

3D Spatial Mapping of the Nanomorphology of Polymer:Fullerene Blends by Highly Selective, Homogeneous Copper Staining

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Bulk-heterojunction absorber layers of organic solar cells (OSCs) consist of three-dimensional (3D) interpenetrating networks of conjugated polymer and fullerene (donor/acceptor) domains [1]. The power conversion efficiency of OSCs depends strongly the intrinsic physical properties such as the exciton diffusion length and the charge carrier dissociation at interfaces of donors and acceptors. It requires a nanomorphology with domains sizes that are on the order of the exciton diffusion length. Thus, the nanomorphology has to be carefully characterized for correlation with solar cell performance. However, owing to their similar material properties, distinction of conjugated polymers and fullerenes in bulk-heterojunctions is always hampered by low contrast in electron microscopy. A common method for contrast enhancement is selective staining where one phase of a material mixture is labeled by heavier elements. This increases the difference of the average atomic number Z and yields Z -contrast imaging. Staining agents like OsO₄/RuO₄, [2] and uranylacetate [3] are commonly used. However, the staining process can lead to swelling of nanoscaled phases, and, more seriously, these staining agents are highly toxic.

To overcome these issues, we describe in this work a facile procedure for highly selective and homogeneous Cu infiltration that can be used as staining procedure to recognize the phase distribution in sulfur-containing conjugated polymer:fullerene absorber layers in OSCs. **Figure 1a** shows a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of a focused-ion-beam (FIB-) milled TEM lamella of a model sample consisting of pure PC₆₁BM (C₇₂H₁₄O₂), P3HT (C₁₀H₁₄S), PC₇₁BM (C₈₂H₁₄O₂) and PTB7 (C₄₁H₅₃FO₄S₄) layers. The lamella was attached to a Cu lift-out grid. The image hardly shows any contrast between the layers apart from thin PEDOT:PSS layers which are located between different layers of the stack (blue arrows) as remnants of the sample-fabrication process. The contrast between layers is drastically enhanced after thermal treatment at 200 °C for 3 h in air where conjugated polymer appear with high intensity (**Figure 1b**). In addition, **Figure 1a,b** show the S and Cu distributions obtained by energy dispersive X-ray spectroscopy (EDXS) mapping. We find a homogenous Cu distribution after thermal treatment that correlates with the S distribution in PTB7, P3HT and PEDOT:PSS. The source of the Cu infiltration is the Cu lift-out grid. High-resolution TEM images (not shown here) demonstrate that Cu is homogeneously dissolved in the polymers without the formation of clusters or crystalline nanoparticles. Fullerene derivatives (PC₆₁BM and PC₇₁BM) do not contain any sulfur and are not infiltrated by Cu. The new selective staining technique is not only suitable for HAADF-STEM imaging but can be also used for secondary-electron scanning electron microscopy (SE-SEM) imaging. This facilitates mapping of the domain structure of polymer:fullerene absorber layers in OSCs

in a cross-section perspective and subsequent reconstruction of the 3D nanomorphology by FIB-SEM tomography.

For this purpose, prototype PTB7:PC₇₁BM absorber layers processed with different additives, which are commonly employed to tailor the nanomorphology of bulk-heterojunctions. As an example we present the nanomorphological investigation of the absorber layer processed with 3% p-anisaldehyde (AA). A thick TEM cross-section lamella was prepared by FIB-milling, which was attached to a Cu lift-out grid. **Figure 2a** shows SE-SEM images of two stacked absorber layers separated by a bright PEDOT:PSS layer in cross-section perspective before and after thermal treatment. PTB7 and PC₇₁BM cannot be distinguished in the pristine state. After thermal treatment, Cu staining strongly enhances the SE-SEM intensity of S-containing polymer domains, which allows to clearly differentiate materials and measure domain sizes. **Figure 2b** shows the two stained absorber layers embedded in a layer stack with pure PTB7 and PC₇₁BM layers. The latter yield reference intensities for the pure compounds and even allow to distinguish local PTB7-rich and PC₇₁BM-rich phases at intermediate SE-SEM intensities. After segmentation, the distribution of different domains is indicated by the color coding on the absorber layers in **Figure 2b**. Irregular-shaped pure PC₇₁BM domains (dark red) with comparably large sizes of 100–200 nm are formed, which are embedded in PC₇₁BM-rich (green) and PTB7-rich (purple) regions. Only narrow pure PTB7 domains (yellow) at the bottom of the absorber layers are observed.

