行政院原子能委員會

委託研究計畫研究報告

白金擔持活性碳的三維斷層電子穿透影像研究

Study of Pt-impregnated activated carbon with 3D

tomography TEM

計畫編號：1002001INER057

受委託機關(構)：國立台灣大學

計畫主持人：白偉武

聯絡電話：02-33665252

E-mail address：wpai@ntu.edu.tw

核研所聯絡人員：曾怡仁

報告日期：100年 11月 30日

中文摘要

　　白金擔戴的活化碳顯示出高儲氫效能。而要瞭解此高儲氫效能的來源，必需要有活化碳上白金的分佈資訊。我們利用掃描穿透電子顯微鏡(STEM)研究了兩批樣品： 一是擔戴白金奈米粒子的原始活化碳(ACB-Pt)，另一是白金奈米粒子擔戴在經過４０分鐘氧化之活化碳(ACB40-Pt). 在ACB-Pt上，由STEM顯像與電子激發X-ray譜，可證明有微細的2～3奈米大小的白金粒子分散在活化碳上。而在ACB40-Pt樣品上，並無明顯的白金粒子，但也許有更細微的白金粒子含在如"竹筍"狀的棒狀結構中。最後，STEM清楚顯示實驗樣品的活化碳孔洞結構非常不規則，也因此無法取得有意義的三維斷層電子穿透影像，實為可惜。將來，有待取得更加高品質的樣品。

Abstract

Platinum(Pt)-impregnated activated carbon(AC) materials show promise for high-efficiency hydrogen storage. In order to examine the cause of efficient H storage, one needs to know the distribution of Pt on AC. We examined two batches of Pt/AC using scanning transmission electron microscope (STEM). One is Pt on pristine AC (ACB-Pt) and the other is Pt on oxidized(40 minutes) AC. For ACB-Pt, clear dispersion of small Pt particles of ~2-3 nm in size was observed by STEM and electron stimulated X-ray spectroscopy. On the other hand, in ACB40-Pt there were no 2-3 nm Pt nanoparticles and Pt appeared to embed in bamboo-shoot-like rods, perhaps forming even smaller Pt particles. Finally, STEM indicated that the porous structure of AC is very irregular. Due to the clear lacking of ordered pores, it excluded any useful tomography experiment on the present batches of samples. Sample quality improvement is definitely needed in the future.

壹、計畫緣起與目的

There is a close connection between the observed hydrogen storage efficiency and the pore size and structure in Pt-loaded porous carbon materials[1,2]. However, details of such three-dimensional (3D) pore structure cannot be easily determined without specialized microscopic techniques. We expect that with high-resolution scanning TEM technique and EDEX or EELS spectroscopy can be used to detect the presence of Pt nanoparticles in the hydrogen storage materials. Furthermore, if the sample quality allow, 3D tomography could also reveal the location distribution of platinum nanoparticles. We then may relate the 3D pore structure, Pt distribution, and hydrogen storage effectiveness.

Hydrogen storage in metal organic framework (MOF) has shown a great enhancement factor of 8, from 0.5 to 4.0 wt % at room temperature and 100 bar[3]. Cheaper activated carbon (AC) was also considered as a plausible candidate but the spillover on AC only gives rise to a marginal enhancement factor of 2, to 1.2 wt%[4]. Recent work by the institute of nuclear energy research (INER), however, found processed porous AC with impregnated Pt nano-particles can yield a hydrogen storage weight near ~5.0 %. The U.S. Department of Energy

(DOE) has established a multistage target for hydrogen storage for fuel-cell applications. The targets for an on-board hydrogen storage system are 4.5 wt % by 2007, 6 wt % by 2010, and 9 wt % by 2015, at moderate temperatures and pressures (in June, 2005)[5]. Therefore, ~5.0 wt% is a significant result. Dr. Tzeng Y.R. at INER contacted me and showed me that some of their Pt-impregnated activated carbon(AC) samples exhibited unusually high efficiency toward hydrogen storage. The conceptual model is that Pt forms nanoparticles blocking the AC pore entry. Hydrogen molecules dissociate at these Pt and H spillovers to the internal volumes of pores and then recombine and trapped. To get support of such a picture, Dr. Tzeng and I wished to use the STEM facility at the center for condensed matter sciences, NTU, to conduct TEM-based spectromicroscopy.

一、目的

(一) Imaging and confirmation of Pt nanoparticles

　　The first goal was to get high-resolution STEM images showing the presence of Pt nanoparticles, with chemical identification. This goal is achieved.

