

SYNTHESIS OF ORDERED MICROPOROUS CARBONS CONTAINING WELL DISPERSED PLATINUM NANOPARTICLES

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Abstract

Microporous carbon containing well dispersed platinum nanoparticles of size 2 ~ 6nm were synthesised in this work. Powdered zeolite NaY was impregnated with platinum salt, $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$, and dried overnight. The dried powder was then further degassed and impregnated with an organic precursor, furfuryl alcohol. The impregnated sample was then polymerized to further stabilize the organic precursor in a vertical quartz reactor and then carbonized to reduce the platinum ion to elemental platinum. After carbonization, chemical vapor deposition was conducted with propylene gas ($5.18 \pm 0.1\%$ in nitrogen gas) immediately for 4 hours and then heat-treated at 900°C for 3 hours. The inorganic support material was leached from the produced sample by immersion in 48% hydrofluoric acid for 3 hours, filtering and washing with copious purified water and finally drying in a vacuum oven at 30°C for 24 hours. Scanning electron microscopy and high resolution transmission electron microscopy images show the produced carbon containing well templated zeolite-like crystal morphologies and very well dispersed platinum nanoparticles of well controlled size around 2nm to 6nm. The platinum loading on the produced carbon sample can be controlled by the impregnation step. Raman analysis reveals graphitization of the final carbon was promoted by the metal loading. Nitrogen adsorption analysis suggested the carbon has mainly micropores. The material is a promising candidate as a shape selective catalyst, or for fuel cell or hydrogen storage applications.

Keywords: microporous carbon, pyrolysis, catalyst, platinum nanoparticles, templated carbon

1. Introduction

Fabrication of porous carbon supports with high surface area have attracted considerable attention, especially for use as catalysts, hydrogen storage materials, and fuel cell use (Barata-Rodrigues, et al., 2003, Chen, et al., 2005, Hou, et al., 2005, Joo, et al., 2006, Kyotani, 2000, Meyers, et al., 2001, Raghuvver and Manthiram, 2005, Yang, et al., 2007, Yang, et al., 2006). However, even though it is relatively easy to synthesize nanostructured carbons, it is not easy to impregnate precious metal nanoparticles uniformly into them while maintaining the control of particle size and shape (Choi, et al., 2005). Conventional techniques for embedding platinum or mixed-metal particles in the porous supports are post-synthesis treatment either by impregnation, adsorption, or ion-exchange methods (Ding, et al., 2005, Raghuvver and Manthiram, 2005, Su, et al., 2005). However, these methods normally lead to uncontrolled growth of metal particle size, shape and aggregation/sintering at elevated temperatures. Recent substantial progress in the field of incorporation of well dispersed metal nanoparticles in carbon support materials has focused on ordered carbon mesoporous materials (CMMs) because of their ordered structure, high surface area and relatively larger pore sizes which will allow the platinum ion to diffuse into the pores and aggregate (Chao, et al., 2006, Joo, et al., 2006, Kim, et al., 2005, Liu, et al., 2006). However, there are few reports on the synthesis of ordered microporous carbon materials containing well dispersed metal nanoparticles because these carbons have pore sizes normally less than 2nm which are apt to be blocked if the above mentioned methods are used.

Chemical vapor deposition (CVD) method is a well-established technique for preparing carbon molecular sieves because of its high degree of pore-filling in a template, enabling the graphitization of the pore walls, and avoiding the formation of

additional mesoporosity. However, there are very few reports on attempting to introduce metal nanoclusters into these carbon molecular sieves by CVD. Recently, Coker, et al. used NaX as a template to synthesize carbon containing dispersed platinum nanoclusters by CVD. However, the procedure is complicated and also the carbons synthesized don't have resolved pore size distribution in the micro-range but have a wide range of pore sizes from micro to meso (Coker, et al., 2007). In the present work, we first report a simpler CVD approach to fabricate fully ordered microporous carbon molecular sieves of extremely high microporosity and also containing well dispersed but highly stable Pt nanoparticles of controllable sizes in the nano-range from 1nm to ca. 6 nm by first doping the NaY zeolite with platinum ions by simple incipient wetness impregnation before furfuryl alcohol impregnation. The platinum ions were reduced during the following carbonization and CVD process. No further hydrogen reduction process is needed. Platinum metal loading on the final carbons and their corresponding particle sizes can be controlled by the concentration of the platinum salts in the impregnation solution. As discussed later, the ordered microporous carbon molecular sieves so fabricated possess high surface area, high micropore volumes, narrow pore size distribution in the micro-range and well dispersed Pt nanoparticles. These materials are suitable not only as adsorbents for hydrogen storage but also as electrocatalytic materials for fuel cell use and catalysis.

