of TCB. As seen in fig. 5, the slow growth allows to grow layer crystals of TCB with a reduced number of grain boundary in the direction perpendicular to the temperature gradient. This method was used not only to obtain large and uniform crystal domains but also to obtain homogeneous films in terms of film thickness. Accordingly, large oriented domains of P3HT can be grown epitaxially on the TCB (fig 5.e). This method of zone melting has also been used for poly(3-alkylthiophenes). As seen the bright field (BF) image in fig. 6, the highly oriented domain of P3DT was obtained by this zone melting method

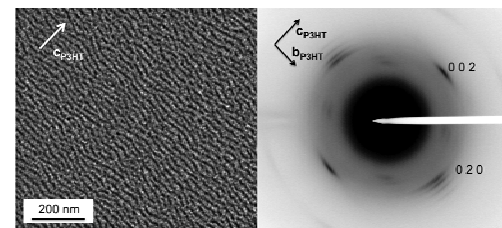


Figure 6: Left: Bright field of a highly oriented P3DT film (hexane fraction) grown by using the zone melting apparatus (see fig. 5). Right: Electron diffraction (ED) pattern in proper orientation relative to the BF image. The ED pattern indicates a preferential (1 0 0) contact plane of P3DT on TCB.

III. 3D-structure of the oriented and nanostructured hybrid films

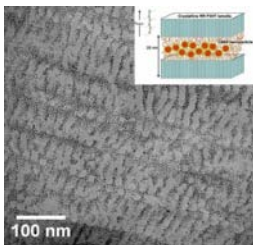


Figure 7: Bright-field (BF) image of a hybrid thin film grown by directional solidification in TCB. Nanocrystals are coated with their initial ligands [2]. The inset shows a scheme of the nanostructure of the hybrid material.

TEM provides 2D projections of the film morphology. However, for the use of the films in photovoltaic devices, it is essential to visualize the 3D dispersion of the NC in the matrix of the polymer. Percolation of the NCs is an essential aspect to reach. Therefore, we use TEM-tomography to establish the 3D distribution of NCs in the bulk of the hybrid thin films. Preliminary results indicate that the spheres are sequestered in the bulk of the amorphous interlamellar zones. However, depending on the relative proportion NCs/P3HT, some excess NCs are rejected on one side of the film.

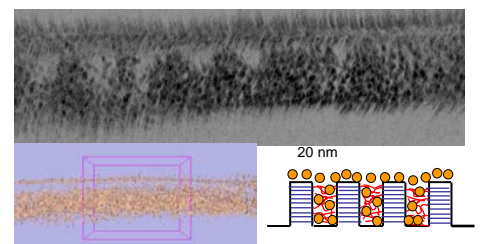


Figure 8: TEM Tomography image of a hybrid film. Top image shows the sum of transverse projections for a 3D reconstruction in the direction perpendicular to the chains of P3HT. On the bottom (right), we represent a 3D model of the hybrid film structure showing the location of the NCs in the films. As shown in the scheme, this sample exhibits both a surface decoration of the layers and a volume distribution of the NCs.

CONCLUSION: Highly oriented and nanostructured hybrid thin films are obtained by epitaxial growth on TCB. These hybrid thin films are of potential interest for the active layers of solar cells because of their nanostructuration on a scale of about 28 nm which is close to the exciton diffusion length in P3HT. Thus it is possible to avoid aggregation and to control the phase separation of NCs and polymer, which is a crucial factor affecting the device performances. In a first attempt to improve the directional epitaxial crystallization method, we designed and used a zone melting apparatus so as to grow highly oriented and very large TCB crystals. In order to improve the charge transport properties, NCs have been functionalized with small conjugated molecules such as alkylthiophenes and 1-10, Phenanthroline. In a close future, some tests with various polypyridine ligands will be performed. It is also planned to perform charge transport measurements on these systems and to integrate them into devices.

In order to further understand the morphology of the films, TEM tomography is used. Preliminary results show that the morphology observed in standard TEM imaging is not only due to a surface decoration, but that NCs are indeed distributed in the whole volume of the sample.

REFERENCES

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