Nanoscale

Electronic supplementary information

Revealing the growth of copper on polystyrene-*block*-poly(ethylene oxide) diblock copolymer thin films with *in situ* GISAXS

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Cu-polymer interfaces in LIBs

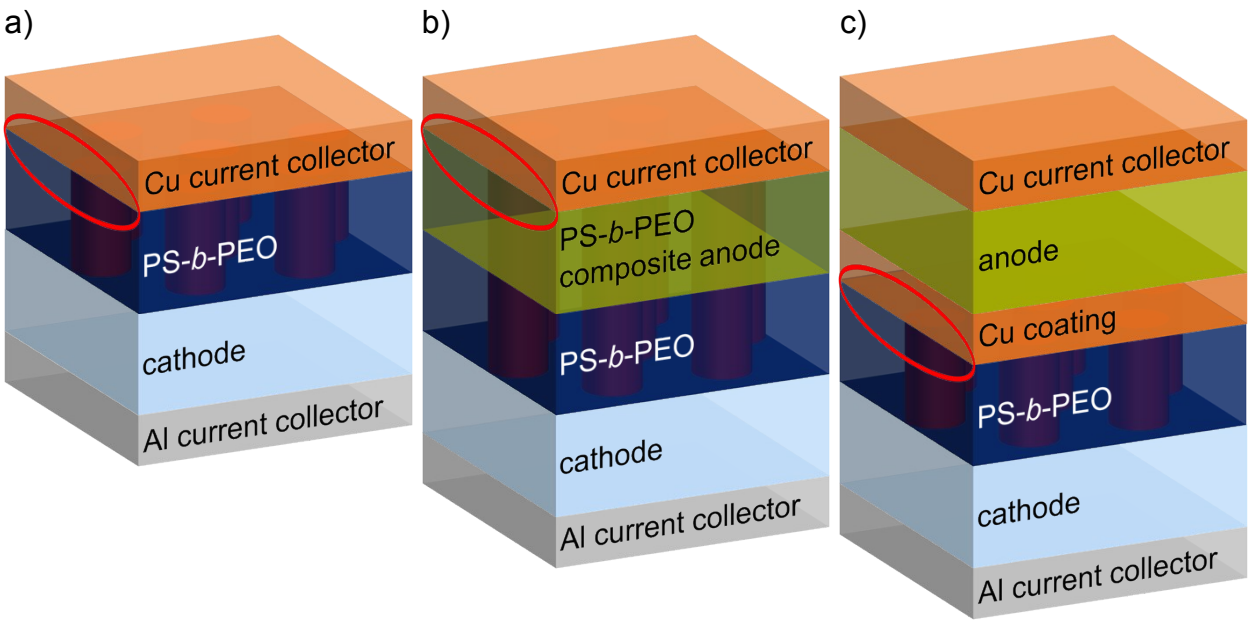

Figure S1 Simplified schematic cross sections of LIBs with Cu/PS-*b*-PEO interfaces (red ellipses): a) anode free LIB, b) LIB with polymer composite anode (*e.g.* with 32 wt% PS-*b*-PEO), and c) LIB with anode Cu coating and PS-b-PEO polymer electrolyte.

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Atomic force microscopy (AFM)

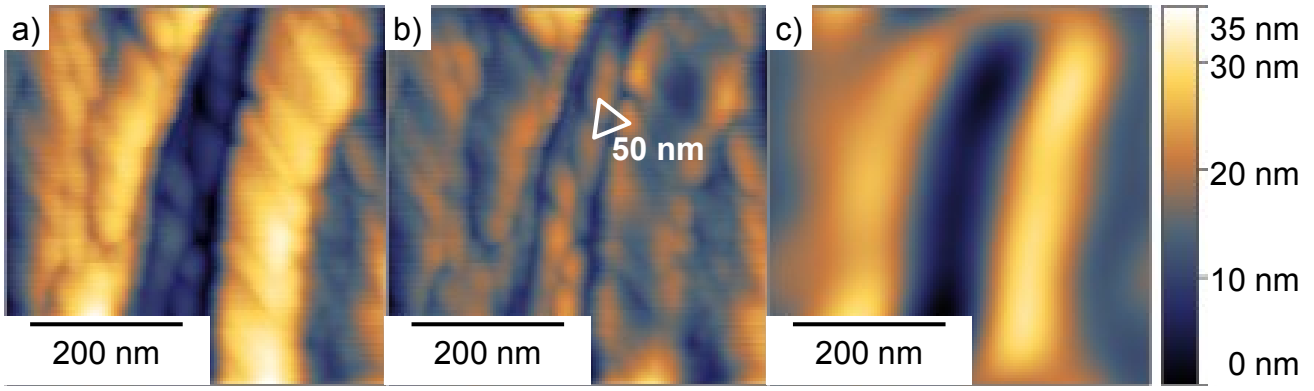

Figure S2 AFM images of bare PS-*b*-PEO polymer thin film surface: (a) without filtering, (b) filtered image and (c) filter residuum. An equilateral triangle (white in b) is visualizing the domain distance of the PS blocks in the PEO matrix. The applied 2DFFT filter is used to highlight the roughness at the PS-*b*-PEO film surface at large distances and the local hexagonal arrangement at smaller distances (around 50 nm).