(二) 3D tomography Imaging

Ideally, we hoped to perform 3D tomography and show the spatial distribution of Pt relative to the pore structure. We note that, due to the limited resolution of TEM tomography (~ 2-3 nm at most), the feasibility of tomography thus depends on the actual sample quality. Unfortunately, this goal is not achieved, mainly because the AC samples turned out to have very irregular pore structures not even discernible in regularly HRTEM or STEM images. Therefore, it became impossible to conduct meaningful tomography analysis.

貳、研究方法與過程

We described the research by two parts:

一、樣品製備

There were two batches of samples selected for STEM study. One we call ACB-Pt and the other we call ACB40-Pt.

(一) ACB-Pt

In this batch, the activated carbon (obtained from景明化工) was first rinsed by pure water to ~pH7 and dried in vacuum at $95°$C for 12 hrs. and then Pt was impregnated onto the AC by reducing a solution mixed with electrocatalyst precursor salt ($H_2PtCl_6 \cdot 6H_2O$), the reducing agents ethylene glycol (EG) and sodium hydrogen sulfite ($NaHSO_3$). The solution's pH is adjusted using 4N NaOH to about pH~4 and then the mixed Pt/AC solution was put on a hot plate at ~$120°$C for 120 minutes under refluxing condition. The corresponding hydrogen storage efficiency, as measured by weighting method in INER, was ~3 %.

(二) ACB40-Pt

This batch is similar to ACB-Pt except that before water rinse and Pt impregnation, the AC sample was subjected to an additional step of oxidation in a solution (100 ml) consisting of 8M HNO_3 and 2M H_2SO_4 at the temperature of ~$95°$C for 40 minutes under refluxing condition. This treatment removes impurities and adds functional

groups on AC. This may reduce the impregnated Pt size. The

corresponding hydrogen storage efficiency, as measured by weighting

method in INER, was nearly ~8 %.

二、電子顯微鏡的檢定

(一)使用的電子顯微鏡

Our studies were conducted with a FEI Tecnai G2-F20 scanning

transmission electron microscope, see below. This instrument has a

HR-STEM resolution < 0.20 nm. It is equipped with high resolution

electron energy loss spectrometer and energy dispersive X-ray

spectrometer. It can also conduct electron holography and tomography.

In CCMS, there is another Cs-corrected STEM (JEOL 2100F). It is not

used for this study because our sample quality requires further

improvement.

The TEM samples were prepared by dispersing sample flakes

onto a carbon film. We selected samples that show flatter geometry in

order to avoid TEM artifacts.

(二) ACB-Pt

Figure 1 shows the low-resolution and high-resolution

(HRTEM)ACB-Pt images. The pore structure is not clear. In the HRTEM

image, the presence of Pt nanoparticles is discernible.
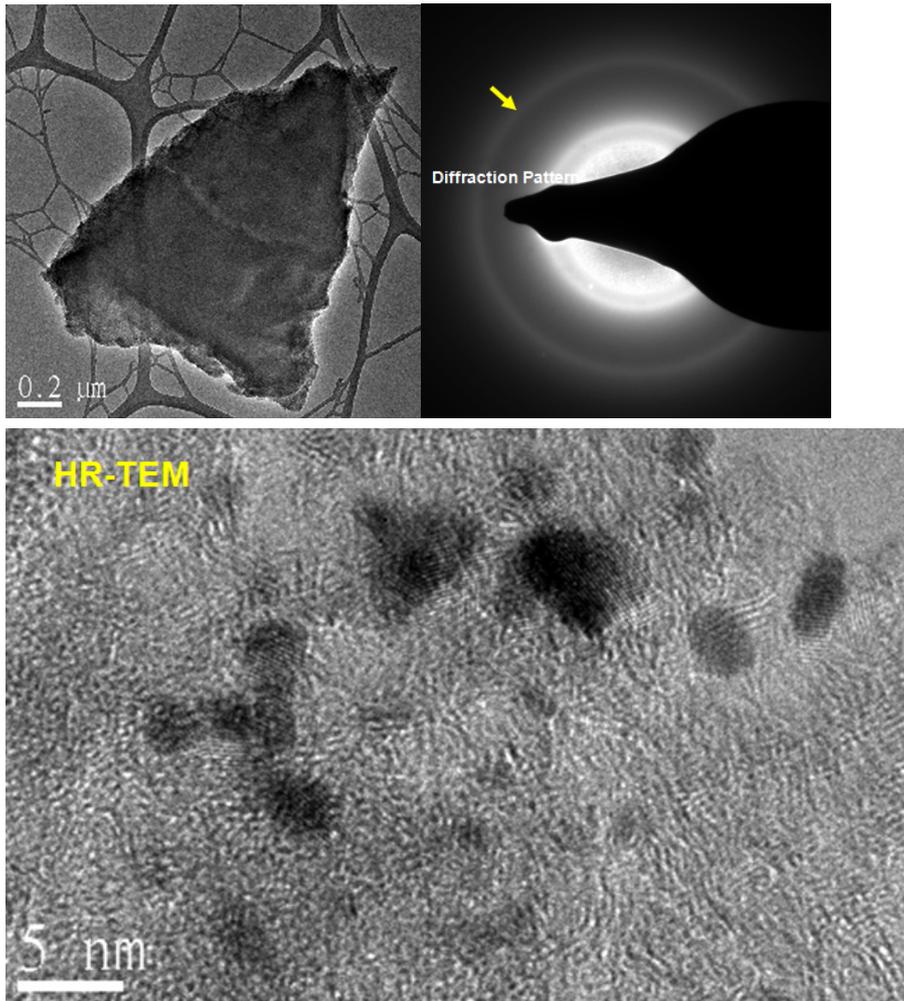
Figure 1 (top left) TEM and (bottom) HRTEM for ACB-Pt. (top right) selected area diffraction shows that the Pt is crystalline.