2. Experimental section

2.1. Synthesis

The microporous Pt-C carbon samples were synthesized according to the following procedure: (i) powder zeolite NaY (CBV 100, ZEOLYST international) was impregnated with $[\text{Pt}(\text{NH}_4)_4](\text{NO}_3)_2$ (99.9+%, Sigma Aldrich) by incipient wetness impregnation, denoted here as parent template, m%-PtY in which m% refers to the platinum loading percentage on the final carbon. The metal loading can be controlled by changing the concentration of the impregnation salt solution. The two parent PtY templates produced in our experiment are 6%-PtY, and 40%-PtY. (ii) The m%-PtY powder was dehydrated by heating to 400°C slowly under inert nitrogen purge and then cooled down. (iii) The dehydrated m%-PtY powder was then impregnated with an organic precursor, 99% furfuryl alcohol (FA, 99%, Sigma Aldrich), in a vacuum Rota-vapor for 24 hours. The sample was then centrifuged and polymerized to further stabilize the organic precursor and the metal ions in a quartz reactor and then the organic material was carbonized by further increasing the temperature to 700°C for 4 hours to reduce the Pt ion to elemental Pt (0). (iv) After carbonization, chemical vapor deposition (CVD) was conducted with propylene gas ($5.18 \pm 0.1\%$ in nitrogen gas) immediately for 4 hours with a gas flow rate of approximately 400 ml/min to further infiltrate carbons into the zeolite framework. Then heat-treatment at 900°C was conducted for another 3 hours to further strengthen the carbon structure. We name samples produced from this step as the composite carbon samples, noted as m%PtCcom (v) the inorganic support material was leached from the composite carbon samples by immersing the composite sample in 48% hydrofluoric acid for 3 hours, washing with purified water and drying in a vacuum oven at 30°C for 24 hours. The final produced carbon is denoted as m%Pt-C.

2.2. Characterization

The as-synthesized carbon samples were characterized using N_2 adsorption analysis at 77K by a volumetric adsorption analyzer (Micromeritics, ASAP 2020). Prior to measurements, the samples were degassed at 350°C for 6 hours under vacuum. The specific surface areas were determined according to the Brunauer-Emmett-Teller (BET) method. Pore size distribution (PSD) is determined by applying Density Functional Theory (DFT) (for slit pore-like) method to the nitrogen adsorption isotherm. The micropore volume was calculated from the Dubinin-Radushkevich (DR) equation using the data of each adsorption isotherm and the mesopore volume was determined by subtracting the micropore volume from the volume of N_2 adsorbed at a relative pressure of 0.97. Powder X-ray diffraction (PXRD) was used to investigate the long range order and graphitization of the final templated carbon sample. Scanning electron microscopy (SEM) FESEM 6300 was used to observe the external morphology of the carbon particles. Transmission electron microscopy (TEM) (CM20 or JEM 2011, Japan) operated at 200kV was used to detect the nano-scale structure of the carbon and metal particles.

3. Results and discussion

3.1. Nitrogen Adsorption/Desorption Isotherms

All N_2 adsorption isotherms obtained for the carbon samples show type I isotherms like their parent templates and have very narrow desorption loops indicating little mesoporosity, as shown in Fig 1a. All the calculated values are summarized in Table 1, where the carbon samples and their parent zeolites are also given for comparison. Kyotani et al. reported that as long as the regularity of zeolite Y was kept in the resultant carbons, their pore structure was always characterized by the following features: high surface area, large micropore volume and high microporosity (Ma, et al., 2002). Such features are indeed observed for all our two produced carbon samples. Reports for pore size distributions are shown in Fig 1b. The resulting PSD curves of all the carbons are very sharp and most of the pore sizes fall within the range of 0.5-2nm. There is a

small difference between the two carbon samples prepared by the same method but having different metal loadings. Sample 40%Pt-C and 6%Pt-C has similar small bimodal pores of size at 0.5nm and 0.7nm but the 6%Pt sample has more pores of sizes in the range of 1-2nm with correspondingly higher micropore volume.

