3D Printing of Colloidal Nanocrystals Using Light

Three-dimensional nanoprinting is a state-of-the-art manufacturing technique that allows maskless fabrication of complex 3D structures with nanoscale resolution. Rationally designed 3D nanostructures exhibit intriguing physical, chemical or mechanical properties beyond those found in nature, such as negative refractive index, artificial magnetism and impact resilience.[1] However, traditional 3D laser nanoprinting relies on photopolymerization and is therefore limited to some light-responsive polymers.

One strategy for meeting the demand for additional 3D-printable materials is to use a 3D polymer skeleton as a mask for conformal adsorption or deposition of inorganic materials, allowing construction of organic–inorganic nanohybrids. Alternatively, functional components can be incorporated into photosensitive resin to form nanocomposites for direct laser printing. Although the polymer in the 3D hybrid structures can be removed by post-sintering or chemical etching, polymer removal can lead to severe structural shrinkage or defects, which causes the properties of the functional architectures to deteriorate.

In recent work, we developed a polymer-free 3D-printing technique called photoexcitation-induced chemical bonding (PEB) to directly assemble and print colloidal nanocrystals into 3D nanostructures.[2] Colloidal nanocrystals are solution-grown, nanometer-sized inorganic particles that present an ideal candidate for the functional feedstocks, thanks to their abundant species and superior properties.[3,4]

In our experiment, we chose water-phase CdSe/ZnS core/shell quantum dots (QDs) capped with 3-mercaptopropionic acid (MPA) as an example. The highest occupied molecular orbital of MPA molecules is located above the valance band maximum of CdSe; hence, under light excitation, the holes generated inside CdSe cores tunnel through the shell barrier and are captured by the MPA ligands. The surface ligands are then desorbed from the nanocrystal surface, exposing the unoccupied bonding sites. Such chemically active sites are connected to surface ligands from neighboring nanocrystals for interparticle bonding and printing. This concept can be extended to other nanomaterials, such as MPA-capped CdSe QDs, CdS QDs and silver nanocrystals.

Using a 780-nm femtosecond laser as the excitation light source, we printed QDs into arbitrary 3D structures in shapes ranging from linear to curved to volumetric by steering the laser focus in 3D space. Through parameter optimization, we achieved a minimum printing linewidth of 77 nm, taking advantage of the threshold effect of two-photon absorption. We also utilized QDs of different colors as feedstocks and demonstrated heterogeneous 3D-printing capability.

We anticipate that PEB will open new avenues in the manufacturing of freeform 3D nanophotonic and optoelectronic devices for many new applications. OPN

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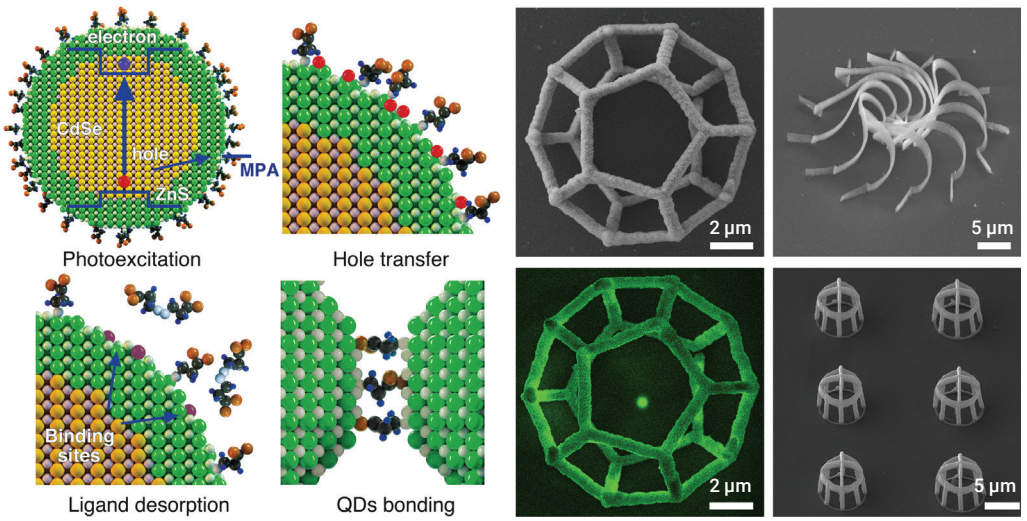

Left: The working principle of PEB. Right: 3D laser printing of complex structures composed of QDs.