Synthesis of Light-Diffracting Assemblies from Microspheres and Nanoparticles in Droplets on a Superhydrophobic Surface

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Crystalline arrays of colloidal particles Periodicity

Light manipulation capability in a manner similar to that in natural opals

colloidal particles into macroscopic spherical structures

Wet self-assembly (WSA) and dry self-assembly (DSA)
The Paper

Colloidal assembly in droplets

Advantages
- Better control over the final shape
- Creation of supraparticles that are easily detached and ready-to-use
- Near-spherical and spheroidal supraballs in dry environments

Droplets reside on superhydrophobic substrates

Result
The experiment

The first step

Surface generation

Mixture of xylene and methyl ethyl ketone

LDPE sheets

Coated with

A solution of LDPE pellets

- Xylene is solvent
- MEK is non-solvent
- Non-solvent is to increase the roughness and contact angle of the substrates
Why LDPE?

- flexible
- naturally hydrophobic
- inexpensive
The next step of the experiments

Preparation of supraparticles from a mixed suspension of latex microspheres and gold nanoparticles

The final step

Drying

The final stages of drying, the gold nanoparticle suspension dewets the latex microsphere network and clusters within some of the crystal domains on the supraparticle surface
Schematics of the process for making spherical colloidal assemblies on superhydrophobic surfaces: a) latex opal ball, and b) latex and gold opal ball. The inset is a scanning electron microscopy image that displays the hexagonal close-packed structure of latex spheres inside an opal ball of 540nm latex.
This method easy to implement
avoids the oil-removal step

Makes the colloidal assemblies ready to collect and use
Timeline of formation of spherical opal assemblies on a superhydrophobic Si-NW substrate: a) latex, b) latex and 0.1 wt % Au nanoparticles, and c) latex and 1.0 wt % Au nanoparticles. The latex microsphere diameter is 540nm in each droplet. The Au nanoparticle diameter is 22 nm. Scale bars: 500nm.
SEM image of the surface of a supraparticle made from a mixture of 540nm latex and 22nm gold nanoparticles. Dark spheres are latex and bright regions are clusters of gold nanoparticles. Scale bar: 5mm.
Optical microscopy images of latex opal balls made from microspheres with varying sizes taken under identical illumination conditions.
Optical microscopy images of latex and gold nanoparticle opal balls containing microspheres of varying sizes.
Figure 6. a) Colored rings in the top-view of a 540nm latex opal ball. b) Side-view schematics of the angles used in the theoretical calculation of wavelength for a particular color ring.
Figure 7. Normalized path difference versus the normalized wavelength for colored ring patterns in latex opal balls and latex/gold opal balls.
\[ m\lambda = d \times \left[ \sin(90 - \alpha) + \sin(\theta - \alpha) \right] \]

- **\( m \)** = 1, 2, 3... for first, second, and third sets of rings, respectively.
- **\( \lambda \)** is the wavelength, \( l \), of the specific spot on a colored ring
- **\( d \)** is the interplanar spacing for (111) planes
- **\( \theta \)** is the angle between the incident beam direction and the horizontal plane.
- **\( \alpha \)** is the angle between the radial direction and the horizontal plane.
Future scopes

methods and the types of supraballs formed can be diversified much in future research

Magnetic functionality can be introduced in latex opal balls by adding magnetic nanoparticles to the initial latex suspension

Further refinements are required for control of the final size of the supraparticles

Owing to their close-packed structure, the latex spheres have maximum contact with their neighboring particles. However, the supraparticles still manifest brittleness because of the low strength of van der Waals attractions at small contact areas between microspheres. This creates the need for further reinforcement procedures to increase the mechanical stability of the structures.
Summary

• Simple yet powerful technique that can be used in massively parallel manufacturing of diffracting particle assemblies in droplets suspended on superhydrophobic substrates.

• The reflection bands in the “opal balls” originate from diffraction by the parallel crystal rows on the surface, instead of bulk Bragg scattering.

• The presence of metallic nanoparticles in the structure does not lead to a shift of the reflection band by plasmon resonance, but enhances the diffraction color by increased reflectance and suppressed backscattering.

• The uniform supraballs can find application in photonics, drug delivery, special coatings, sensors, and microfluidics