AN EFFICIENT HYDRO THERMAL SYNTHESIS AND CHARACTERIZATION OF Pd-HHTP COMPOUND

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ABSTRACT

In this study, the synthesis of a palladium-HHTP (2,3,6,7,10,11) hexahydroxytriphenylene) metal-organic framework (MOF) was aimed initially. The hydrothermal procedure adopted resulted in the metallic-organic compound but not MOF, as powder XRD revealed the formation of palladium nanoclusters. Further, SEM and EDX analysis showed encapsulation of Pd nanoclusters with varying sizes from 200 nm to 400 nm inside the organic moiety. Thermal analysis showed that the compound was stable up to 214 °C. Remarkably high resistance of 75 GW and 25 GW were recorded at 153 °C and 175 °C measured by a powder-packed two-probe measurement system made in-house.

Keywords: Palladium hexahydroxy triphenylene, MOF, XRD, SEM, EDX.

INTRODUCTION

The development of materials toward better living is a part and parcel of human civilization. In particular, the development of coordination compounds envisaged an organic ligand linkage to a metal ion. Following is the realization of big molecules called crown ethers (cyclic oligomers of dioxane) where the metal ions are caged in an organic moiety. Other side, zeolites – inorganic long chain/cyclic structures of hydrated alumino silicates of alkaline and alkaline earth metals are known for centuries for their high surface area, porosity, and adsorption capacity. The topological design of organic crystalline compounds resulted in covalent organic frameworks. Combining the properties like high surface area, porosity, crystallinity, and catalytic activity of metal ions for varieties of applications was envisaged in the past three decades through the development of a new class of

compounds called metal - organic frameworks (MOF). Another class of metal organics called metal-organic cages (MOC) is also envisaged which also exhibit large surface area and are competent to MOFs with enhanced structural stability. In this work we aim to prepare palladium-based MOF. A brief note on MOF is presented in the following sub-section.

Metal-organic Frameworks

Metal-organic frameworks (MOFs) are a class of compounds consisting of metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures. The organic ligands included are sometimes referred to as “struts” or “linkers”. The metal ions form nodes that bind the arms of the linkers together to form a repeating, cage-like structure.

Due to this hollow structure, MOFs have an extraordinarily large internal surface area further, the porosity with enhanced surface area of these open structures with catalytic activity of metal and conductance of conjugated linkers are promising for gas sensing applications.

MATERIALS AND METHODS

Palladium, hexa hydroxyl triphenylene, isopropyl alcohol, Nitric Acid was the products of Aldrich (Coimbatore, India). Ethanol was purchased from Sigma Aldrich, India.

Instrument

A double beam UV–Visible spectrophotometer, Jasco–V 630 is used for absorption measurements using 1cm path length cells and IR spectroscopic study (M/s Bruker, for functional group analysis. Further, the morphology and elemental analysis of the sample were envisaged by SEM and EDX respectively (M/s FESEM, ZEISS Crossbeam 340). The thermal stability of the samples was carried out by TG-DTA (M/s SETARAM) and DSC (M/s Mettler) measurements. The surface area of the samples was measured using BET isotherm (M/s Thermo Scientific.

Preparation of palladium nitrate solution

About 102 mg of palladium was dissolved in 5 to 10 m of nitric acid with constant stirring and heating to about 65 °C with intermittent ultrasonication and the solution was made up to 100 mL in a standard measuring flask

Preparation of 2, 3,6,7,10,11 - hexa hydroxyl triphenylene (HHTP) solution

The UV-Vis spectra of as procured HHTP (M/s Alfa Aesar) were presented in

Appendix. About 487 mg of hexa hydroxyl triphenylene was dissolved in 20 mL of 75% of isopropyl alcohol in water and the solution was diluted to 100 mL in a standard measuring flask.

30% ammonia solution was added drop wise to ~ 1 mL of palladium nitrate solution in a test tube till the solution become colorless and the odor of ammonia was observed from the solution. Also, ammonia solution was added to a sample solution of HHTP in IPA that resulted in a dark blue solution (resembling permanganate coloration). The ammonical solutions of palladium and HHTP were mixed and that resulted in a black precipitate.

Hydro thermal synthesis

About 10 to 25 mL of 30 % ammonia solution was added to the stoichio-metric amounts of HHTP and palladium nitrate solutions (table 2) in a 100 mL capacity Teflon (PTFE) container. Water was added to make up a total of 75 to 80 mL and sealed tightly with a Teflon lid. The Teflon container with a lid was kept in side a stainless steel autoclave and tightened. The stainless steel autoclave was kept in a preheated oven to the desired temperature.