We resorted to high-angle annular dark-field STEM imaging of a selected area (yellow rectangle), see figure 2. The HAADF image shows clearly decorated nanoparticles, which are crystalline. To verify that these nanoparticles are Pt-containing, we used SAE (selected area EDX). Indeed, when the selected area contains bright particles, Pt EDAX signal was clearly detected. In contrast, for regions with no observable

particles, Pt signal was not detected. We also note that the Pt

nanoparticles were located at different TEM focal depths. Therefore,

they must be at different height. This could come from two possibilities:

(1) the Pt nanoparticles are loaded at surface but the surface has a very

rugged morphology. (2) the Pt nanoparticles are loaded in different depth

of the AC bulk structure. We noted that the sample flakes were prepared

by brief ultrasonication in solution. Therefore, the flake surface is likely

fractured from bulk AC during TEM sample preparation. The Pt

nanoparticles seem unlikely purely loaded at the original surface. We

thus believe that Pt nanoparticles are formed throughout the bulk AC

structure.
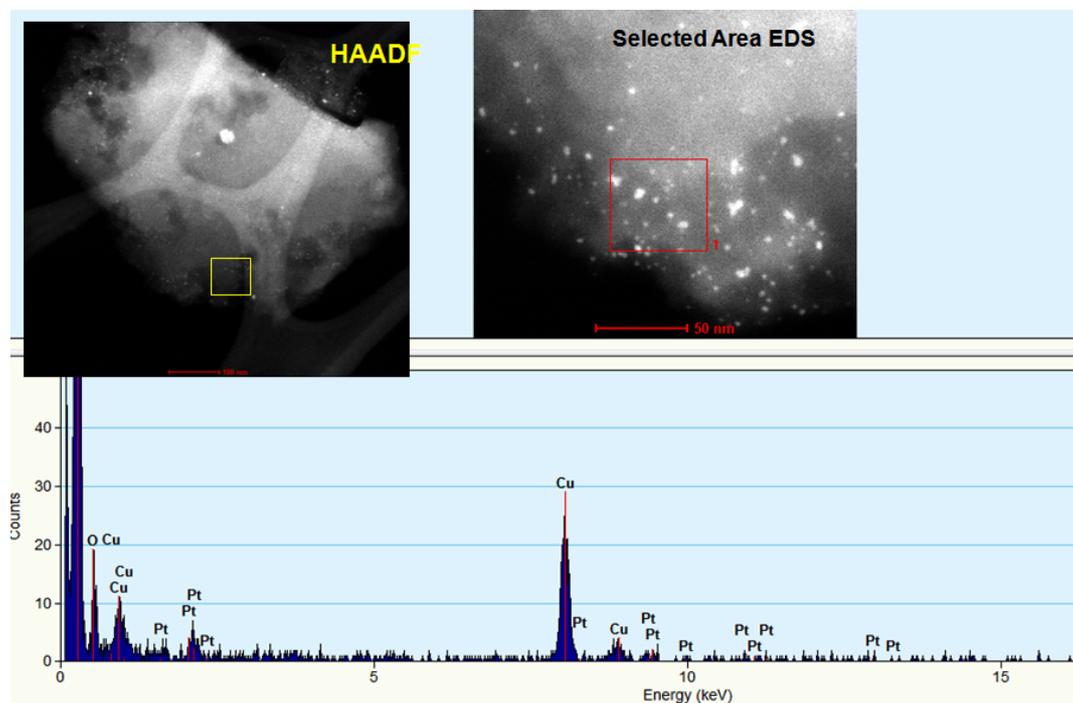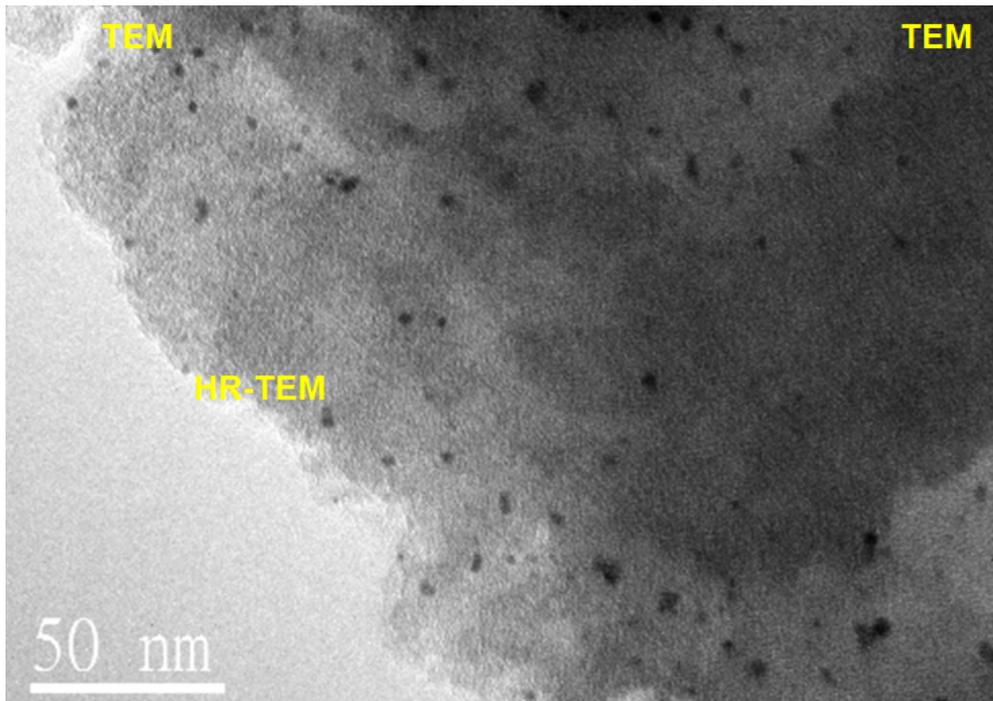
Figure 2HAADF (STEM) and SAE of ACB-Pt. The middle panel is the EDAX spectrum showing the presence Pt. The bottom one is a HRTEM picture, which also shows clearly the presence of Pt nanoparticles.