Table 1. Porous properties obtained from N₂ adsorption isotherms for the templates and the final carbons.

samples	Pt loading (wt%)	BET specific surface area (m ² /g)	Pore volume (cm ³ /g)	
			V _{micro} ^a	V _{meso} ^b
NaY	0	786	0.36	0
6%-PtY	1.2	791	0.38	0
40%-PtY	6.2	621	0.28	0
6%Pt-C	6	1347	0.65	0.12
40%Pt-C	40	912	0.43	0.05

^a Micropore volume, ^b Mesopore volume

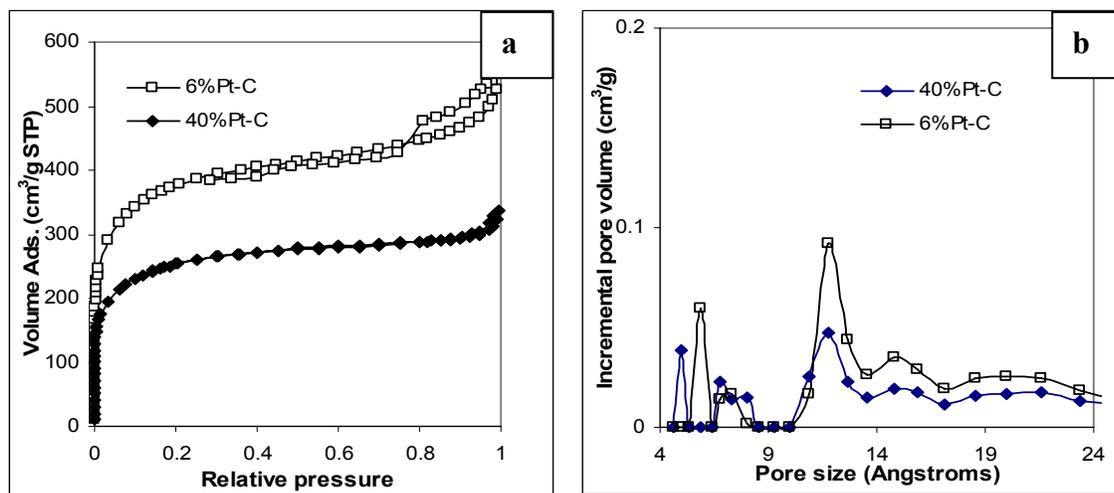


Figure 1. a, adsorption-desorption isotherms and b pore size distribution curves determined by applying DFT method to the N₂ adsorption isotherms for the produced carbons 6%Pt-C and 40%Pt-C.

3.2. XRD patterns

In the XRD patterns as shown in Fig. 2a, compared to the original template NaY, parent templates 6%-PtY, 40%-PtY show a deteriorating crystallinity with increasing [Pt(NH₄)₄](NO₃)₂ loading. Especially the peak at 2 • 6° corresponding to the supercage in the framework reduces significantly with increased metal loading, indicating that most [Pt(NH₄)₄]²⁺ ions assume the positions in the supercages because they are too big to penetrate the 6 ring of the zeolite framework. Fig. 2b is the XRD patterns for the produced composite carbon samples. After heat-treatment at 900°C, we observed that in the composite sample 6%PtCcom, the peaks related to the parent templates were retained and did not collapse but in sample 40%PtCcom, framework collapsed occurred because platinum ions migrate and aggregate into large particles which break the supercages. Fig. 2c shows that peaks related to the templates have disappeared after removing the templates by HF leaching and water wash for all the final carbon samples. Small and broad peaks at 2 • 39.8, 46.2, 67.8, and 81.3° reveal the existence of crystalline platinum metal nano-particles with a face centered cubic (fcc) structure. Based on the Scherrer formula, the average size of Pt deduced from the XRD profiles of the Pt-C samples was found to be around 6 nms for 40%Pt-C, and 2 nm for 6%Pt-C, coinciding with those determined from TEM images (see below). The peak at 2 • 6° indicates existence of long-range carbon structural order corresponding to the carbon replication in the supercage of the Y zeolite. With decreasing

platinum loading on the carbon samples, the 6° diffraction peak in the final carbon becomes increasingly stronger indicating better carbon replication in the supercages.