RESULTS AND DISCUSSION

Figure-1 Represents the powder XRD patterns of as procured HHTP and products obtained Figure 1(a) corresponds to as procured HHTP and figure (b) shows.

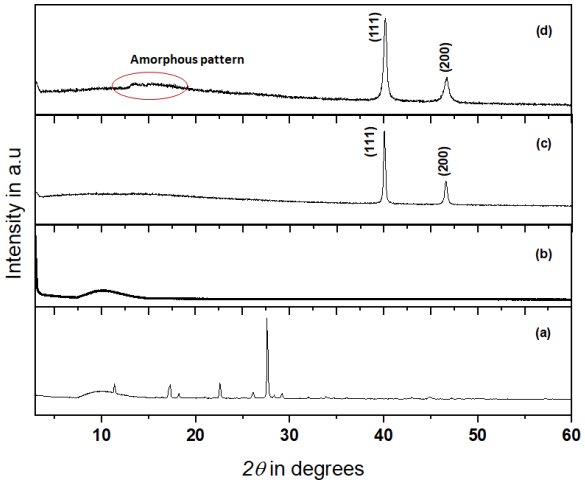


Figure-1 Powder XRD of (a) HHTP as procured and products obtained

Only an amorphous signature around 2θ of 10°. Figures1(c) and 1(d) corresponds to the oven- dried products obtained after cleaning respectively. The peaks are identified as that of metallic palladium (COD#96-900-8479) with miller indices (111) and (200). The amorphous hump is might be due to the organic moiety surrounding palladium nano clusters. The XRD patterns reveal no formation of crystalline metal-organic framework. It makes to think that the precipitation of nano palladium from the solution by

reduction during the addition of ammonical HHTP. Further, powder XRD confirms the reproducible formation of nanopalladium with varying sizes. Figure 2 is the vibrational spectra recorded by ATR-FTIR mode.

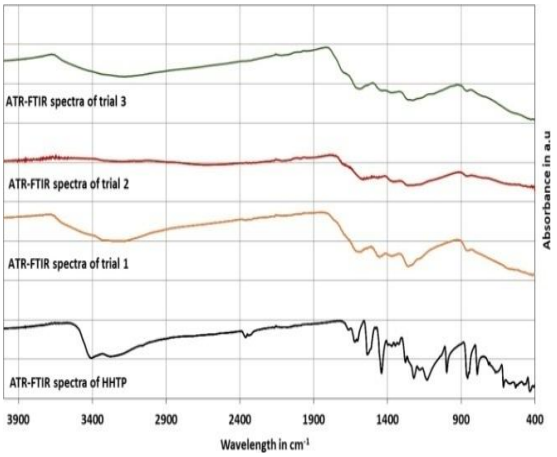
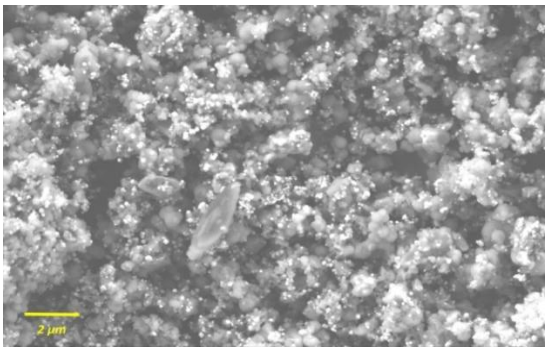
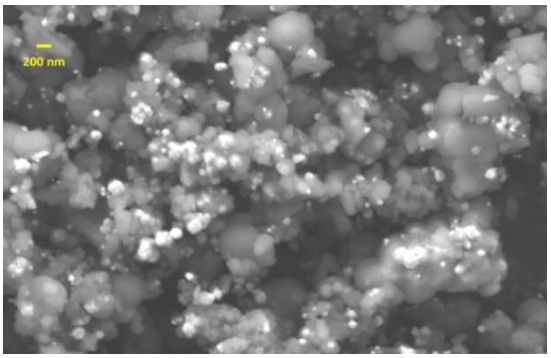


Figure-2 ATR-FTIR spectra of as procured HHTP and products obtained.

