



Room-temperature sintered metal-organic framework nanocrystals: A new type of optical ceramics

Jia-Wen Ye¹, Xuehong Zhou², Yu Wang¹, Rui-Kang Huang¹, Hao-Long Zhou¹, Xiao-Ning Cheng¹, Yuguang Ma² and Jie-Peng Zhang^{1*}

Ceramic is a rigid material consisting of an infinite three-dimensional network of sintered non-oriented inorganic, non-metallic crystalline grains, which are generally non-transparent. If the inner light scatter is eliminated, ceramics can become transparent or optical ceramics [1,2]. With great potentials in optical windows, sensors and lasers, optical ceramics have received great attentions since 1950s [1]. As the gain medium of solid-state lasers, optical ceramics can combine the advantages of large size, high transparency, high mechanical and thermal stabilities, and ease for dispersing the luminous atoms and groups [3]. For comparison, single-crystal gain mediums can suffer high power density but are difficult to grow into large size, while glasses and polymers have reversed characteristics.

To make ceramics transparent, the inner pore and impurity should be minimized to zero, which requires highly pure, nanosized, and very uniform crystallite precursors as well as complicated fusing technology (Fig. 1) [4,5]. The cubic crystal symmetries (absence of the birefringence which causes extremely high scattering losses) are generally required for the crystallites of optical ceramics, meaning that only a few inorganic materials can be used. Besides, ceramics sintering usually operates above 1000°C, which excludes organic and organic-inorganic hybrid materials [1].

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) are crystalline materials consisting of metal ions and organic ligands, which have captured widespread attentions for adsorption, catalysis, sensing, optics [6] and also laser gain mediums [7–11]. As can be seen in membranes and photonic crystals [12,13], MOF nanocrystals may merge to form seamless microscopic blocks under mild conditions [14–16]. Nevertheless,

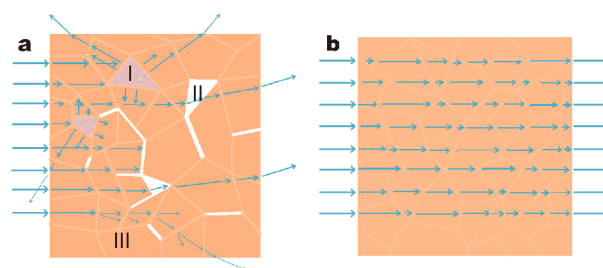


Figure 1 Schematic illustrations of the light propagating pathways in (a) opaque ceramics (I, II, and III represent light scattering sources of impurity, residual pore, and birefringence, respectively) and (b) transparent ceramics.

macroscopic and optical transparent blocks of MOF nanocrystals/microcrystals are still unknown so far. Just like single crystals and optical ceramics, increasing the block size with high optical quality is always a great challenge for many materials. Here, we show that by simply slowing down the solvent evaporation rate, nanocrystals of the prototypical MOF SOD-[Zn(mim)₂] (MAF-4/ZIF-8 [17,18], Hmim = 2-methylimidazole, Fig. 2) with the cubic crystal symmetry can fuse at room temperature to form large transparent blocks. After doping laser dye, this metal-organic optical ceramic (MOOC) can show the amplified spontaneous emission (ASE) with a very low energy-density threshold.

MAF-4 nanocrystals with uniform size (ca. 20 nm) can be easily synthesized by reaction of Zn(NO₃)₂ and Hmim in methanol or ethanol at room temperature (Fig. S1). Compared with the commonly used solvent methanol [19], ethanol is nontoxic and more environment-friendly. After centrifugation and washed, the residual nanocrystals and solvent form a white gel-like (semi-fluidic) block. As reported previously, when the residual solvent me-

¹ MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China

² Institute of Polymer Optoelectronic Materials & Devices, State Key Laboratory of Luminescent Materials & Devices, South China University of Technology, Guangzhou 510640, China

* Corresponding author (email: zhangjp7@mail.sysu.edu.cn)

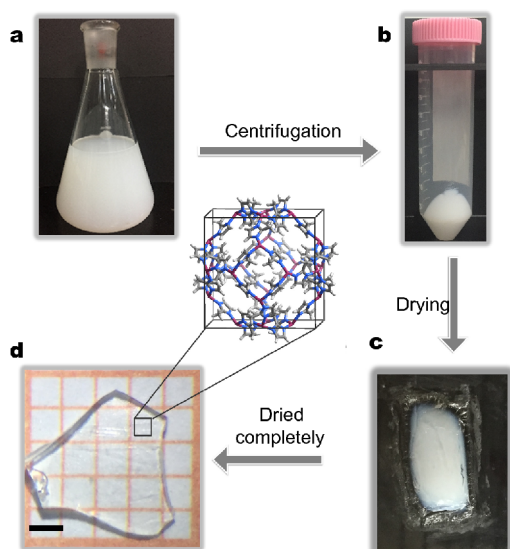


Figure 2 Optical photographs of (a) a colloidal solution of MAF-4 nanocrystals, (b) a gel-like (semi-fluidic) block of a mixture of MAF-4 nanocrystals and ethanol, (c) a semi-dried/shrunk gel of a mixture of MAF-4 nanocrystals and ethanol, and (d) a typical piece of MOOC-1 (scale bar 1 mm). Inset: a portion of the crystal structure and the unit cell of MAF-4.