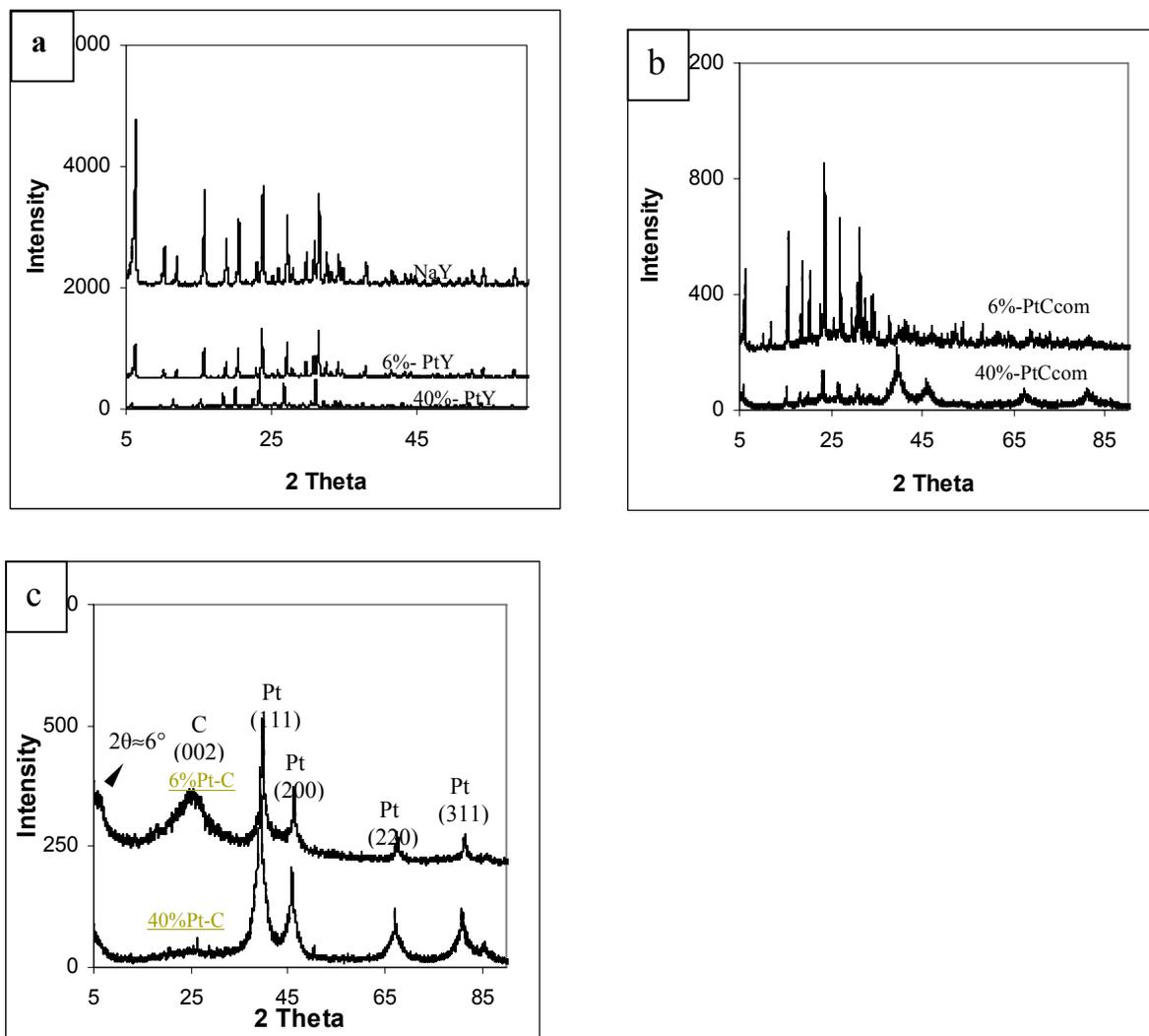


Figure 2. XRD a: 40%PtY, 6%PtY, NaY; b: corresponding composite samples produced from the previous templates, 40%PtY, 6%PtY; c: final carbon samples after HF and water wash.

