Optical ceramic meets metal-organic frameworks

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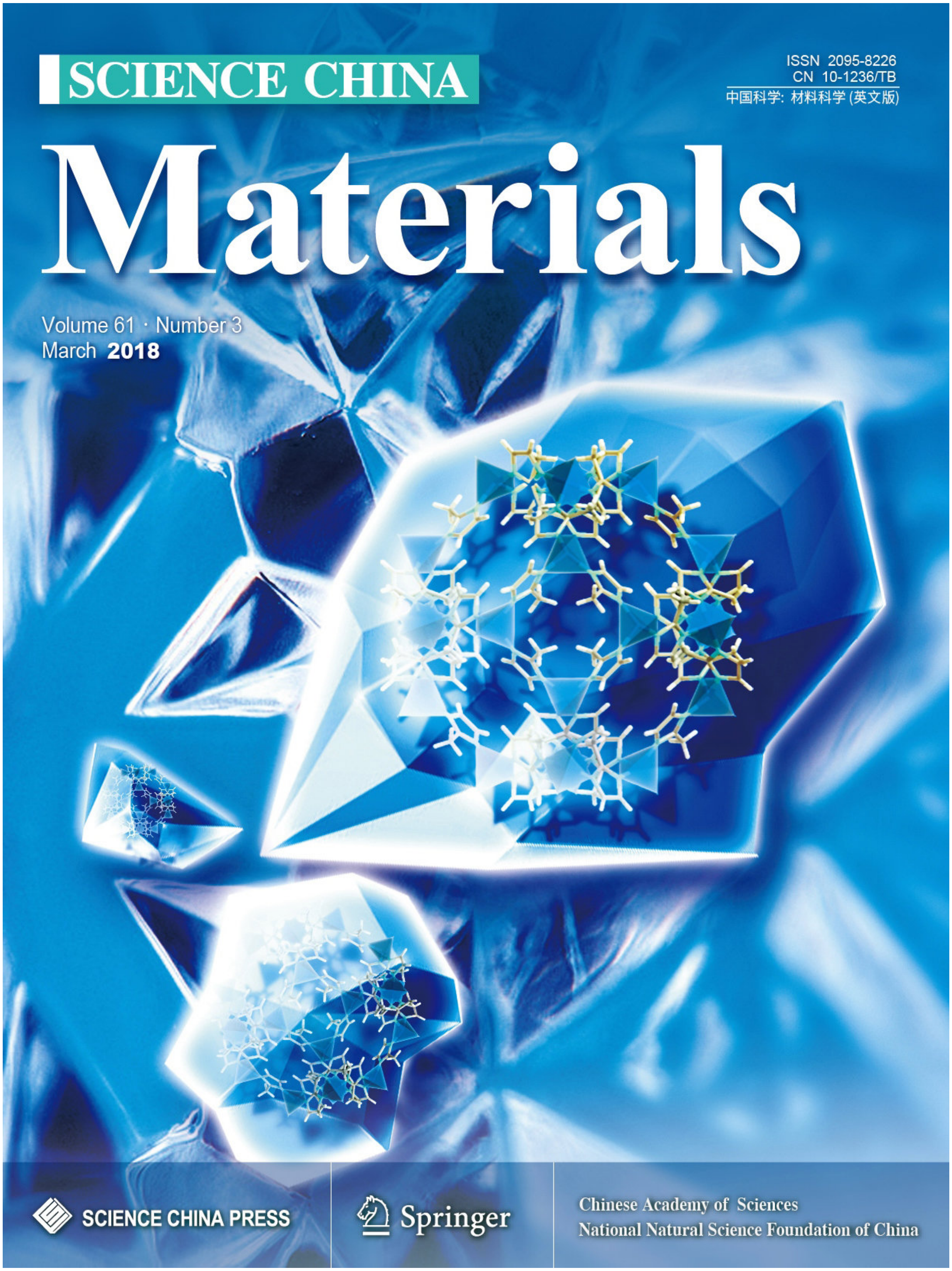
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Recently, researchers from Sun Yat-Sen University reported that by simply slowing down the solvent evaporation rate, metal-organic framework nanocrystals can fuse at room temperature to form transparent ceramic-like monoliths with optical transmittance up to 84 percent and a low energy threshold for the amplified spontaneous emission. Credit: ©Science China Press