The 3D reconstruction of the domain structure provides more information than 2D images on the interconnectivity and morphology of the absorber layer. Thus, FIB-SEM tomography was performed by alternating FIB milling and SE-SEM imaging (see scheme in **Figure 2c**) leading to a stack of images for 3D reconstruction. The blue color in the reconstructions in **Figure 2d** represent pure PC₇₁BM phase while mixture and possible pure PTB7 phase are transparent. Different perspectives of the total reconstructed volume (thickness ~0.47 μm) show irregular-shaped and well-connected PC₇₁BM domains. The 3% AA-processed blend exhibits a rather coarse PC₇₁BM domain structure with sizes in the 100 to 500 nm range.

To summarize, a new selective staining method has been developed leading to selective Cu staining of S-containing polymers with a Cu lift-out grid as Cu source. The resulting strong contrast between S-containing polymers and fullerene derivatives is the prerequisite for the visualization of the domain structure with high contrast and for 3D reconstruction of the nanomorphology of polymer:fullerene absorber layers. We expect the stimulation of more studies of metal staining for phase identification in block copolymers and OSCs candidates and even studies how metal infiltration can be used to tune the electronic and optical properties in organic semiconductors [4].

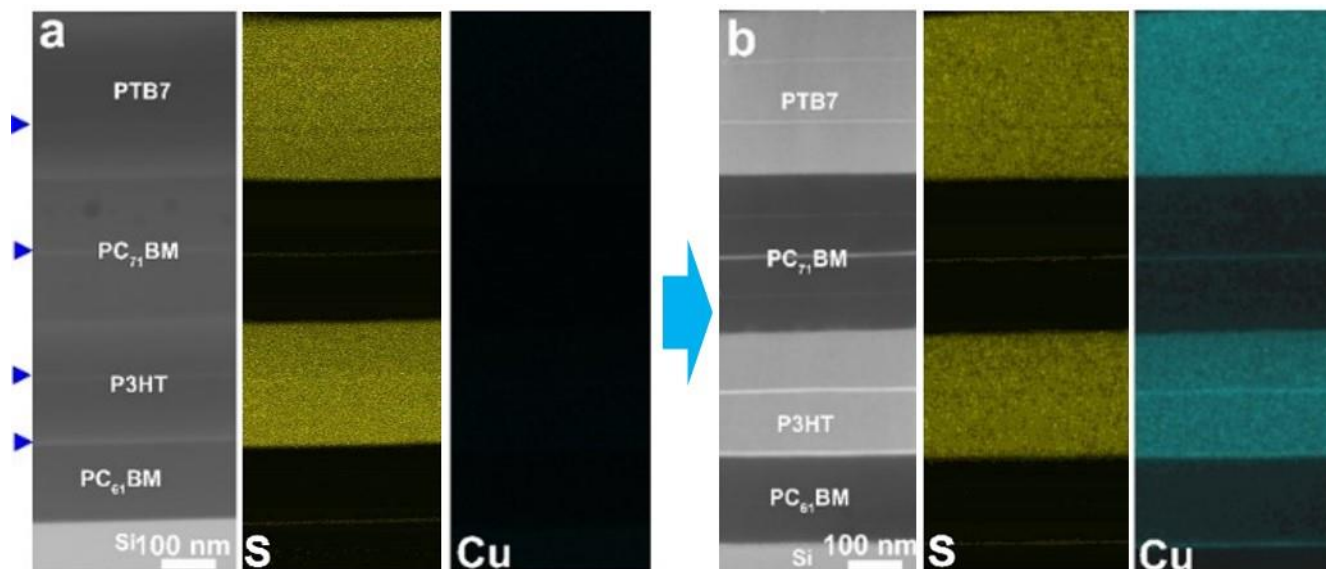


Figure 1. Observation of a selective Cu distribution in S-containing polymer layers. Comparison of 200 keV HAADF-STEM image and S/Cu distributions of the PTB7/PC71BM/P3HT/PC61BM multi-layer stack on a Si substrate in the (a) as-prepared TEM lamella and (b) after thermal treatment at 200 °C for 3 h in air.

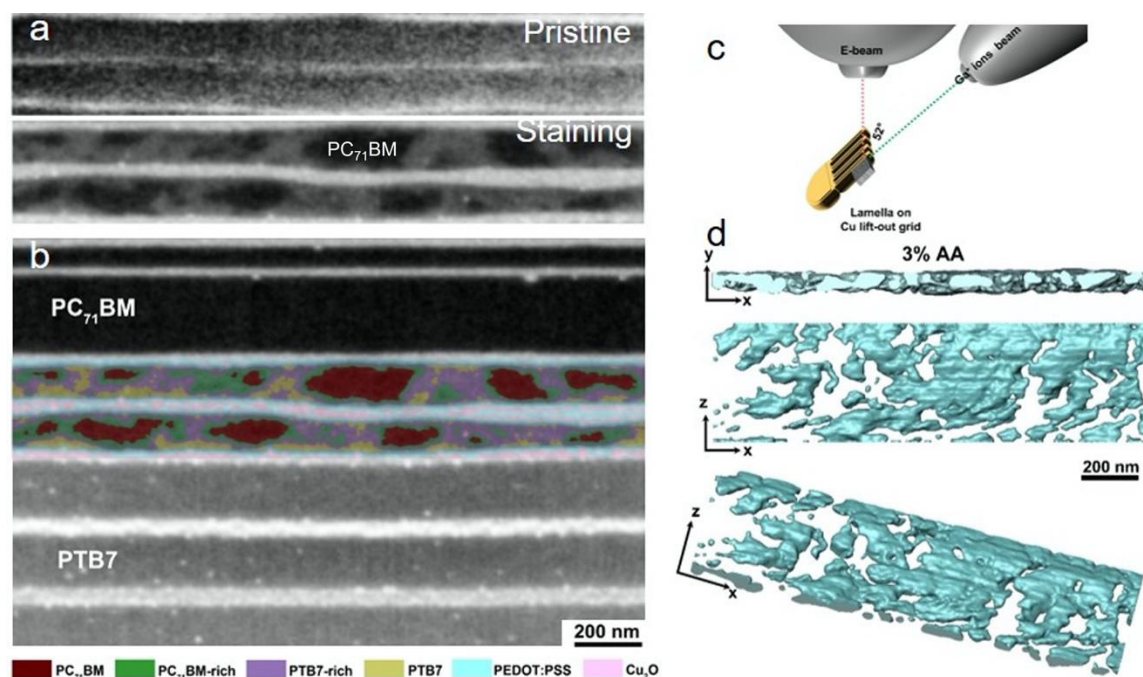


Figure 2. Application of selective Cu staining in PTB7:PC71BM absorber layers that were fabricated with 3% AA as processing additive. (a) 2 keV SE-SEM cross-section images of PTB7:PC71BM absorber layers in the pristine state and after thermal annealing. (b) 2 keV SE-SEM cross-section images of PTB7:PC71BM absorber layers in a multi-layer stack with pure PC71BM and PTB7 layers as reference for phase segmentation. Pure PTB7 and PC71BM, as well as PTB7-rich and PC71BM-rich mixtures are color coded (see legend). (c) Scheme of the experimental setup for FIB-SEM tomography and (d) 3D-rendered reconstruction of the domain structure with PC71BM domains in light blue. Mixture and pure PTB7 are transparent.

References

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