While figure 2 shows Pt particles are generally quite small (<2~3 nm in size typically), occasionally there were large Pt particles. This is shown in figure 3. The SAE EDEX encircling a large nanoparticle indeed shows a much stronger Pt signal. This indicates that Pt are aggregated. However, such a large Pt nanoparticle was not commonly observed. The majority of Pt nanoparticles remained fine and well-dispersed. We also note the presence of some Mg and Al signals in the EDAX spectrum.
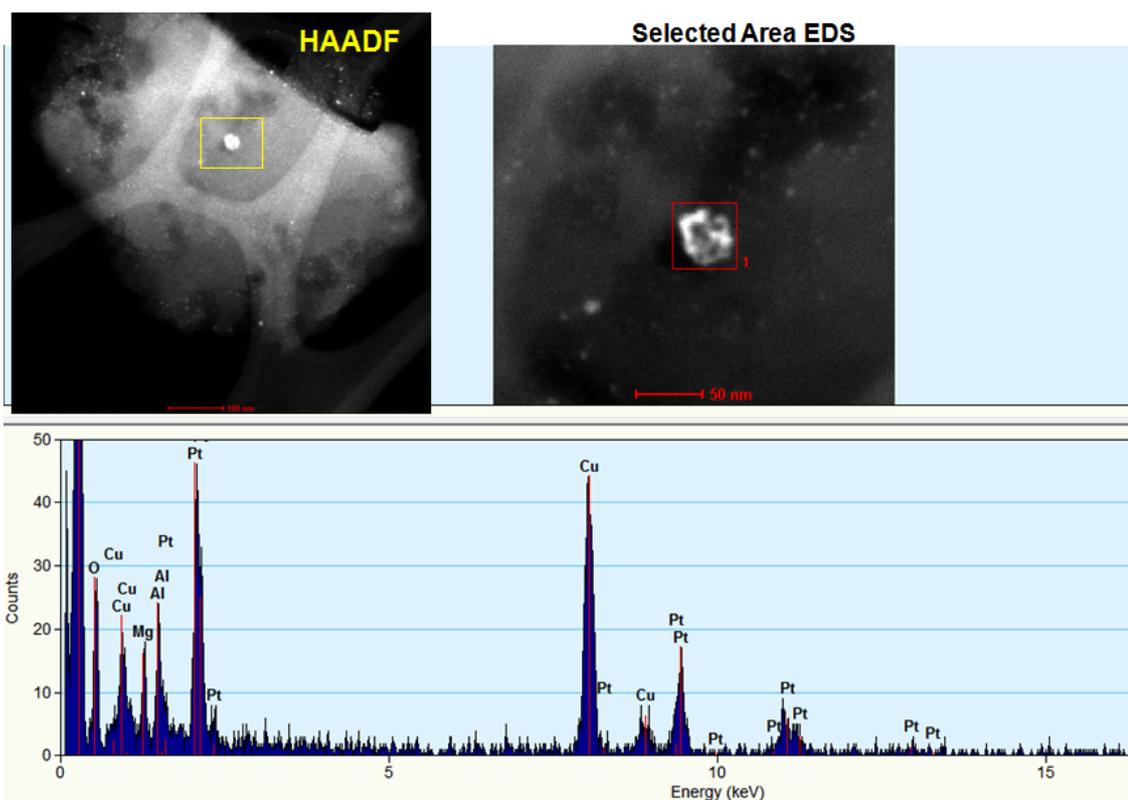
Figure 3 HAADF (STEM) and SAE of ACB-Pt on a "large" particle. The bottom EDAX spectrum of stronger Pt signal suggests aggregation of Pt.

(三) ACB40-Pt

In contrast to the ACB-Pt sample, there are two major differences. First, ACB40-Pt seems to have formed some crystallization of AC. This is shown in the spotty diffraction pattern of figure 4. We have not understood what the exact crystallization is. TEM Ronchigram also indicates some crystallization. X-ray diffraction study at INER also showed that the activated carbon after oxidation treatment will possess some degree of crystallization, as evidenced by those C-related

