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Grant Title: Synthesis of Bumpy Core-shell Polymeric Nanoparticles for Coffee Ring-free Assemblies
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Synopsis: Colloidal particles are of interests to create photonic colors because they are low cost and versatile. However, colors obtained from highly ordered colloidal crystals are angle-dependent. Moreover, coffee-ring effect is often observed during assembly where an order structure is formed predominantly at the droplet edge. Uniform structural colors have been demonstrated from quasi-amorphous colloidal assemblies. The goal of this proposal is to synthesize core-shell nanoparticles (NPs) and fine-tune the morphology of the shell to suppress the coffee-ring effect and enhance reflectivity, thus, color contrast. We will study the self-assembly mechanisms for potential applications such as 3D color printing, smart windows, and mechanosensors.

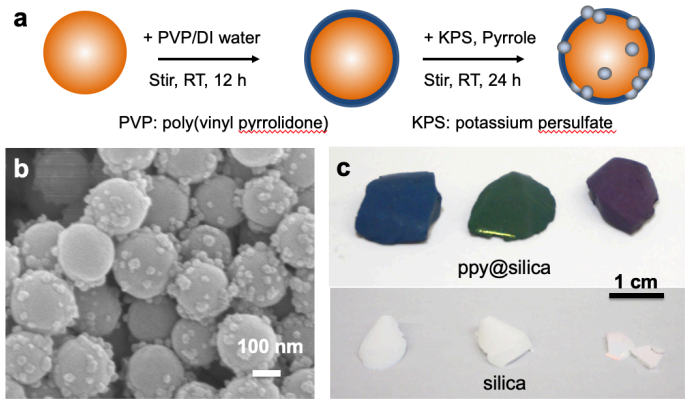

Fig. 1 (a) Schematic illustration of the synthesis of bumpy PPy@silica NPs, where silica NPs are first coated with poly(vinyl pyrrolidone) (PVP), followed by in situ polymerization of pyrrole. (b) SEM images of the bumpy PPy@silica NPs. (c) Optical images of the drop cast films from the assemblies of PPy@silica NPs vs. those from assemblies of silica NPs of different sizes.

Synthesis and assembly of bumpy colloidal NPs for ultrasmooth and uniform structural colors. Polypyrrole (PPy) black coated silica NPs (PPy@silica NPs) were synthesized with a low coverage (~10.7 wt%) of bumpy PPy nanogranules (10–30 nm in diameter, see Fig. 1 and the corresponding scanning electron microscopy, SEM images). After drop-casting the colloidal ink on a glass slide, followed by solvent drying in air, we observed uniform color from PPy@silica NPs and the color could be tuned by the silica NP size. In contrast, the drop-cast films from the pristine silica NPs appeared white or opalescent due to the Bragg reflection from the relatively ordered structure (Fig. 1c).

As seen from the optical images, the pristine silica NPs were assembled in highly ordered fashion but mainly localized at the outskirt of the droplet, a typical coffee-ring effect (Fig. 2a). In contrast, the bumpy

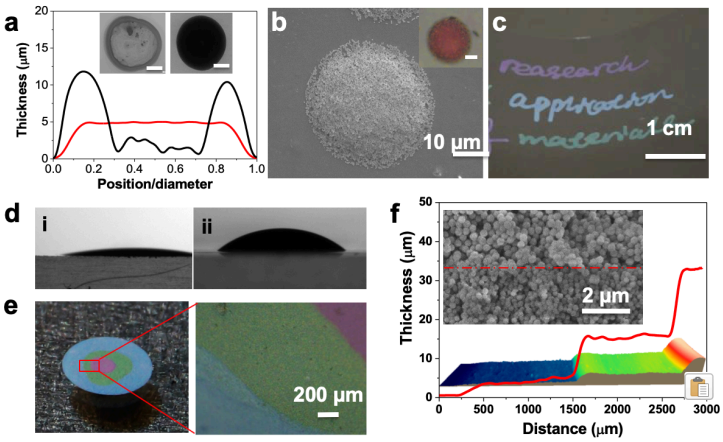

Fig. 2 (a) Optical microscopy images of drop cast from (left) silica NPs (diameter, 300 nm) and (right) bumpy PPy@silica NPs dispersed in IPA, and the corresponding thickness profile of the dried droplets consisting of silica NPs (black line) and the bumpy PPy@silica NPs (red line) on glass. Scale bar: 200 μm. (b) SEM image of the droplet showing the nanoparticle assembly and the corresponding color. (c) Photo of letters written on the 3M inkjet printable PET film from the bumpy PPy@silica NP/IPA solution as ink. (d) Contact angles of a drop of bumpy PPy@silica NP/IPA solution on (i) a glass slide and (ii) on a dried PPy@silica NP film, respectively. (e) Optical microscopy image of a three-layer stacked PPy@silica NP film. Scale bar: 50 μm. (f) Confocal microscopy image and height profile of the three-layer stacked PPy@silica NP films. Inset: Cross-sectional SEM image of the stacked NP film, where the red line indicates the interface between two layers of different sized NPs.

