Color Printing by Polymer-Assisted Photochemical Deposition of Metallic Thin Films

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Structural color printings (SCPs) have been widely studied for their higher resolution and better sustainability compared to conventional pigment-based printing technologies[1]. The most widely adopted designs of SCPs rely on the use of micro- or nano-structured materials, e.g. plasmonic or dielectric nanostructures, to modulate the light-matter interaction and accordingly display colors[2]. However, such designs usually demand complicated, time-consuming, and expensive fabrication processes from nanolithography to vacuum deposition and etching.

Here, we demonstrated micro-scaled SCP by employing our recently developed 3D printing technology, i.e. polymer-assisted photochemical deposition (PPD)[3]. Briefly, using a water-soluble ink containing metal salt, reductant (sodium citrate dehydrate) and a polymer (poly(allylamine)), the PPD process produces metal nanoparticles (MNPs) in the presence of ultra-violet (UV) illumination (Fig. 1a). To prove the concept of SCP, a Fabry-Perot (FP) cavity was created, consisting of a bottom metal (silver) reflector, a mid-layer dielectric (silicon oxide) film, and a top-layer printed microscale silver structures. Our PPD-printed films (as thin as < 5 nm) were found slightly smoother (Fig. 1b) and more continuous (Fig. 1c) than physical vapor deposited (PVD) ones. Interestingly, the PPD film had significantly different optical refractive indexes from PVD films in the visible wavelength range (400 nm – 800 nm) (Fig. 1d). This was found to be caused by the unique formation of nanocomposite consisting of interconnected MNPs and polymer matrix[4]. In fact, this more lossy composite film is more desirable to produce more broadened optical response than PVD film for more vivid color display.

The design of FP cavity allowed us to flexibly design the printing color by changing the dielectric layer thickness (*d*) and/or the metal film thickness (*t*) (Fig. 2a), as shown by Finite-difference time-domain (FDTD) simulation (Fig. 2b-c). With the same *d*, multiple colors can be produced in a single print, simply by modulating *t* though overlaying two image patterns in consecutive UV illumination steps (Fig. 2d). As demonstrated (Fig. 2e-g), complex SCPs with ultrathin film thickness (< 5 nm) and a spatial resolution down to ~ 6.5 µm were successfully demonstrated. Further, utilizing thick PPD-printed silver as bottom reflector and polymethyl methacrylate (PMMA) films as the dielectric spacer, our technology can be extended to flexible substrates, e.g. polyethylene terephthalate (PET) (not shown here)[5]. Our demonstration may inspire future additive manufacturing of metallic micro- and nano-structures in nanophotonic and electronic applications.

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[1] Z. Xuan et al., The Innovation, Vol. 2, 10081, 2021.
[2] F. Cheng et al., Sci. Rep., Vol. 5, 11045, 2015.
[3] Z. Zhao et al., Mat. Today, Vol. 37, 10-17, 2020.
[4] V. Vodnik et al., Polymer Composites, Vol. 33, 782-788, 2012.
[5] S. Choi et al., manuscript submitted.

