



Communication

In situ generation of palladium oxide nano-crystals

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ARTICLE INFO

Article history:

Received 9 December 2008
 Received in revised form 20 January 2009
 Accepted 22 January 2009
 Available online 30 January 2009

Keywords:

Porphyrin
 Palladium oxide nano-crystals
 Nano-structures
 Metal–organic framework

ABSTRACT

Synthesis of metal–organic framework (MOF) based on tetra-pyridyl porphyrin and palladium (II) salt resulted in the formation of palladium oxide nano-crystals. The palladium oxide nano-crystals were characterized by PXRD, TEM, HRTEM, ED, UV–Vis spectroscopy, DLS, SEM and AFM. A plausible mechanism for the *in situ* generation of nano-crystals has been proposed.

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1. Introduction

In recent times, porous metal–organic frameworks (MOFs) have been explored extensively due to their potential applications as molecular sieves, in gas storage, ion exchange and in catalysis [1–4]. A careful selection of appropriate ligands and metals may lead to MOFs with desirable structure and functionality based on their coordination tendencies and geometries. In this context, porphyrins have been exploited owing to their ability to chelate with various metal ions such as Cu, Zn, Fe, Pd, Pt to form porous MOFs [5–8]. Porphyrins have significant implications in nature as small molecule binders, transporters, catalysts, light harvesters, and as energy movers [9]. Synthetic porphyrins are of immense interest in molecular electronics and as supramolecular building blocks [10–12]. Amongst these, pyridyl substituted porphyrins are the excellent candidates for chelation with several metal ions as they form fascinating supramolecular arrays as shown in Scheme 1 [13–14]. Interestingly our attempts to synthesize such metal mediated superstructure resulted in the formation of palladium oxide nano-crystals (5–7 nm in diameter) along with random MOF.

The nano-crystals were characterized using powder X-ray diffraction, transmission electron microscopy, high-resolution transmission electron microscopy, particle size analyzer, atomic force microscopy and electron diffraction.

2. Results and discussion

For the preparation of palladium oxide nano-crystal, *meso*-tetraakis(pyridyl)porphyrin (TPyP) and Na₂PdCl₄ were taken in the molar

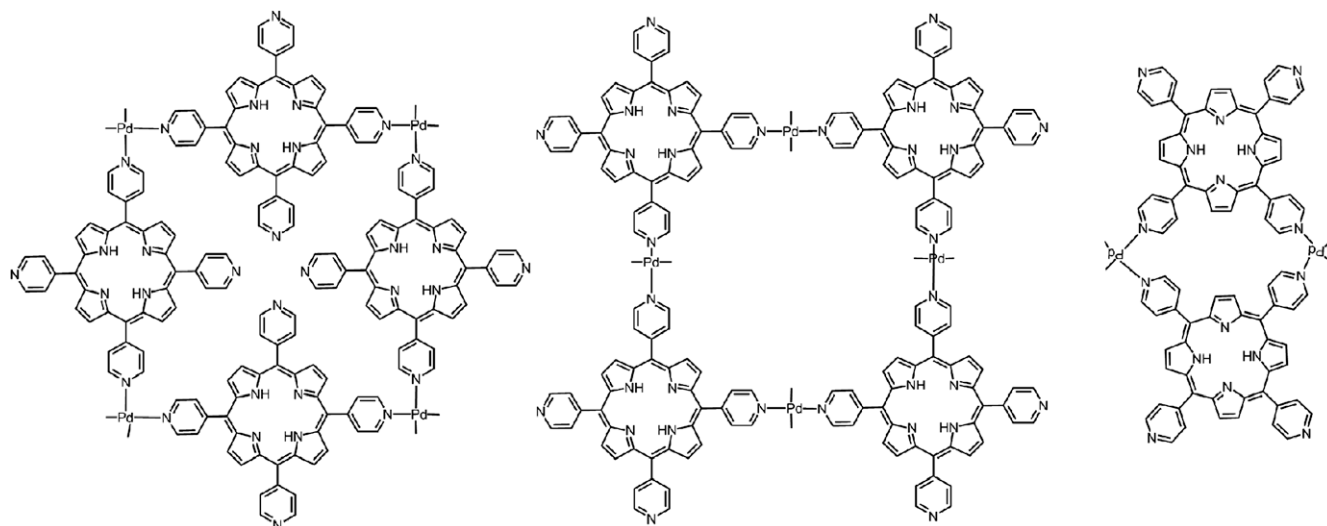
ratio of 1:4 in dimethyl formamide (DMF). The mixture was heated at 80–100 °C in oil bath with continuous stirring for 12 h. During the course of the reaction, the color of the reaction mixture was changed from pale orange to deep wine-red. The reaction was monitored by UV–Vis spectroscopy. The UV–Vis spectra revealed a red shift of the Soret of about 3–4 nm with broadening of the band and the Q-band remains 4-line, instead of 2-line as has normally been observed in metalloporphyrins. This indicated that palladium was not inserted in the porphyrin macro-cycle core rather it was coordinated to the pyridyl groups present on the periphery of the porphyrin ring (Supplementary material, Fig. S-1) [15]. The coordination mode would probably be similar to that is shown in Scheme 1.