The aromatic C-H deformation modes around 700 and 800 cm^{-1} in HHTP spectra were clearly visible; along with the broad hump around 3400 cm^{-1}corresponding to –OH / -NH stretching. The IR spectra of the products obtained during the trials look alike with remarkable features around 850 cm^{-1} and 545 cm^{-1} possibly to that of Pd-nonmetal linkages.





The scanning electron microscopic images of the product obtained during trial 3 were shown in Fig. 3 (a) and (b). The exposure of electrons resulted in charging effects on the metallic centers. That indicates the dispersion of palladium nano clusters in the amorphous organic matrix that is in line with the XRD results.

The average size of Pd-clusters varies between 200-400nm.ThePd cluster presence was further confirmed by Energy Dispersive X-ray analysis (EDX

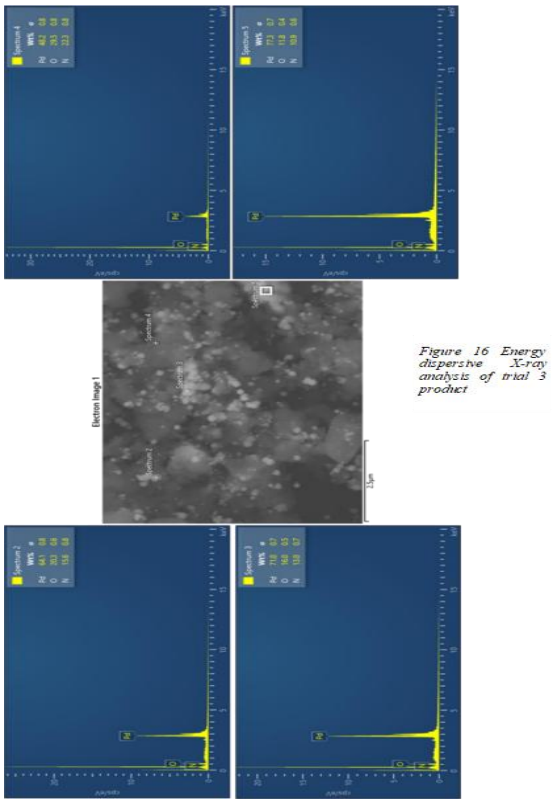
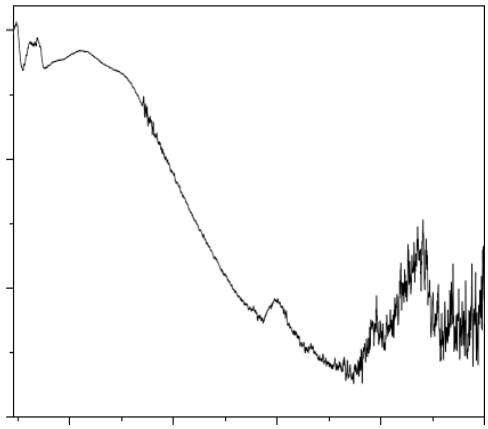


Figure 16 Energy dispersive X-ray analysis of trial 3 product

Figure.4 shows the distribution of palladium at different selected areas as labeled.



The UV-Vis-spectra of as procure pd-HHTP was shown in Figure 5.

The surface area of the sample was measured using BET adsorption isotherm and the result was found to be a very high value of about 6000 m^2/g. The sample was subjected to the duplicate measurement for concurrence.

The thermal stability of the compound was analyzed by TG-DTA. The heating and cooling curves of TG-DTA are presented in Fig. 6 (a) and (b) respectively. During heating from room temperature two decomposition on-sets could be seen at 226.6 °C and 363.7 °C with weight loss.