3.3. SEM and TEM

The TEM and SEM images of the Pt-C samples exhibited well templated morphology like crystal Y zeolite, shown Fig 3a-d. Fig. 1a is the SEM overall image for the 40%Pt-C, which clearly reflects the crystal morphology of the zeolite templates. No observed external deposition and the very smooth carbon surface suggest carbon deposition inside the zeolite channels (Hou, et al., 2005). Fig. 3b shows the high magnification image for the 6%Pt-C at a very think edge with the arrows showing the templated carbon fringes. Fig. 3c is the low magnification image of the 40%Pt-C carbon particles containing dense but well dispersed platinum metal nanoparticles of sizes ranging from 2nm to 6nm shown in inset. Fig. 3d is the high magnification image of a selected area in which is shown some platinum metal nanoparticles having well aligned crystal fringes along the $\{111\}$ plane and faceted morphology. The well resolved diffraction spots in the diffraction pattern taken for this selected area further reveal single crystalline structure properties of the synthesized platinum metal nanoparticles Figure 3e is the SEM image for the 40%Pt-C.

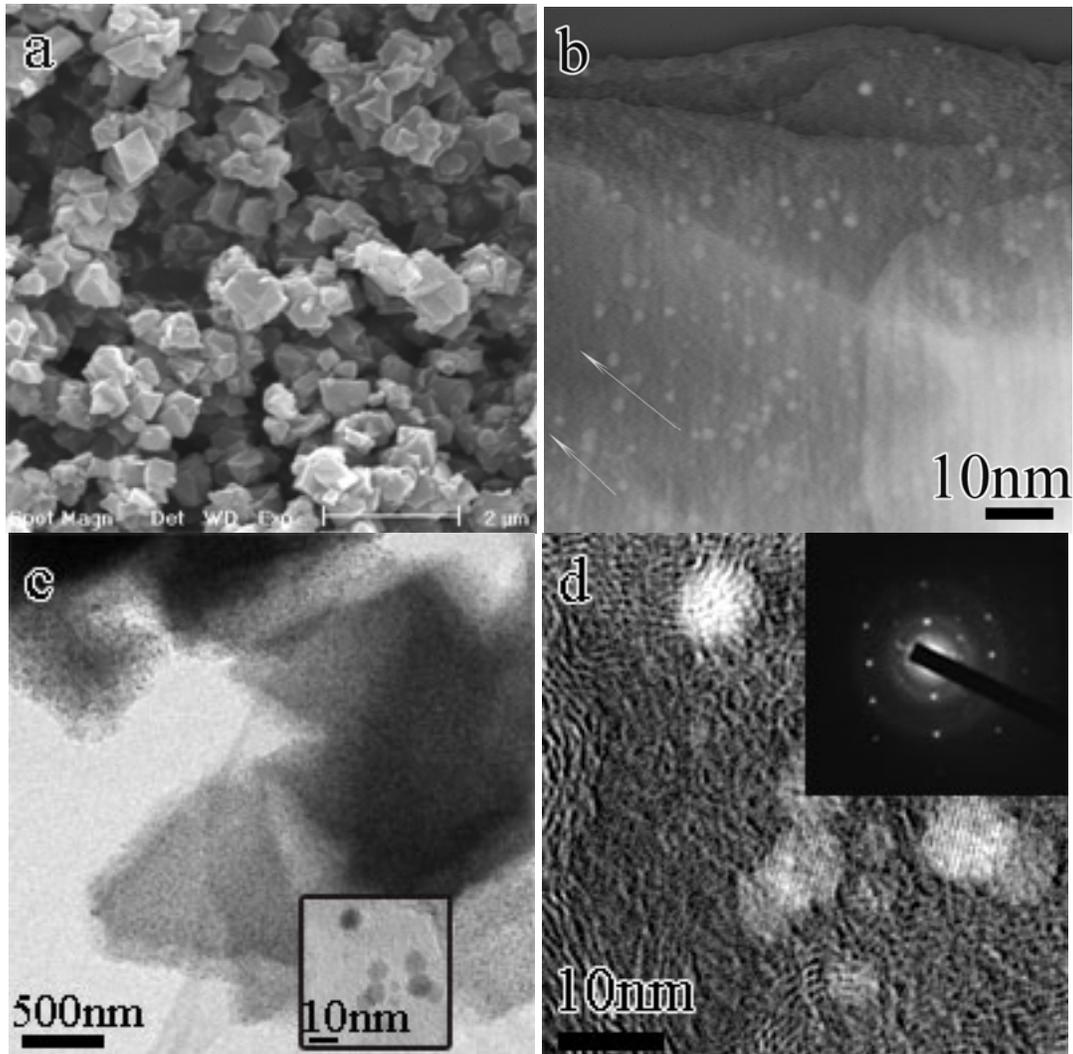


Figure 3. SEM and TEM images for the Pt-C samples: a, SEM image for the 40%Pt-C; b, high magnification of 6%Pt-C; c, d: low and high magnification images for the 40wt%Pt-C.