PPy@silica NPs are loosely packed into quasi-amorphous structures and the coverage is rather uniformly across the entire droplet without coffee-ring effect (Fig. 2a-b). We believe that the bumpy surface on the core-shell NPs could deform the air-water interface, forming arrested structures (or aggregates) because of the high surface area and the mechanical occlusion by the PPy nanogranules, which acted like gears to interlock each other, preventing them to be swiped to the edge of the droplet. In turn, it effectively suppressed the coffee-ring effect during the drying of the colloidal ink, leading to ultrasmooth surfaces with submicron thickness and uniform structural colors with wide viewing angles (Fig. 2c-d). The color can be fine-tuned by the size of silica NPs, and the presence of PPy black significantly enhances the color contrast by suppressing incoherent and multiple light scattering. Moreover, the bumpy colloidal ink can be formulated from both low and high surface tension liquids as solvents and applied to a hydrophilic or hydrophobic substrate. The ultrasmooth surfaces of the colloidal drop allowed to stack different color drops on top of each other, creating a "3D" color.

Synthesis and assemblies of metallic nanoprisms. Despite the success in creating angle-independent colors, the reflectance from the silica based colloidal assemblies remains relatively low. To enhance the color intensity and contrast, we began to synthesize metallic nanoparticles and metal@silica core-shell nanoparticles, investigate their assemblies in liquid crystal phases, and add chiral dopant to form lamellar structures. Specifically, we have synthesized Au and Ag NPs with different sizes and shapes, including spherical nanoparticles, nanorods, and nanoprisms. Metallic NPs can generate localized surface plasmonic resonance (LSPR) such that the color from metallic NPs is angle-independent but with high contrast. Due to the shape anisotropy, nanoprisms could be assembled into unique geometries, hexagonal packing, layer-by-layer stacking, or the combination (Fig. 3). Here, the surface chemistry on nanoprisms is critical to their aggregation in solution and later assembly behaviors, and thus the colors from the assemblies. Currently we explore the mechanism to control the assembly behaviors, e.g. forming higher-order liquid crystal phases by varying ligand chemistry and salt concentration. Importantly, NPs should disperse well in the liquid. Therefore, chemistry of ligands on NPs is critical.

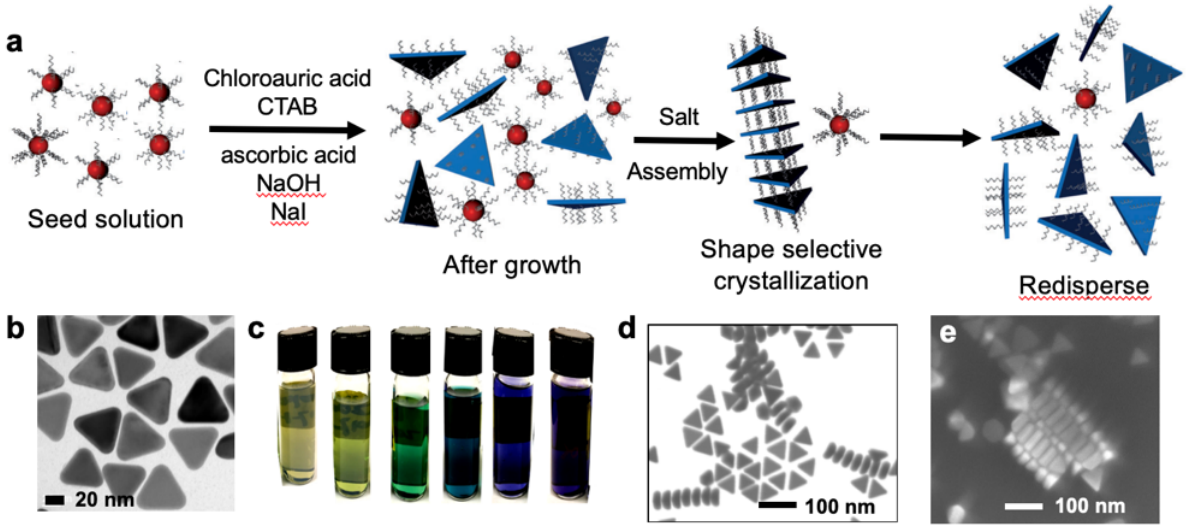

Fig. 3. (a) synthesis of Au nanoprisms. (b) TEM image of Au nanoprisms. (c) Optical images of Au nanoprisms in water. (d) TEM and (e) SEM images of the assemblies of Au nanoprisms.

Impact of the research: This project allows the PI to build a new research direction in synthesis of various NPs and establish a fundamental understanding of how the surface chemistry and morphology of the NPs could dictate the assemblies, which in turn affect the structural colors (evenness of the films, angle-independence, and color contrast). The research project involves a set of polymer synthesis, nanoparticle synthesis, and characterization. This project also trained the postdoc and student involved in the project to learn different characterization techniques, including dynamic light scattering (DLS), SEM and transmission electron microscopy (TEM) for examining nanoparticle size, distribution, and morphology, and transmission/reflectance measurement to characterize the optical properties. Our study of creating angle independent structural colors from colloidal assemblies also enabled us to explore potential applications such as colorimetric biosensors, where molecular imprint polymers will be grafted onto NP surface for the target drugs whereas the assembly of the NPs will be important to create smooth, color films for sensing.