diffraction peaks in figure 4X. The second difference is the
disappearance of the 2-3 nm nanoparticles. Instead, we now often
observed "bambo-shoot" like rods.
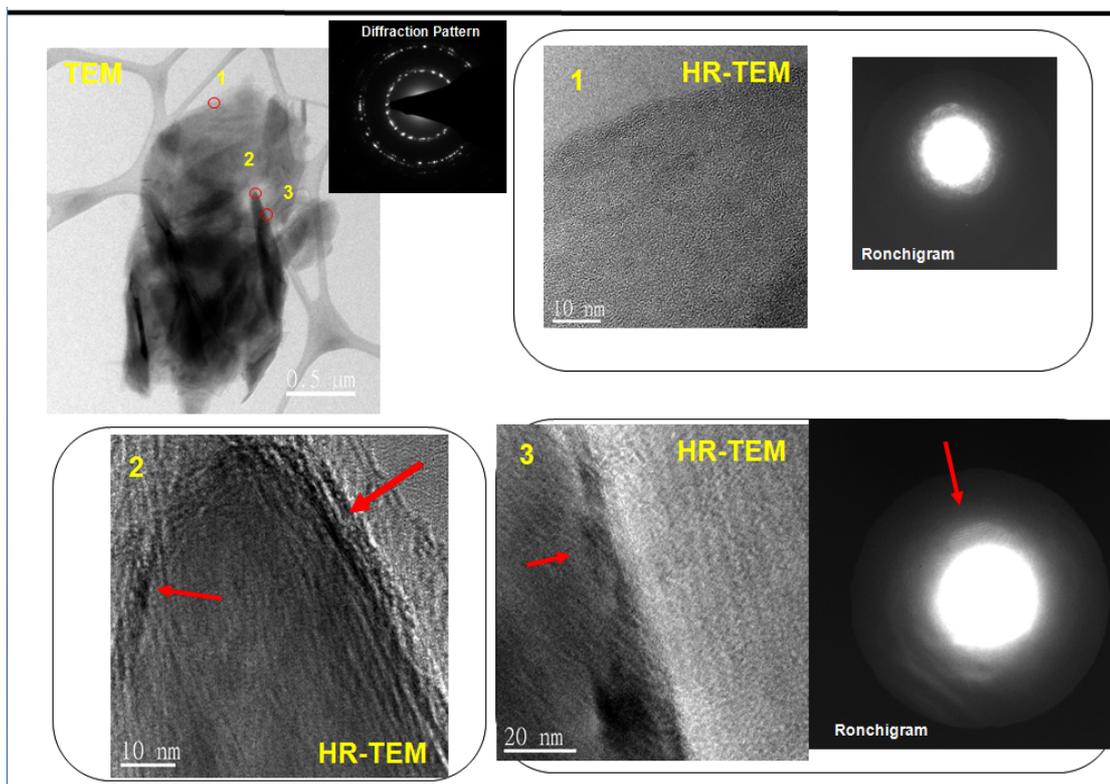
Figure 4 TEM and HRTEM of ACB40-Pt. In some areas, the diffraction
