Physical vapor deposition of conductive metal–organic framework thin film

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[Introduction] Metal–organic framework (MOF) is a porous material that consists of coordinated metal ions and organic ligands. Among various MOFs, conductive MOFs attract considerable attention owing to diverse applications such as electrocatalysis, charge storage, and chemiresistive sensing [1]. For electronics device applications, the fabrication of MOF thin films is required. So far, MOF thin films are mostly fabricated in wet processes, not suitable for multilayer devices. In contrast, there are only limited reports on the fabrication of MOF thin films in dry processes. In this study, we utilize infrared-pulsed laser deposition (IR-PLD) as a method of physical vapor deposition and fabricate a conductive MOF thin film, $Cu_3(HHTP)_2$ (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene).

[Experiment] $Cu_3(HHTP)_2$ thin films were deposited on glass and Al_2O_3 (0001) substrates (4 mm × 5 mm) using an IR-PLD system [2]. As precursors for metal and ligand, we chose $Cu(OAc)_2$ (copper acetate anhydrate) and HHTP. These powders are mixed with Si powder and pelletized separately. Each pellet is fabricated in the Ar-filled gloved box and transferred to the IR-PLD chamber with no exposure to air to prevent degradation. The 88-nm-thick HHTP layer was first deposited on the substrate, followed by the 68-nm-thick $Cu(OAc)_2$ layer. The substrate temperature was kept at 150 °C during all the deposition processes. The fabricated thin films were characterized by IR spectroscopy, ultraviolet-visible (UV–vis) optical transmittance spectroscopy. The total thickness of the thin films was ~96 nm using a stylus profiler.

[Results and discussion] Figure b shows IR-spectra of a $Cu_3(HHTP)_2$ thin film deposited on Al_2O_3(0001) substrate. We observed two peaks at 1,174 cm^{-1} and 1,421 cm^{-1}, corresponding to the C–O stretching and C–H scissoring vibration of $Cu_3(HHTP)_2$, respectively [3]. On the other hand, the O–H band near 3,200–3,500 cm^{-1} of ligand, disappeared in the fabricated thin films (Figs. a,b). Next, UV-vis optical transmittance spectra show the decrease in transmittance near 680 nm (Fig. c), originating from the ligand-to-metal charge transition absorption band [4]. These results indicate the coordination of Cu and HHTP and the formation of $Cu_3(HHTP)_2$ network in the thin film by IR-PLD.

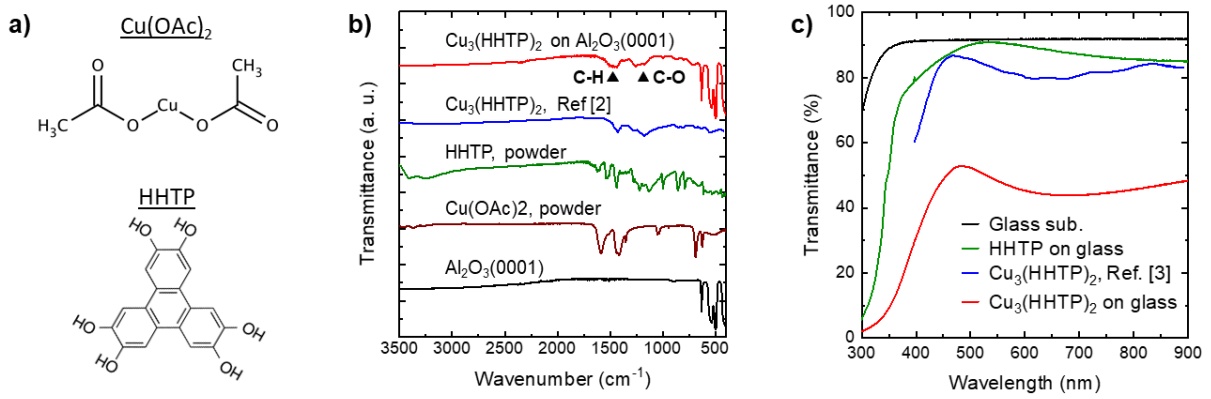

Figure: (a) Molecular structures of $Cu(OAc)_2$ and HHTP, (b) IR spectra of $Cu_3(HHTP)_2$ thin film on Al_2O_3(0001) substrates and (c) Optical transmittance spectra of $Cu_3(HHTP)_2$ on glass substrates.

References

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