For further analysis, the reaction mixture was diluted 20 times with DMF (V/V). Part of the diluted dispersions were kept for 1, 2 and 3 days separately (represented by A, B and C, respectively, as shown in Scheme 2). TEM of the wine-red dispersions A and B (Scheme 2) showed the formation of palladium oxide nano-crystals of diameter 5–7 nm (Supplementary material, Fig. S-2). However DLS measurements of the corresponding dispersions showed an increase in the mean particle size from 14.5 nm ($\sigma_n = 1.47$ nm) to 55.54 nm ($\sigma_n = 12.67$ nm). This indicates that probably aggregation of porphyrin assemblies around the palladium oxide nano-crystals occur which results in a larger particle size. The colloidal dispersion was ultra-centrifuged at 15000 rpm and the residue was washed with ethanol, dried and analyzed using powder X-ray diffraction (PXRD). The PXRD pattern of the residue matched well with PdO (JCPDS No. 655261) (Supplementary material, Fig. S-3). The crystalline nature of the palladium oxide nano-crystal was further evident from the HRTEM and electron diffraction (ED) pattern as shown in Fig. 1.

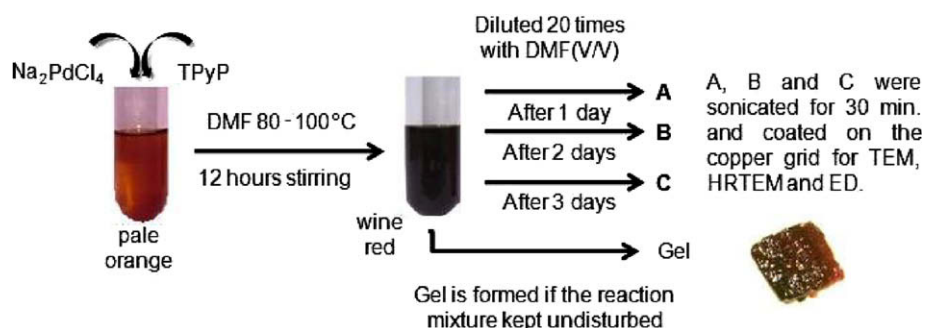
The pattern could be indexed in cubic system ($a = 5.65$ Å). The schematic [002] zone-axis diffraction pattern of palladium oxide

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Scheme 1. Proposed structure of palladium mediated supramolecular arrays with a pyridyl substituted porphyrin. N–Pd–N links between adjacent pyridyl substituted porphyrins results in various flat open 2-D networks (for clarity, atoms coordinated to palladium atom have not been shown). Further chelation of uncoordinated pyridyl nitrogens with palladium (II) salt would result in infinite 3-D network.



Scheme 2. Synthesis and characterization procedures of palladium oxide nano-crystals.