thanol was removed quickly by vacuum and/or heating, the gel transformed to white/opaque solid blocks, which can be easily crushed to form white powders (Fig. S2) [20–22]. Interestingly, when the solvent was ethanol, the gel transformed to small transparent granules after the vacuum/heating treatment (Fig. S2). Further, when the gel, synthesized using either methanol or ethanol as the solvent, was slowly dried at room temperature in ambient air, it shrunk and finally transformed to much larger transparent coherent masses (MOOC-1). Although a gel-like block tends to break into several pieces after drying, large pieces of transparent blocks with size of $4 \times 4 \times 1 \text{ mm}^3$ can be easily obtained (Fig. 2).

X-ray diffraction confirmed that MOOC-1 is composed of randomly oriented nanocrystals (Fig. 3 and S3). As expected from the cubic crystal symmetry of MAF-4, polarizing microscope showed no birefringence (completely dark when the Nicol was cross) in MOOC-1 (Fig. S4). No defect or residual pore was found by optical microscope and scanning electron microscope (SEM), and the block surface is very smooth (Fig. S5). The optical transmittance of MOOC-1 gradually increases from 69% at 400 nm to 84% at 700 nm (Fig. 3), being similar with those of Nd:YAG optical ceramics [4]. In other words, MOOC-1 possesses similar optical properties of conventional optical ceramics. Preliminary studies showed that, besides MAF-4, several other types of MOF nanocrystals

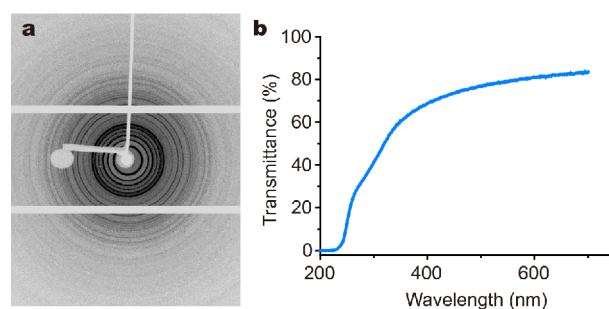


Figure 3 (a) Two-dimensional X-ray diffraction and (b) UV-vis absorption spectrum of MOOC-1.

can also fuse at similar conditions to form MOOCs (Fig. S6). The close contacts between MOF nanoparticles have been rarely studied [14–16]. It is well known that crystals in solvent are not static but actually undergoing recrystallization. The recrystallization rate depends on many factors such as the composition, structure, and size of the crystal, the solvent, and the temperature. Although MOF nanocrystals are generally regarded as insoluble in common solvents in the macroscopic point of view, many MOFs actually can readily undergo metal ion/ligand exchange [23]. Further, smaller crystals and crystal surfaces with bigger curvatures have higher surface energies and recrystallization rates. Therefore, the close-packed MOF nanoparticles can optimize their shapes to form closer contacts and even completely fuse together. Nevertheless, slowing down the solvent evaporation rate, which provides enough time for the fusing process and avoids destroying the crystal boundaries, should be the key for obtaining large coherent masses of fused MOF nanoparticles.

MAF-4 is well known for its ability to encapsulating small molecules, either inside the SOD cage or into the crystal defect [24,25]. Sulforhodamine 640 (SRh) is a good laser dye with high photoluminescence quantum yield, and low energy-density thresholds of $30\text{--}95 \mu\text{J cm}^{-2}$ for laser/ASE had been achieved by using this dye [26]. SRh can be doped into MAF-4 by adding SRh during the synthesis of the MOF nanocrystals. Using the same drying process for MOOC-1, the desired SRh doped optical ceramic (hereafter denoted as SRh@MOOC-1) was obtained as rose-bengal transparent solid blocks (Fig. 4 and S3). Excited by a monochromatic xenon lamp at 532 nm (the second harmonic of a Nd:YAG laser, convenient for comparison with the ASE test), SRh@MOOC-1 showed the characteristic broad emission band of SRh peaked at 613 nm (Fig. S7). The fluorescence lifetime and quantum yield were determined as 6.25 ns and 63.6%, respectively

