

Operation of the ~740 nm OLED using Pt(II) complex 1. [Reproduced from Ref. 2]

Future Porous Materials: A Highly Flexible Inorganic Framework

In inorganic framework system, researchers have succeeded to develop an efficient method to perform a systematic reproducible synthesis of a flexible inorganic framework with different nanosized pores.

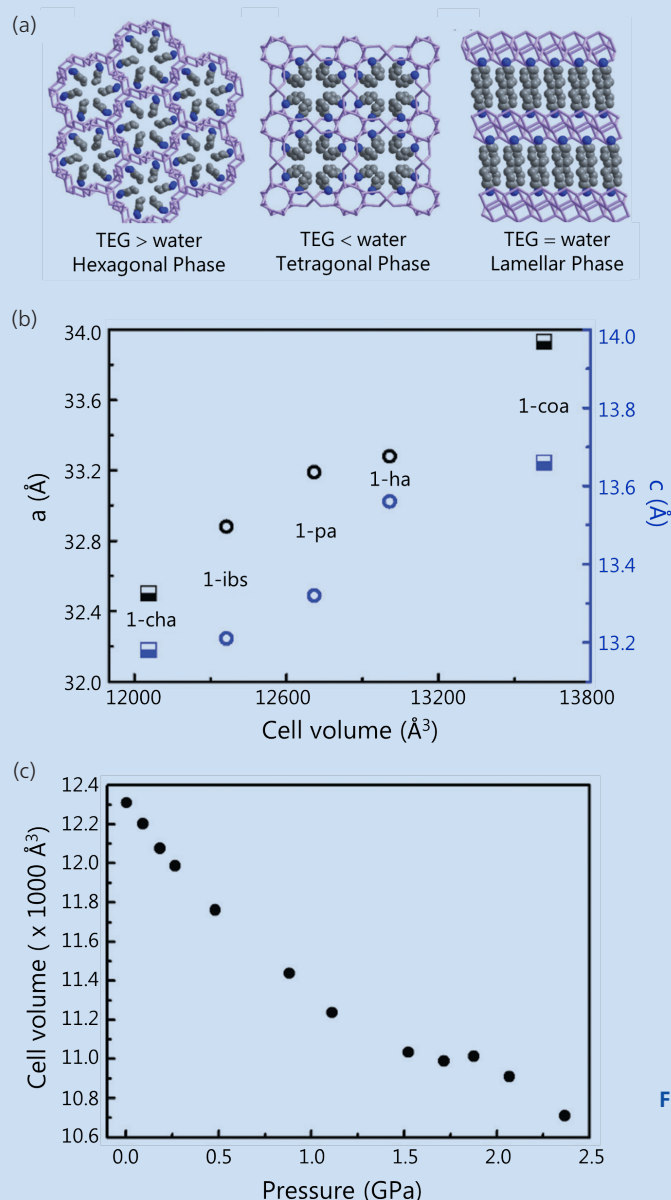
Over the past decade, chemists have endeavored to develop a series of practical porous materials for greenhouse gas capture and chemical catalysis. These porous materials include metal organic frameworks (MOFs),¹ covalent organic frameworks (COFs)² and inorganic frameworks. These materials are well known for their high thermal stability and exceptional surface area. In MOFs structures, the highly modular syntheses make modification of pore sizes possible and it is now known that the organic linker dominates the pore size. However, it is still a challenge to control inorganic frameworks in a similar manner to achieve a desirable pore sizes. In this work, Sue-Lein Wang (National Tsing Hua University) and her co-workers successfully developed a systematic synthesis procedure to control the pore size of an inorganic framework³ and this work provided a new insight into the design of porous inorganic frameworks, with practical applications.

A series of five zinc phosphite-phosphate frameworks $(\text{HA})_2[\text{Zn}_3(\text{HPO}_3)_{4-x}(\text{HPO}_4)_x]$ ($\text{A} = \text{C}_4\text{H}_9\text{NH}_3^+$, $\text{C}_5\text{H}_{11}\text{NH}_3^+$, $\text{C}_6\text{H}_{13}\text{NH}_3^+$, $\text{C}_6\text{H}_{15}\text{NH}_3^+$, and $\text{C}_8\text{H}_{15}\text{NH}_3^+$; $x = 0.3-1$) with nanometer-scale channels were synthesized. This kind of system has a low framework density ($\text{FD} = 9.25$), an extremely high surface area to volume (SAV) exceeding 60.3%, a large hydrophobic empty volume

in the interior of the framework (20% of the unit cell). Inside the crystal, the organic template molecules were aligned parallel to the channel direction and the hydrogen bondings were found between the ammonium functional group of template molecules and the wall of frameworks, which leads a high temperature stability (up to 210°C).

The formation of different templates is critical. Three different template assemblies were generated, which leads to three products: hexagonal-rod-like, tetragonal-rod-like and bi-layer sheet-like structures (**Fig. 1(a)**). In this study, the ratio between Triethylene glycol (TEG) and water was manipulated to control these amine assemblies. For example, a high proportion of TEG facilitates the formation of the hexagonal phase structure.

It is rare that an inorganic framework system has flexibility due to the lack of adaptable structure units, such as organic ligand. Remarkably, as the unit cell volume increases while filling up with different amine template molecules, the void space expands significantly (**Fig. 1(b)**). More interestingly, from a crystallographic point of view, the bond distances remain similar in the five framework systems. However, the Zn–O–P bond angles were found to stretch (up to



maximum of 11.48°), resulting in great flexibility. *In-situ* pressure dependent powder X-ray diffraction was performed at **TLS 17A1**, no phase transition was observed in these framework systems when pressures up to 2.37 GPa were applied. The corresponding cell volume however reduced by 13% (**Fig. 1(c)**). These data suggest that these inorganic frameworks are the most flexible and compressible reported amongst microporous metal oxides. (Reported by Yu-Chun Chuang)

*This report features the work of Sue-Lein Wang and her co-workers published in Dalton Trans. **46**, 364 (2017).*

TLS 17A1 W200 – X-ray Powder Diffraction

- PXRD
- Materials Science

References

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Fig. 1: (a) Three different assemblies of amine assemblies. (b) Flexibility of framework system with different templates. (c) Lattice volume under high pressure. [Reproduced from Ref. 3]

Plasmon-Induced Suppression of Hydrogen Peroxide Formation in Oxygen Reduction Reaction

A photo-dependent property, corresponding to Localized Surface Plasmon Resonance (LSPR) in an Ag–Pt nanostructure, reveals that the plasmon-induced hot electron transfer provides the suppression of peroxide formation, which makes the oxygen reduction reaction more efficient.

Oxygen reduction reaction (ORR) is mainly attributed to two pathways, from O₂ to H₂O or from O₂ to H₂O₂. As previous studies demonstrated, the catalytic activity of O₂ reduction reaction is highly correlated to element type and to the crystalline facets of electrocatalysts. However, the formation of hydrogen peroxide H₂O₂ as an intermediate compound plays a key role in the reduction of the catalytic performances. Platinum is recognized as the best element to catalyze the oxygen reduction until now.¹ The disadvantage of Pt is its expensive cost and motivated chemists to develop other systems with comparable activities. In this paper, Hao Ming Chen (National Taiwan University) and his co-workers demonstrated that in the bimetallic nanocage system Ag–Pt, the silver is