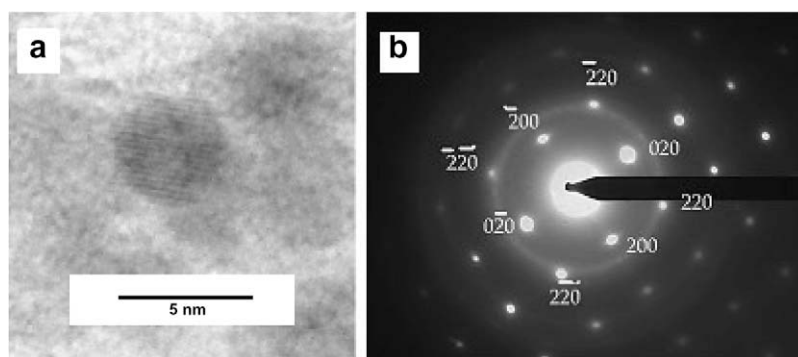


Fig. 1. (a) The HRTEM image of the nano-crystal observed in the colloidal dispersion A. The size of the nano-crystal is ~ 4.2 nm having d spacing ~ 2 Å. (b) Selected area electron diffraction pattern of the palladium oxide nano-crystals of dispersion A, along the zone-axis [002] (Scheme 2).

nano-crystals is shown in Fig. 1b. Experimental data therefore obtained from PXRD, HRTEM and ED is in agreement with the formation of PdO nano-crystals. The PdO nano-crystals can be generated *in situ* either directly from $[\text{PdCl}_4]^{2-}$ or from the oxidation of reduced Pd^0 centers during the reaction in DMF under air at 80°C . It has been reported earlier that DMF can reduce metal ions [16–18]. Therefore the Pd^0 perhaps undergoes aerial oxidation during the course of reaction to form palladium oxide nano-crystals [19,20]. It was also

found that only palladium nano particles were formed when the reaction was conducted in Argon atmosphere. The PXRD of the residue was taken which clearly shows the formation of palladium particles. The powder pattern is shown in Fig. S-3b, Supplementary material.

DLS of dispersion C showed mean particle size of 164 nm ($\sigma_n = 14.33$ nm) (Supplementary material, Fig. S-2). This indicated that upon aging, the porphyrin moieties aggregate to form larger

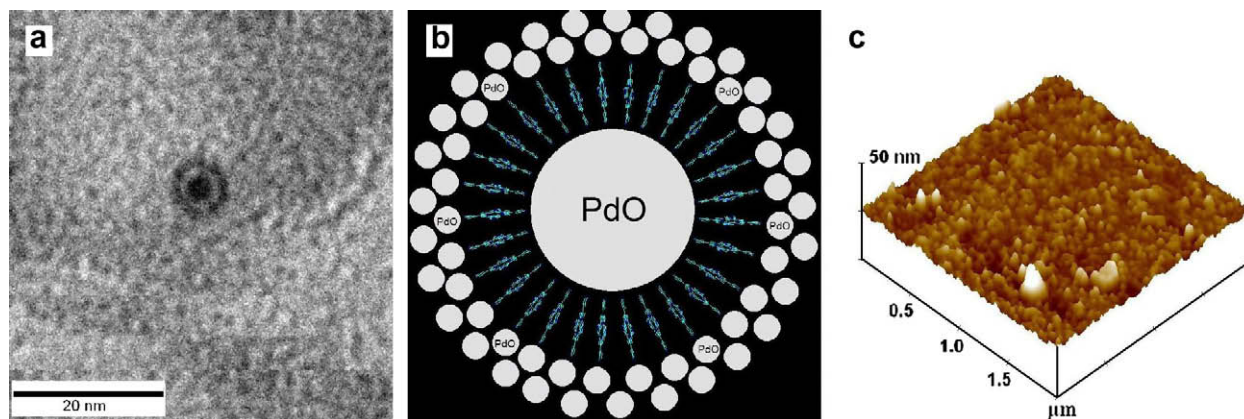


Fig. 2. (a) TEM of dispersion C. (b) Model showing small palladium oxide nanoparticles forming a concentric circle around a central nano-crystal. The smaller particles are stabilized due to coordination with pyridine N of porphyrin. (c) AFM shows the agglomeration of the particles.

particles. TEM of the dispersion C showed clustering of nanoparticles of diameter about 1–2 nm forming concentric outer ring around the nano-crystals.