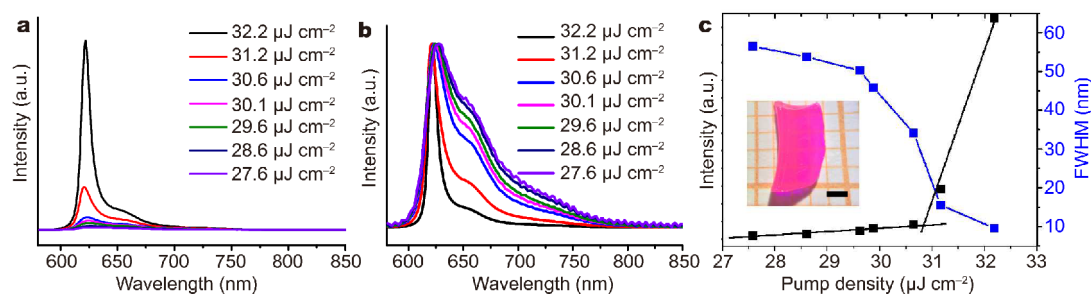


Figure 4 The pumping-energy-density dependent fluorescence of SRh@MOOC-1. (a) Original emission spectra. (b) Intensity-normalized emission spectra. (c) The relationships of the peak intensity (black) and the FWHM (blue) of the fluorescence emission against the excitation pump laser power (Inset: a photograph for SRh@MOOC-1, scale bar 1 mm).

(Fig. S8), which were similar to the normal values reported for rhodamine dyes [26,27]. Note that a high luminescence quantum yield can greatly improve the performance of the gain medium [28].

The lasing performances of gain mediums can be studied by measuring their ASE properties. A piece of SRh@MOOC-1 with size of $6 \times 3 \times 1 \text{ mm}^3$ was excited with 532-nm laser pulses and the luminescence spectra were detected by a fibre optic spectrometer. At low excitation energy densities ($27.6\text{--}30.6 \mu\text{J cm}^{-2}$), the emission spectra were similar with that observed in the ordinary luminescence test with a broad emission band. As the excitation energy density increased above $30 \mu\text{J cm}^{-2}$, the emission band suddenly narrowed, indicating an ASE appeared above a certain energy-density threshold (Fig. 4). The energy dependence of the luminescence intensity and the full width at half maximum (FWHM) of the emissions gave a very low energy-density threshold of $31 \mu\text{J cm}^{-2}$ (Fig. 4), which is the lowest among all reported values for MOF-based gain mediums ($41\text{--}7.5 \times 10^6 \mu\text{J cm}^{-2}$) [28–29] and also lower than the values reported for SRh-doped polymers ($53\text{--}95 \mu\text{J cm}^{-2}$) [26], illustrating the very good optical quality of MOOC-1. What is more valuable that the volume of SRh@MOOC-1 is at least 10,000 times bigger than the biggest MOF single crystals used for ASE or laser tests (Table S1), and we believe that MOOCs can grow into bigger size and better optical property by further optimization of the synthetic and drying procedure.

In summary, we found that MOF nanocrystals can fuse at room temperature to form large blocks with good optical transparency, serving as a new type of optical ceramic preforming good ASE property. Considering the vast diversity of their structures and functions, MOFs can serve as an innovative type of raw material for ceramics and optical ceramics, which can enlighten future developments of not only new laser mediums and optical de-

vices, but also applications related with adsorption, separation, sensing, etc.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.



Jia-Wen Ye was born in 1990. He is a PhD candidate of inorganic chemistry at Sun Yat-Sen University (SYSU). His research focuses on optical properties of MOFs.



Jie-Peng Zhang obtained his BSc in 2000 and PhD in 2005 at SYSU, and was a JSPS postdoc at Kyoto University from 2005 to 2007. He joined SYSU as an associate professor in 2007, and became a professor in 2011. His research focuses on the chemistry and applications of MOFs.

室温烧结的金属—有机框架纳米晶：一种新型光学陶瓷

叶嘉文¹, 周学宏², 王昱¹, 黄瑞康¹, 周浩龙¹, 程小宁¹, 马於光², 张杰鹏^{1*}

摘要 光学陶瓷是一种透明的特种陶瓷, 可兼备单晶的高稳定性和玻璃、流体和其他非晶材料的大尺寸的优点, 是有潜力的激光增益介质。因为对晶体尺寸和对称性有严格要求, 而且需要高温烧结过程, 只有少数无机非金属材料可用于制备光学陶瓷。本文报道了一种由配位聚合物(或称金属—有机框架)组成的新型陶瓷。通过简单地降低溶剂挥发速度, MAF-4(即SOD型二甲基咪唑锌, 也称ZIF-8)的纳米晶即可融合形成致密的陶瓷状块体, 甚至具有毫米级尺寸和高达84%可见光透过率。该金属—有机光学陶瓷MOOC-1可以负载荧光染料sulforhodamine 640并保持其发光特性, 包括很高的量子产率63.6%和极低的放大自发辐射阈值 $31 \mu\text{J cm}^{-2}$ 。其他几种金属—有机框架的纳米晶也可以在类似条件下融合成陶瓷或光学陶瓷。考虑到金属—有机框架的结构和功能多样性, 金属—有机陶瓷不但可用作光学器件, 还可能在吸附、分离、传感等相关领域展现潜力。