Scanning electron microscopy (SEM)

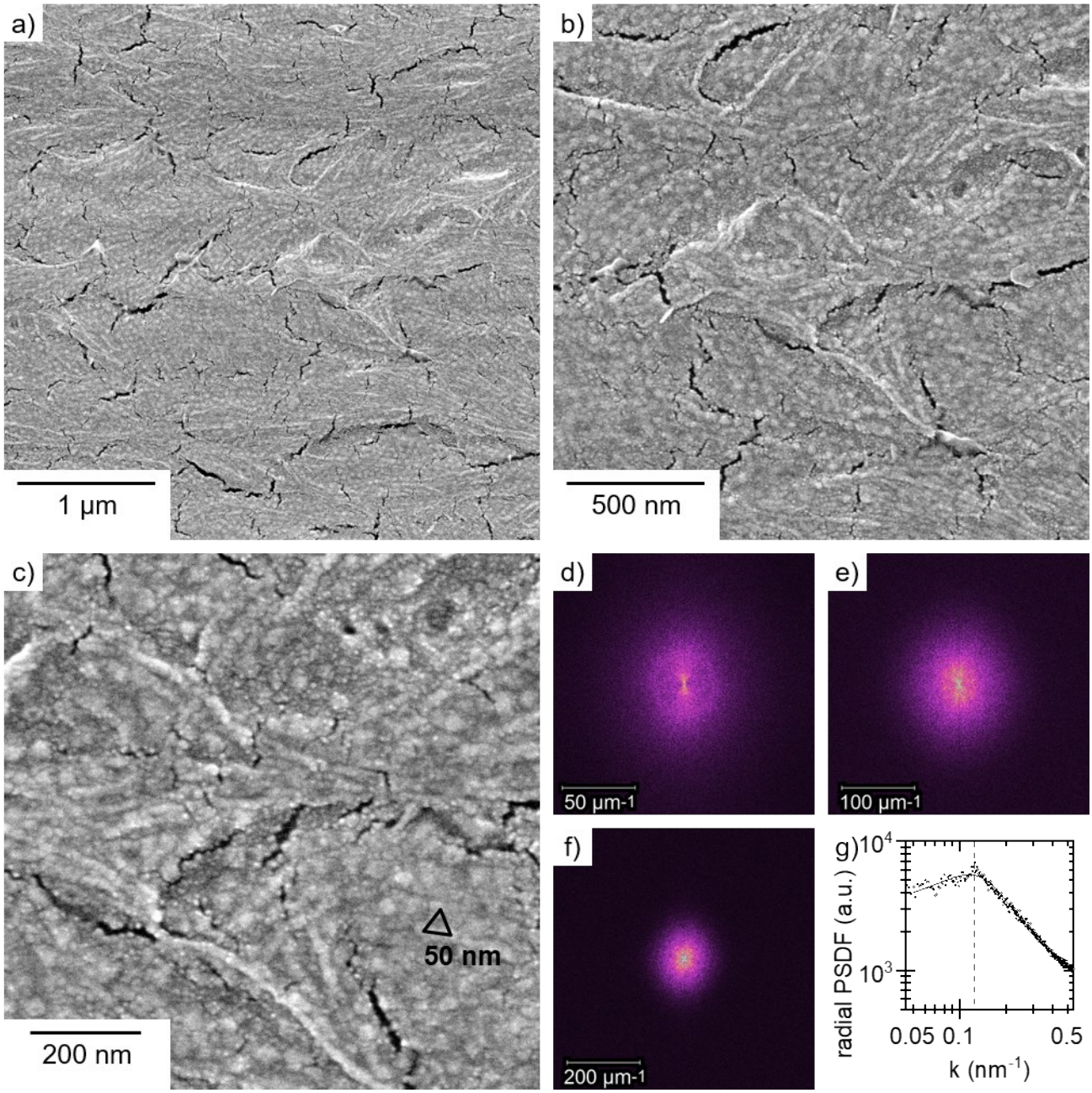

Figure S3 Scanning electron microscopy (SEM) images of (10.7 ± 0.1) nm Cu sputter deposited on PS-*b*-PEO at taken at magnifications of (a) 20000, (b) 40000, and (c) 80000 with an acceleration voltage of 5 keV. An equilateral triangle with side length of 50 nm highlights the local hexagonal arrangement. 2D power spectral density functions (PSDF) of the SEM data with (d) 20000, (e) 40000, and (f) 80000 magnification reveal the lack of long range order. (g) Radial integration (points) of the PSDF (d) is shown with a Lorentzian fit (line) and the maximum at 0.125 nm^{-1} (dashed line), corresponding to a distance of 50 nm.