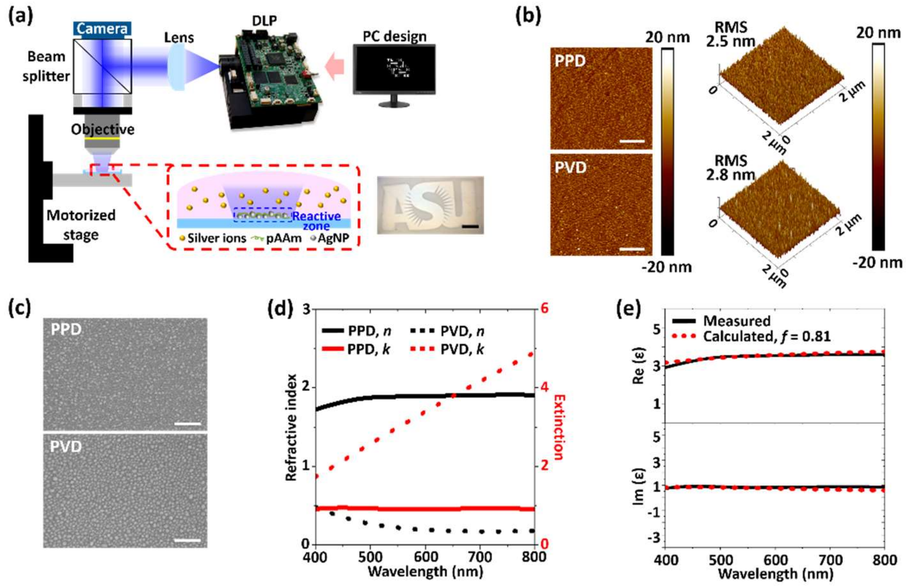

Figure 1: Structural and optical characterization of PPD and PVD thin films. (a) Schematic illustration of the PPD printing setup (b) 2D (left, scale bar: 500 nm) and 3D (right) profile of atomic force microscopy (AFM) images. (c) Scanning electron microscopy (SEM) images (scale bar: 200 nm). (d) Measured optical properties (n, in black; k, in red) of PPD (solid lines) and PVD (dot lines) films, respectively. (e) Measured (black solid line) and calculated (red dotted line) permittivity of PPD film. Top: real part. Bottom: Imaginary part. *f*, the filling factor of metal.

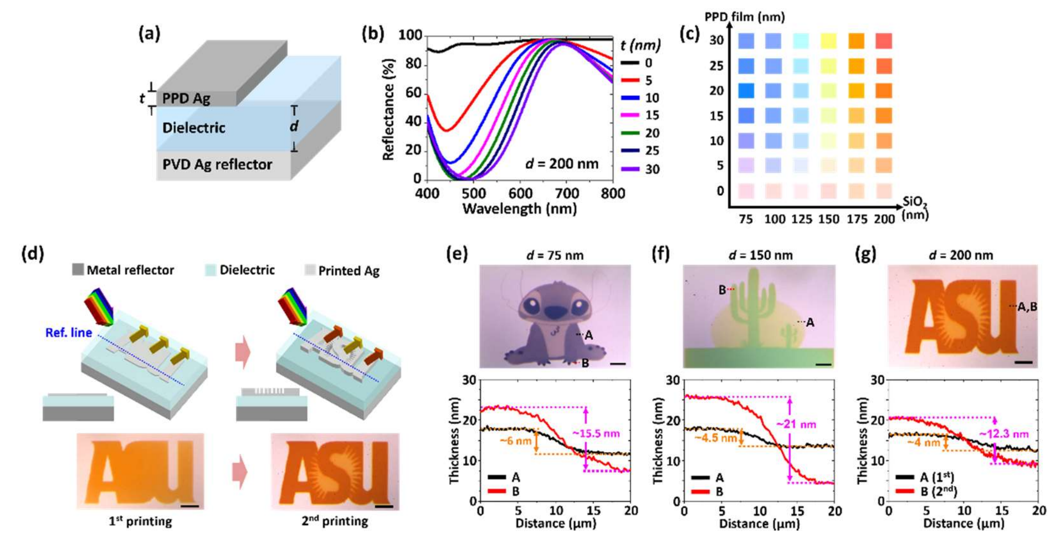

Figure 2: Characterizations of SCP. (a) 3D schematic of the FP cavity, with the top-layer PPD film thickness *t* and dielectric spacer thickness *d* as variables. (b) FDTD reflectance spectra with varied printed Ag thickness, where Ag and SiO_2 substrate thicknesses are set as 85 nm and 200 nm, respectively. (c) Generated color palette based on simulated spectra results, mapped on CIE 1931 color space. (d) Schematic illustration of fabricated FP cavity using PPD (top) and microscopic images for exhibited colors corresponding to each structures (bottom). (e-g) PPD based SCPs for complex structures. (e) Cartoon character 'Stitch', (f) a symbol of Arizona 'Cactus', and (g) 'ASU' logo. All scale bar is 100 μm.