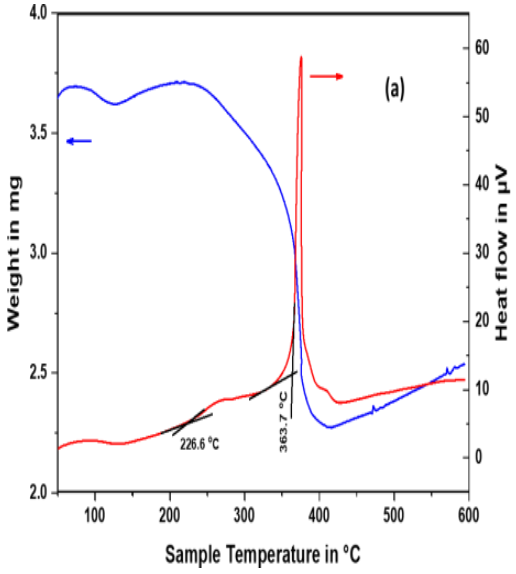
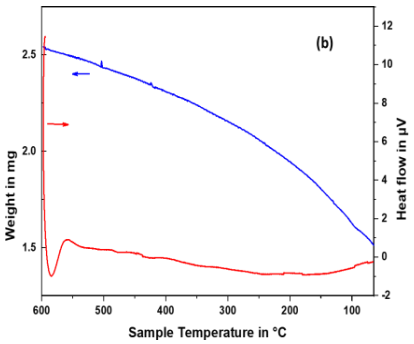
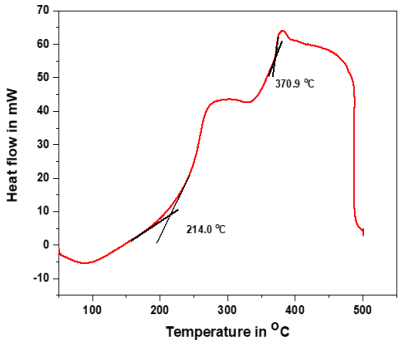


Figure. 6 (a) Heating and (b) Cooling curvesof TG-DTA exhibited by-product

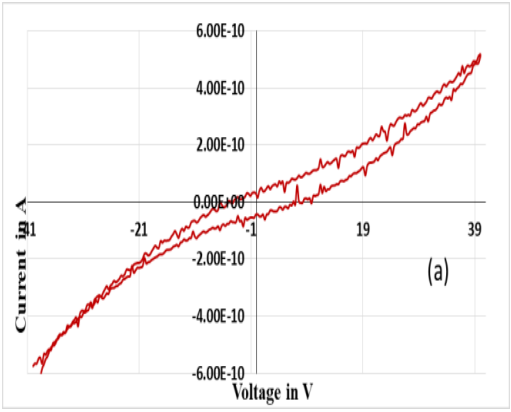


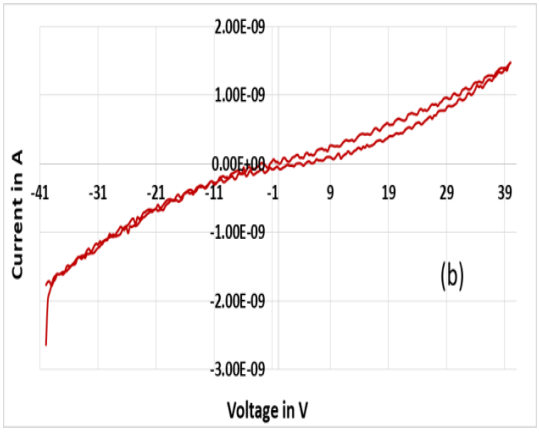


During cooling, the weight loss continued, and finally about 55.9 % weight loss was observed. The heats of decomposition were further confirmed by differential scanning calorimetry that is more sensitive over DTA. Figure .7 shows the heat flow measurement during DSC run from room temperature to 500 °C.

The current-voltage characteristics were studied at two temperatures 153 °C and 175 °C. Figure 13(a) and (b) shows current raise with voltage ramp from -40 Vto +40 V in forward and reverse order. The I-V curves infer the very high resistance nature of the sample of about 75 G and 25 G at 153 °C and 175 °C respectively.

The supernatant collected during washing by centrifugation was concentrated to about 50 mL in all three trials individually and analyzed for the palladium content. Table x shows the amount of unbounded/unreacted palladium from the amount estimated by ICP-OES in the supernatant and the initial weight taken.





CONCLUSION

- Hydrothermal synthesis was adopted for the realization of palladium based metal-organic compound with HHTP.
- Powder XRD revealed the formation of Pd nano clusters dispersed in an amorphous organic matrix. This also indicates no formation of MOF as expected at the beginning of the project. Further analysis by different characterization techniques was continued to elaborate the scientific findings.
- ATR-FTIR study showed that Pd-nonmetallic linkages and signatures correspond to aryl groups.
- Energy dispersive X-ray analysis and Scanning electron microscopy showed the dispersion of Pd nanoclusters in the organic matrix as expected from XRD.
- Thermogravimetry with differential thermal analysis and differential scanning calorimetry showed that the compound starts decomposing above 214 °C.
- The current-voltage characteristics also indicated a very high resistance nature of the compound.

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