pattern and Ronchigram both indicate some crystallization.
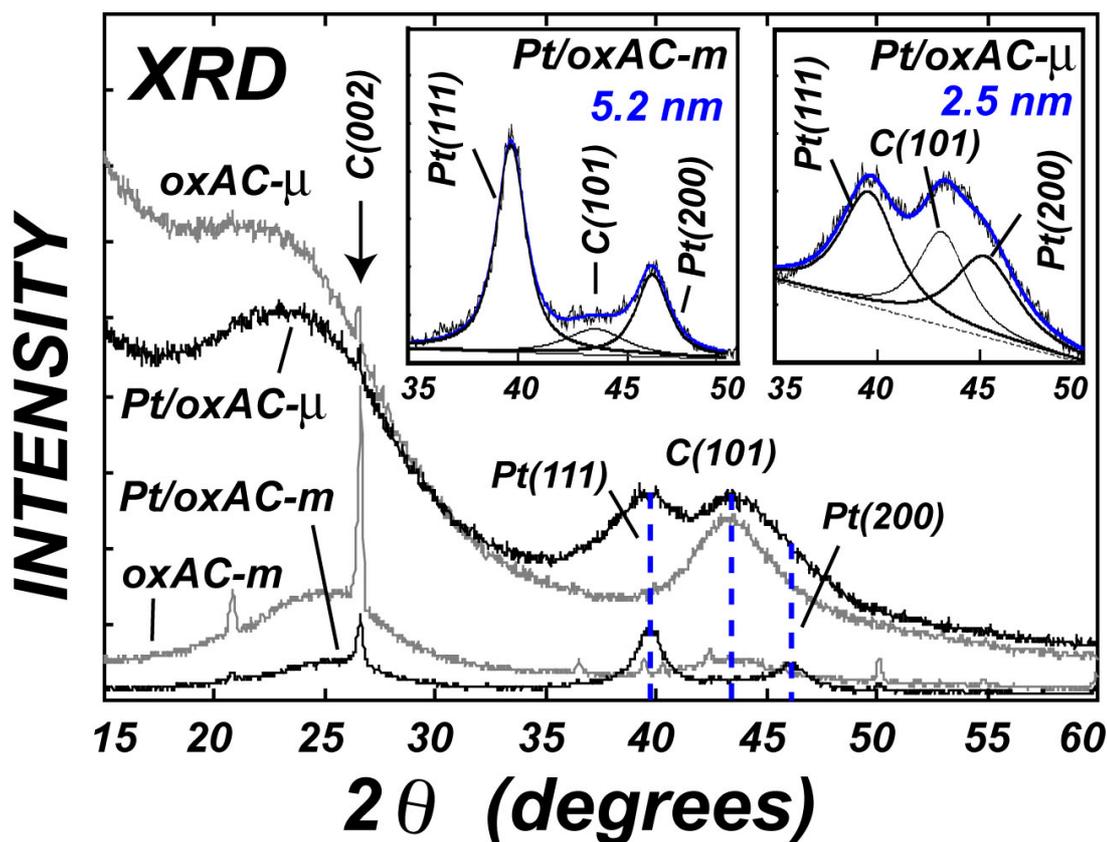
Figure 4X   X-ray diffraction of oxidized activated carbon measured by INER. Our ACB40-Pt corresponds to the Pt/oxAC-μ shown in the figure. Note that in all cases the carbon matrix shows some degree of crystallization.

