

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

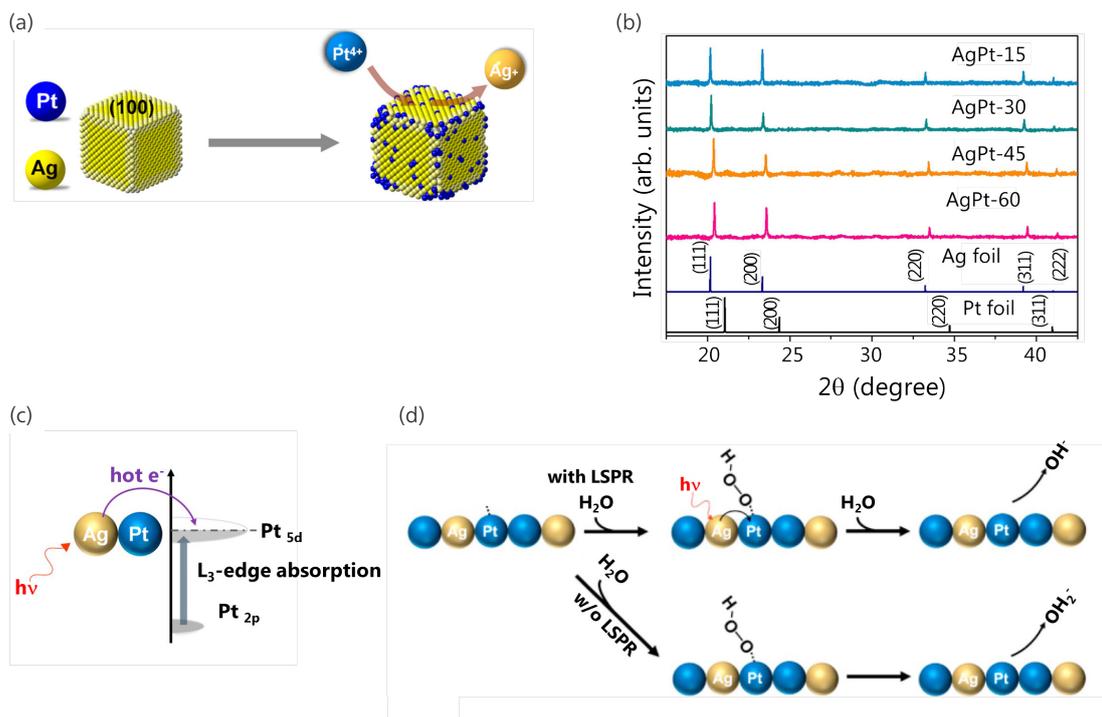
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**Fig. 1:** (a) Three different assemblies of amine assemblies. (b) Flexibility of framework system with different templates. (c) Lattice volume under high pressure. [Reproduced from Ref. 3]

## 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 O<sub>2</sub> to H<sub>2</sub>O or from O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. As previous studies demonstrated, the catalytic activity of O<sub>2</sub> reduction reaction is highly correlated to element type and to the crystalline facets of electrocatalysts. However, the formation of hydrogen peroxide H<sub>2</sub>O<sub>2</sub> 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.<sup>1</sup> 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



**Fig. 1:** (a) Schematic diagram of galvanic replacement between Ag and Pt<sup>4+</sup>. (b) X-ray diffraction patterns of four AgPt bimetallic nanocages. (c) Schematic diagram of Pt L<sub>3</sub>-edge XANES and hot electron transfer. (d) Schematic diagram of mechanism in suppressing hydrogen peroxide through hot electron transfer. [Reproduced from Ref. 2]

able to generate localized surface plasmon resonance (LSPR), reducing the formation of undesired hydrogen peroxide during the ORR.<sup>2</sup>

Ag nanocubes with well-control shape, a mean edge size of 81 nm and smooth {100} facets exposed to electrolyte, were synthesized and structurally and chemically characterized. Four Ag–Pt nanocage samples, in different amount of PtCl<sub>6</sub><sup>2-</sup> solution, were introduced into Ag nanocubes solution, and a subsequent replacement reaction between Ag and Pt<sup>4+</sup> occurred (Fig. 1(a)). The individual powder diffraction patterns of all samples showed the characteristic features of a bimetallic nature (Fig. 1(b)).

To realize the light-induced effects upon peroxide yield during the ORR, a custom-made 'rotating disk electrode/rotating ring disk electrode' (RDE/RRDE) station was designed. The sample with high Pt amount exhibited the smallest light-induced features in limiting current, suggesting that light-induced phenomenon might be attributed to the LSPR effects from Ag and not to Pt. The X-ray absorption near edge structure (XANES) of the Pt L<sub>3</sub>-edge was performed to further investigate the affects from LSPR upon the interaction. When the plasmon-induced hot electron transfer occurred, a decline in absorbance of Pt L<sub>3</sub>-edge XANES was observed, indicating a plasmonic hot electron transfer from Ag to Pt (Fig. 1(c)).

Synergetic LSPR effects in Ag–Pt nanocages were observed, where Pt atom behaves as reactive sites with binding to oxygen and adjacent Ag atom makes the hot electron transfer into antibonding of oxygen more efficient. Plasmon induced hot electron transfer processes populate more electrons in antibonding orbital of O<sub>2</sub> and weaken the bonding of O–O bond. This weakening of O–O bond can cause the bond breaking of O–O bond and leaving of desired H<sub>2</sub>O. Without the weakening effect, it might lead bond breaking of O–Pt bond and formation a peroxide ion HO<sub>2</sub><sup>-</sup> (Fig. 1(d)).