The clustering of the nano particles indicates that pyridyl porphyrins which surround the PdO nano-crystal are also coordinated to the nanoparticles through the pyridine N on the other side (Fig. 2b) [21–22]. $\pi \cdots \pi$ interactions between the porphyrin rings further stabilize the parallel stacking of the macro-cycle rings [23]. From HRTEM it was inferred that the distance between the nano-crystal and the ring was around 1.5 nm. This is in good agreement with the size of the porphyrin ring (1.54 nm) and also consistent with the proposed model (Fig. 2 and S-8).

If the wine-red reaction mixture was kept undisturbed for three days, it resulted in the formation of a gel as shown in Scheme 2. The gel once formed was insoluble in most of the solvents such as hexane, dichloromethane, chloroform, dimethyl formamide, acetone, acetonitrile, ethyl acetate, methanol, ethanol and water. The volume of the gel reduced to about 20 times as compared to the initial volume if the solvent was removed. This indicates the presence of large voids in the porphyrin network. However, if the gel was heated to remove DMF, the structure collapsed. This suggests that DMF was probably actively involved in stabilization of the gel by coordinating directly to the palladium (II) salt. The formation of highly agglomerated particles was witnessed by AFM (Fig. 2c). SEM of the xerogel is shown in the Supplementary material, Fig. S-9.

To conclude, a simple methodology for the *in situ* generation of palladium oxide nano-crystals has been proposed. The palladium oxide nano-crystals were characterized using PXRD, TEM, HRTEM, ED, AFM and SEM. UV–Vis spectroscopy and AFM revealed the formation of agglomerated MOFs. Upon aging the solution, a deep red gel was formed, which was stable in presence of oxidants such as pentafluoro iodobenzene, meta-chloroperbenzoic acid and hydrogen peroxide. The catalytic activity of the palladium oxide nano-crystals trapped in the gel is under investigation.

3. Experimental

Na_2PdCl_4 (126 mg, 0.4 mmol) and meso tetrakis(4-pyridyl)porphyrin (62 mg, 0.1 mmol) were taken in 10 ml of dimethyl formamide (DMF) and the mixture was stirred in air in a preheated (80–100 °C) oil bath for 12 h. During the course of the reaction, the color of the reaction mixture was changed from pale orange to wine-red (Scheme 2). Part of the wine-red solution was diluted with DMF and was sonicated for 30 min for further experimental analysis. Use of any other solvent such as dichloromethane, chloro-

form, acetonitrile, ethyl acetate, acetone, ethanol, methanol or water for dilution resulted in precipitation. If the wine-red solution was left undisturbed for three days it resulted in the formation of a gel, which is insoluble in DMF and other solvents (mentioned above) as well.

Room temperature powder X-ray diffraction (PXRD) studies were carried out on a Bruker D8 Advance diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation. Data were collected with a step size of 0.03° and a count time of 1 s per step over the range $2^\circ < 2\theta < 60^\circ$. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on an FEI Technai G2 20 electron microscope operated at 200 kV. AFM and SEM were performed using VEECO METEROLOGY GROUP, NANOSCOPE-IIIA and ZEISS EVO 50, respectively. UV–Vis measurements were done with AGILANT 8453 (diode array detector) spectrophotometer. DLS were done using MALVERN ZETASIZER NANO SERIES (ZS 90) particle size analyzer.

Acknowledgments

This work was supported by the Department of Science and Technology, Delhi (Project No. SR/ S1/ IC - 04/ 2007). We thank Prof. A. Ramanan, Department of Chemistry, IIT Delhi, for helpful discussion. We also thank CSIR for providing funds to VB. SEM, TEM and HRTEM facility provided by IITD is gratefully acknowledged.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.01.037](https://doi.org/10.1016/j.jorganchem.2009.01.037).

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