The "bambo-rod" regions seem to correspond to where the Pt concentration is higher. In figure 5, SAE EDEX were taken at two points either away from or positioned on a rod (right bottom and right top, respectively). The Pt EDAX signal on rods is stronger whereas the not-on-rod Pt EDAX is near the detection limit. Since no 2-3 nm Pt nanoparticle was found but EDAX shows Pt, it suggests that the Pt

exists in a form that is smaller in size, perhaps smaller than nm and

evaded our STEM imaging.
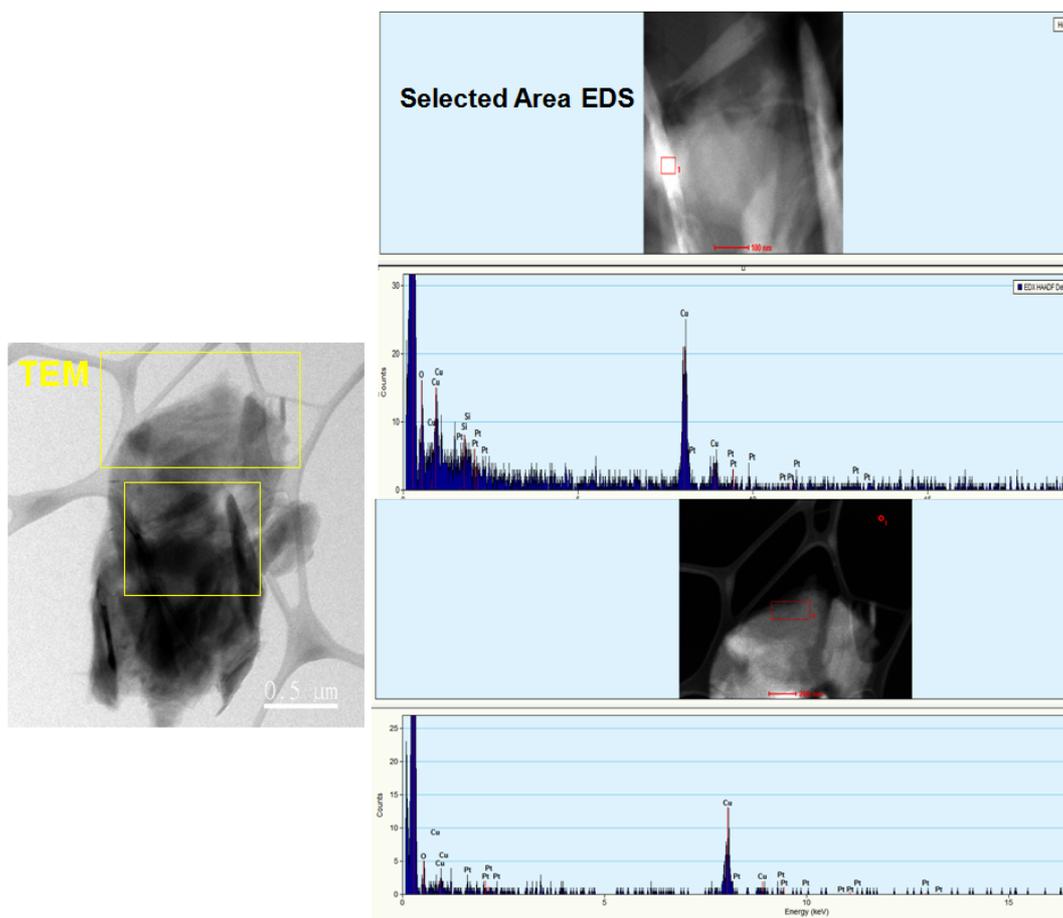
Figure 5 Selected area EDX for ACB40-Pt. In "rod-free" region, the EDX shows very little (if any) Pt signal. On rods, the Pt signal is stronger. However, no clear Pt nanoparticles were detected.

