Site-Selective Formation of Coordination Polymer consisting of Cu-Thiolate Ligands using Metal Ion-Doped Polymer Substrate

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○Takaaki Tsuruoka, Yuri Miyashita, Ryuki Yoshino, Myu Fukuoka, Yohei Takashima, Kensuke Akamatsu
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A variety of flexible, lightweight, and portable solid-state optoelectronic devices consisting of coordination polymers (CPs) have been proposed owing to the ease of synthesis of CPs with high crystallinity as well as their unique photoluminescence properties. However, the significant challenges in CP-based thin films should be addressed to realize CP optoelectronics by device integration. The poor processability of CPs considerably limits their applicability, as CP materials exhibit intrinsic instability against a range of process parameters to form the desired shapes and patterns. Therefore, facile synthetic approaches to fabricate thin films of CPs on flexible substrates are in significant demand, such as the in situ one-pot synthesis of CPs on substrates under mild reaction conditions.[1]

Herein, we demonstrate an interfacial synthetic approach for fabricating CPs comprising d^{10} coinage metals and thiolates on polymer substrates.[2] In this study, we selected a $[Cu(p\text{-SPhCOOH})]_n$, $[Ag(p\text{-SPhCOOH})]_n$ and mixed-metal $[Cu_xAg_{1-x}(p\text{-SPhCOOH})]_n$ CPs. We employed the polyimide substrate bearing cation-exchangeable group by hydrolyzing alkali solutions for precursors and template for CP-based films. The metal ion-doped polymer substrate led to the selective formation of CPs on the surface and the construction of mixed-metal CPs. In addition, a pattern of polymethyl methacrylate (PMMA) photoresist on a metal ion-doped polymer substrate was fabricated in a positive-type with vacuum ultraviolet (VUV) light illumination, enabling the formation of CP thin films with the desired patterns.

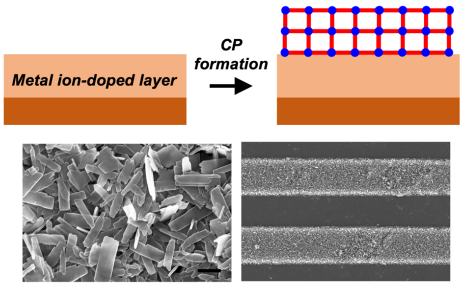

Figure. Schematic illustration of the developed interfacial approach for formation of CPs on a substrate. SEM images of the obtained sample (scale bar: 1 μm).

1) T. Tsuruoka et al., *Cryst. Growth Des.* **2020**, *20*, 1961. 2) T. Tsuruoka, et al., *submitted*