3.4. Raman analysis

In Fig. 4a, Raman spectra of the three samples with different Pt loadings show D and G bands centered around 1300 and 1585 cm^{-1} , where they have been deconvoluted with two Lorentzian lines. As a reference, Raman spectrum of graphite is also presented. Intensity ratio of D to G bands, $R(I_D/I_G)$ is an important parameter to represent the structure of carbon materials in which the D band is attributed to the presence of defects and G band arises from sp^2 graphitic structure in carbon materials, respectively (Ferrari and Robertson, 2000). According to our spectra results, $R(I_D/I_G)$ of each samples decreased from 3.98 to 3.13 with increase of Pt loading amount from 1% to 40% , approaching to 2.95 which is the $R(I_D/I_G)$ of the provided standard graphite, representing the well developed ordered graphitic structure. Together with $R(I_D/I_G)$, the G band FWHM (full width at half maximum) is also often used to interpret Raman spectra in which it is known to be closely related to the crystallinity of graphitic structure (Schwan, et al., 1996, Yoshida, et al., 2006). The more defects the structure has, the wider G band is. According to the spectra, introduction of platinum metal in the carbon samples resulted in the broadening in G band FWHM compared to the standard graphite sample. G band FWHMs calculated from the samples' Raman spectra are plotted with $R(I_D/I_G)$ s in Fig. 4b. It clearly shows when Pt loading increases, $R(I_D/I_G)$ decreases and the G band FWHM becomes narrower, showing that more graphitic sp^2 characteristic is produced when larger amounts of Pt are used during the synthesis.

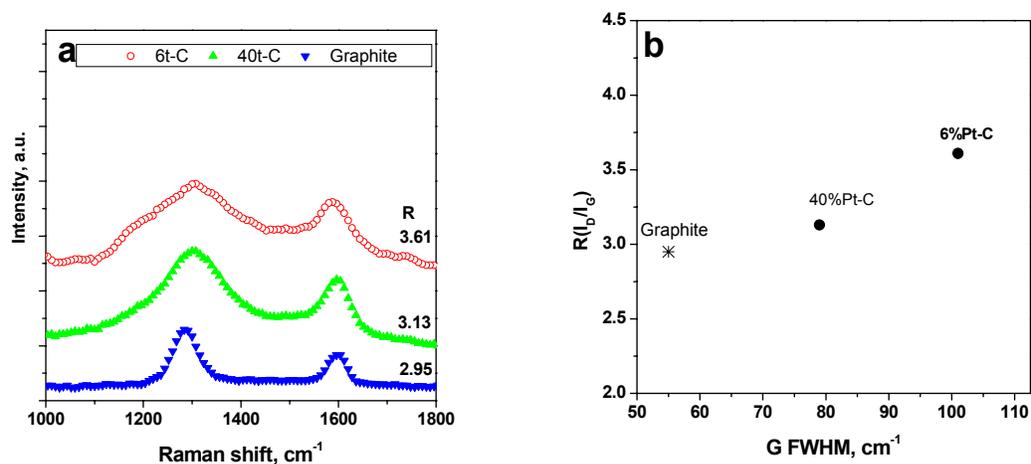


Fig. 4. FT-Raman spectra of the produced carbon samples, **a**, and relationship between R(ID/IG) and G band FWHM, **b**.

4. Conclusions

Microporous carbon molecular sieves containing well dispersed platinum metal nanoparticles of controllable sizes in the fine nano range from 1nm to 6nm were synthesized. These carbons possess very high surface area, very high micro-pore volumes and exclusive pore size distribution in the micro-range (< 2 nm). Dispersion of platinum loading as high as 40% was achieved with mono-dispersed platinum nanoclusters of average size around 4nm which can be further tuned by the reaction conditions. SEM, TEM and XRD have confirmed the structure periodicity and metal dispersion, especially for the low metal loading sample, 6%Pt-C. Raman spectra has shown graphitization of the sample will increase with the metal loading, which will create a potential use of our samples for catalysis and fuel cell membranes.

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