Ceramic, a kind of poly-crystalline monolith sintered by inorganic, non-metallic crystallites, is normally opaque due to defects, voids and birefringence. Eliminating the inner light scatter creates transparent or optical ceramics.

Jie-Peng Zhang and co-workers from Sun Yat-Sen University developed new metal-organic frameworks for preparation of optical ceramics. They've published their results in *Science China Materials*.

Zhang's group has been engaged in the development of metal-organic frameworks and their applications in adsorption, separation and sensing for a long time. Optical ceramics are a special type of ceramics, and, like single crystals, they are optically transparent. The development of optical ceramic heavily relies on the precursor materials.

"To make ceramics transparent, the inner pore and impurity should be minimized to zero. This is a very stringent demand," says Zhang. "The precursors not only need high purity and uniform size distribution, but must be crystallized in cubic symmetry to remove birefringence effect."

In addition, preparing ceramics requires a high-temperature sintering process. Therefore, to date, only a few materials can be used for optical ceramics.

Porous coordination polymers, also known as metal-organic frameworks

(MOFs), have captured widespread attention for adsorption, catalysis, sensing and optics. "However, commonly, they are microcrystalline powders," he says. "It is still challenging to prepare MOF membranes and single crystals with high quality and large size."

Despite low solubility in common solvents, the nanocrystals and building units of MOFs have a notable exchange rate, especially in grains with small size and large curvature. Zhang says, "It is essential to the crystal growth and ion/ligand exchange processes of MOFs." A condensed monolith may be formed by healing the defects inside the aggregates which are assembled by MOF nanocrystals.

Zhang says, "This philosophy motivates us to employ MOF nanocrystals as precursors and then fuse them into a transparent monolith, i.e., metal-organic optical ceramics (MOOC)."

The SOD-type zinc(II) 2-methylimidazolate, namely MAF-4 or ZIF-8, is the first MOF with natural zeolite topology and crystal symmetry, extensively studied for its special pore structure and high stability. Zhang says, "Experimentally, we used ethanol as solvent to produce MAF-4 nanocrystals in diameter of 20 nm, and the gelatinous substance obtained by centrifugation was dried in air at room temperature naturally, which is finally transformed to the colorless and transparent monoliths or MOOC-1, with 84 percent optical transmittance. If you dry the samples at high temperature or in a vacuum, just like general processes in MOF syntheses, you can only obtain the MOF as common white powders."

X-ray diffraction analysis indicates that MOOC-1 is polycrystalline instead of single crystal or glass. The porosities inside MOF-4 and its assemblies allow the luminescent dye, sulforhodamine 640 (SRh), to be doped in MOOC-1 to form a luminescent optical ceramic SRh@MOOC-1, which produces amplified spontaneous emission (ASE) with a low energy threshold of 31 micro-Joule per square centimeter stimulated by a 532 nm laser. "This value is lower than previous reports of MOF-based ASE/lasing. In addition, lowering the solvent evaporation rate is an effective method for fusing MOF nanocrystals into a dense and transparent crystal," Zhang says.

Prof. Xiao-Ming Chen at Sun-Yat Sen University, the founder of MAF-4, says, "This strategy extends the candidate scope of optical ceramics and paves a new way to develop MOF-based devices for optical, adsorption, separation and sensing applications."

More information: Jia-Wen Ye et al, Room-temperature sintered metal-organic framework nanocrystals: A new type of optical ceramics, *Science China Materials* (2018). DOI: 10.1007/s40843-017-9184-1

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