Improvements in the performance of electrocatalysts can provide novel opportunities in designing competitive reactions. The localized surface plasmon resonance in nanocages potentially offers synergetic strategies toward altering the chemical reactions or reaction pathways in various fields. (Reported by Yu-Chun Chuang)

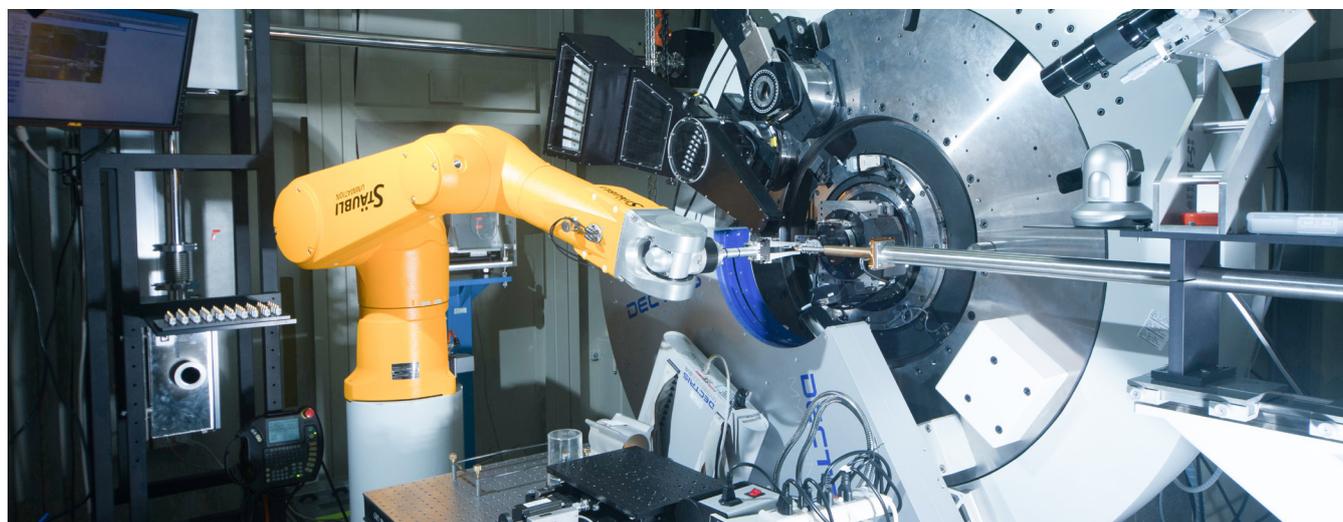
*This report features the work of Hao Ming Chen and his co-workers published in J. Am. Chem. Soc. 139, 2224 (2017).*

#### TPS 09A Temporally Coherent X-ray Diffraction

- HRPXRD
- Materials Science

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TPS 09A: High-resolution PXRD by multi-crystal analyzer detector.

# Photo-Enhanced Ferromagnetism in K–Ni–Cr Prussian Blue Analogues

*Researchers have succeeded to discover a large enhancement of the Ni and Cr ferromagnetic moments under UV light irradiation on K–Ni–Cr Prussian blue analogues.*

Prussian blue analogues (PBAs) demonstrate many fascinating magnetic behaviors. In this study Wen-Hsien Li (National Central University) and his co-workers examine PBAs, with the general chemical formula of  $A_xM[M'(CN)_6]_y \cdot nH_2O$  ( $A-M-M'$ ), where  $M$  and  $M'$  indicate divalent or trivalent transition metal ions and  $A$  indicates monovalent alkali ions that are accommodated in the voids enclosed by the  $MN_6$  and  $M'C_6$  octahedra. It has been shown that a significant reduction in magnetization occurs as a consequence of light irradiation in layered Rb–Ni–Cr/Rb–Co–Fe/Rb–Ni–Cr heterostructures comprised of a photo-sensitive Rb–Co–Fe film sandwiched between two pressure-sensitive Rb–Ni–Cr films.<sup>1,2</sup> No photo-induced magnetism has been identified in isolated K–Ni–Cr, but light irradiation leads to a noticeable reduction (~8%) of the magnetization when this material is coated on a Rb–Co–Fe nano-cube.<sup>3</sup> This work aims to develop K–Ni–Cr PBAs, where light irradiation will enhance the magnetic strength of the compound. Li's group demonstrates that K–Ni–Cr can become photoactive in the high  $K^+$ -containing compound.

They detected significant increases of the Ni as well as Cr magnetic moments upon UV light irradiation in a 55 nm thick high  $K^+$ -containing K–Ni–Cr shell coated on a 240 nm Rb–Co–Fe cube. Surprisingly, the photo-enhancement of the magnetic moments for the  $K_{0.98}Ni-Cr_{0.70}$  phase was as large as that for the  $Rb_{0.76}Co-Fe_{0.74}$  phase.

The neutron diffraction measurements were conducted at the Bragg Institute, ANSTO, Australia, using the high-intensity powder diffractometer Wombat, employing an incident wavelength of  $\lambda = 2.41 \text{ \AA}$  defined by Ge (113) crystals. For these measurements, ~1 g of the sample was loosely loaded into a cylindrical aluminum holder (9 mm in diameter and 30 mm long) with a shiny inner surface. The device was equipped with a quartz tube (5 mm in diameter) located along the central axis of the holder to facilitate light irradiation. The PBA powder was loosely packed 2 mm thick in the quartz tube allowing 35% light transmission, which, combined with the shiny inner face of the Al holder that acted a light reflector, allowed the light to