Cu cluster growth and agglomeration

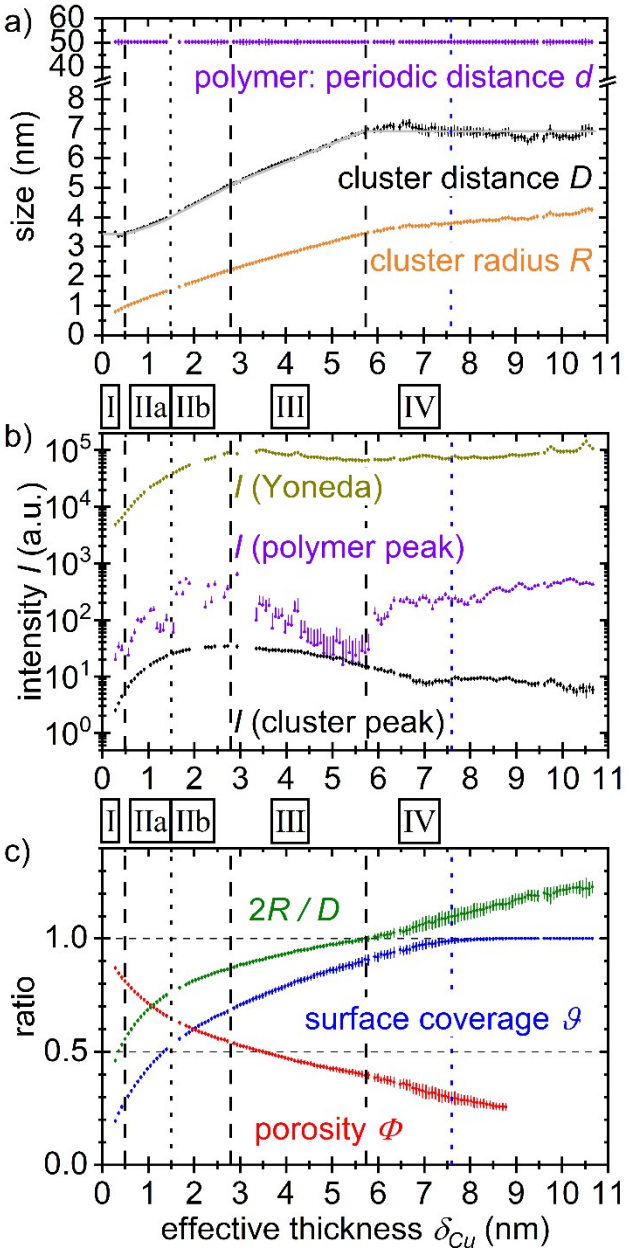

Figure S4 Evolution of structural and morphological parameters of Cu on PS-*b*-PEO during sputter deposition with 10 points binned. (a) The periodic distance of the polymer *d*, the cluster distance *D*, and the cluster radius *R* are plotted *versus* the effective thickness δ_{Cu}. The grey lines are linear fits (regimes I, IIb, III, IV) and exponential fits (regime IIa) of the cluster distance *D*'s evolution characterizing the different growth stages (nucleation, diffusion-driven growth, adsorption-driven growth, grain growth). (b) Evolution of the peak intensities at $q_y = 0$ nm^{-1} (*I* (Yoneda)), of the structure factor of the polymer at q_d (*I* (polymer peak)), and of the Cu clusters at q_D (*I* (cluster peak)) with increasing effective thickness δ_{Cu}. The polymer peak intensity increase in stage II indicates a selective wetting of the PS domains. (c) Evolution of the 2R/D ratio, surface coverage ϑ and porosity Φ with increasing effective thickness δ_{Cu}. Dashed lines divide between different regions of the cluster growth (I, II, III, IV), while dotted lines mark transitions within one region (IIa to IIb). The blue dotted line indicates $\delta_{Cu}(\vartheta = 1) = (8.1 \pm 0.7)$ nm, the point at which a full surface coverage is reached. A version of this graph without binning is shown in Figure 4.