Additive Manufacturing towards Color Printing via Polymer-Assisted Photochemical Deposition of Metal Thin Films

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Metal-based color filters (MCFs) have been widely studied as an essential components for various applications with higher resolution and better sustainability to surmount conventional colorant-pigment based filters[1]. However, majority of MCFs require photolithography and vacuum-based metal deposition process in fabrication. Additive manufacturing (AM) is advantageous in fast and economic production, since it allows a direct unit-by-unit deposition without requiring a mask or template. However, the mainstream AM techniques for metal printing rely on thermal or laser-induced fusion of metal particles, which introduces high temperature and is incompatible with most organic or soft materials. This limits the use of AM in flexible electronics, soft robotics and bio-sensors.

Recently, we have developed a polymer-assisted photochemical deposition (PPD) process for metal printing without lithography and vacuum-deposition (Figure 1). Using a water-soluble ink containing metal salt, reductant (sodium citrate dehydrate) and a polymer (poly(allylamine), or pAAm), this process forms metal nanoparticles (MNPs) in the presence of ultra-violet (UV) illumination. Different from conventional AM techniques that usually leave voids in the film, this process allows the MNP growth into continuous metal films. Additionally, the use of UV light also enabled flexible tuning of printing pattern and film thicknesses. We have demonstrated the versatility of printing on various substrates, including silicon, glass, plastics, and temperature-sensitive gels (Figure 2a) and capability of producing a variety of metal materials, including gold, silver, and platinum (Figure 2 b-c). The printed metal structures were found to have small surface roughness (~ 3 nm), high reflectivity (~ 95%), and high conductivity (3×10^5 S/cm), comparable to vacuum-deposited metals[2].

Based on our prior work, we prove the concept of creating MCFs using PPD. Here dielectric (silicon oxide) film was deposited on a metal (silver) reflector, and then microscale silver structures were printed on the dielectric/metal substrate, creating a Fabry-Perot (FP) cavity. The optical resonance of the FP cavity can be tuned by using different dielectric film thickness or changing metal thickness (Figure 3a) by UV illumination time (T_n). Finite-difference time-domain (FDTD) simulation was utilized to assist the design of desired silver thickness to produce different colors (Figure 3b-c), and the simulated colors were found consistent with fabricated MCFs (Figure 3d-e). Importantly, we demonstrate the feasibility of fabricating complex MCFs with ultrathin film thickness (<10 nm) and a spatial resolution down to ~5 μm. We believe that this demonstration will serve to inspire fabrication of metallic micro- and nano-structures in many nanophotonic and electronic applications.

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[1] N. Dean, Nat. Nanotechnol., vol. 10, 2015.

[2] Z. Zhao, J. Bai, Y. Yao, C. Wang, Mat. Today, vol. 37, 2020.

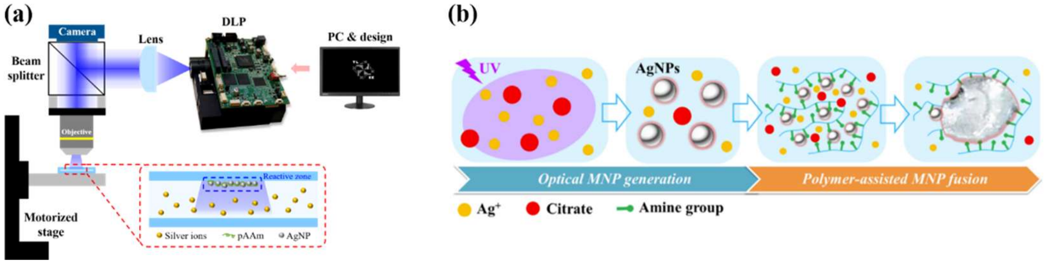

Figure 1: Polymer-assisted photochemical deposition (PPD). Schematic illustration of (a) the metal printing setup and (b) hypothesized two-steps reaction mechanism of PPD.

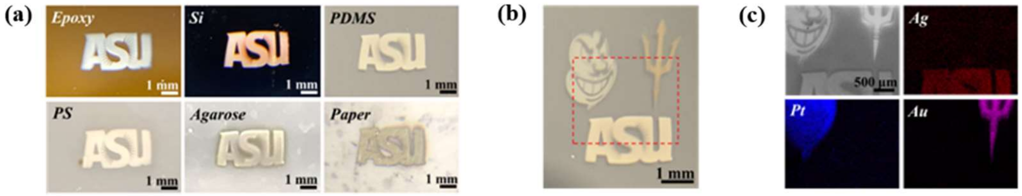

Figure 2: Demonstration of versatile PPD printing. (a) Silver structures printed on various substrates. (b) Printed ASU logo containing multiple metallic materials (ASU mascot "Sparky": Pt, The pitchfork: Au, and ASU sunburst logo: Ag). (c) Scanning electron microscopy (SEM) image and energy dispersive X-ray (EDX) mappings of the boxed region in (b).

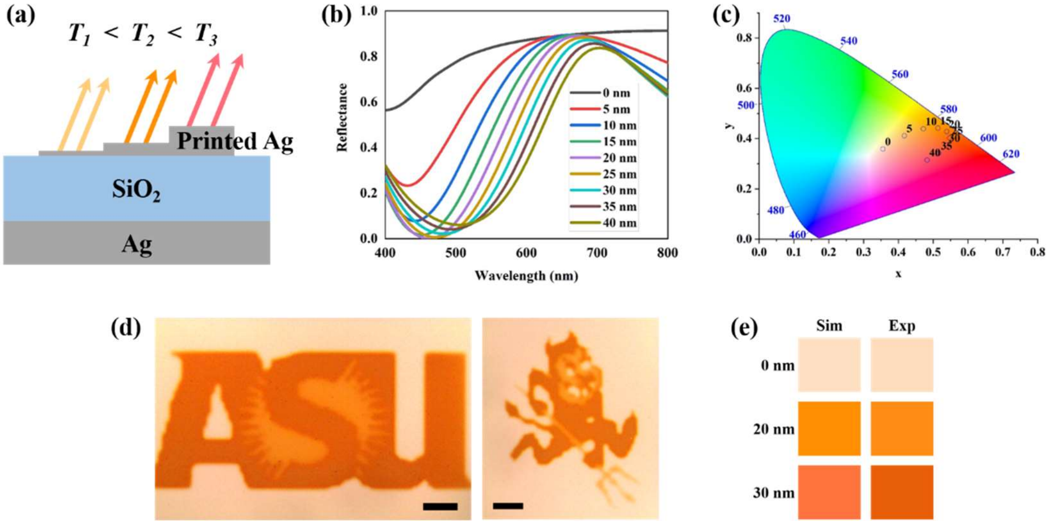

Figure 3: Characterization of PPD fabricated MCFs. (a) Schematic illustration of fabricated FP cavity with film thicknesses controlled by UV illumination time (T_n). (b) FDTD reflectance spectra with varied printed Ag thickness, where Ag and SiO_2 substrate thicknesses are set as 30 nm and 195 nm, respectively. (c) Color mapping on CIE 1931 color space using chromaticity diagram and spectra from (b). (d) Fabricated MCFs based on PPD: ASU logo and mascot (scale bar: 50 um) (e) Color comparison between simulation results and experimentally extracted results from (d).