(三) Attempt of 3D tomography
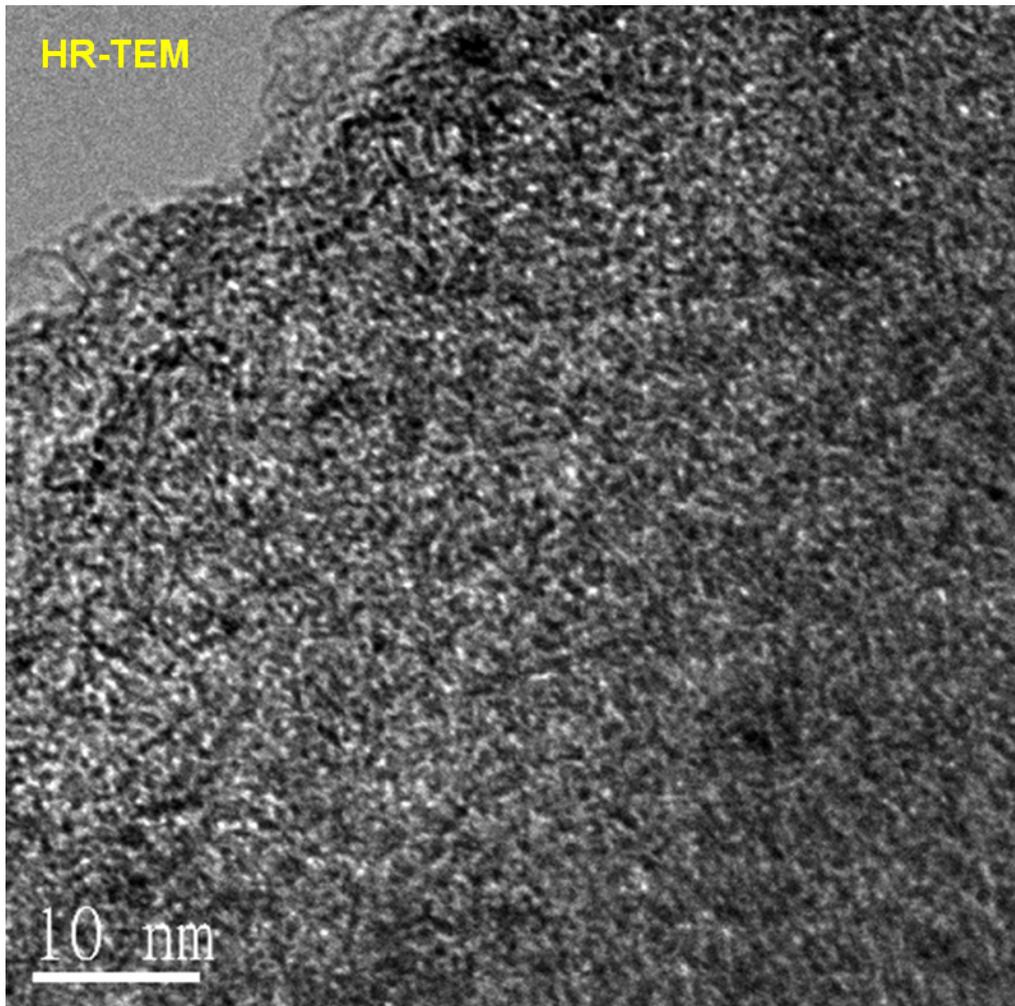
3D tomography, if applicable, provides a direct view of the 3D structure of the sample. Here, because one wants to know the relative spatial position of the Pt nanoparticles and the pore structure, tomography would be very useful. Tomography involves taking a series of TEM images at different sample angles, and uses a mathematical model to reconstruct the 3D real-space geometry. While in a single STEM image one can achieve sub Å resolution, the tomography resolution is much worse at ~2-3 nm. This turns out to be quite close to

our observed Pt particle size, and the expected nanopore diameter as derived from a small-angle neutron scattering experiment. While we were hopeful initially, the AC samples turned out to have very irregular pore structure. We were not able to detect any sign of regular pore structure in HRTEM, unlike e.g., anodized alumina (see figure to the right). This indicated that any attempt of 3D tomography will be fruitless. Therefore, tomography experiment must await for better samples, i.e., with more ordered pore structures. This, of course, is the requirement of analytical microscopy but not necessarily a pre-requisite for good hydrogen storage materials.

參、主要發現與結論

Figure 6 shows our "guess" model of a Pt-loaded AC sample, which has meso-size and micro-size pores. Neutron scattering has been used and suggests such a structure. Here, by direct HRTEM and HAADF images we did detect small Pt nanoparticles on the ACB-Pt samples. The Pt appears to locate inside the AC bulk structure. However, the present data still cannot establish a definitive relation between the Pt and pore entry locations. The present poor sample pore structure and limited tomography resolution, we could not yet reveal the 3D structure of Pt in AC. This is shown in Figure 7. We previously studied MCM and obtained clear pore structure but here with ACB-Pt we did not see any clear sign of pore structure. We believe this is due to a highly-disordered pore structure, rather than the absence of pore structure. SEM pictures show ACB-Pt does have pores on exposed surface, but SEM of course cannot reveal the internal pore structure in the bulk.
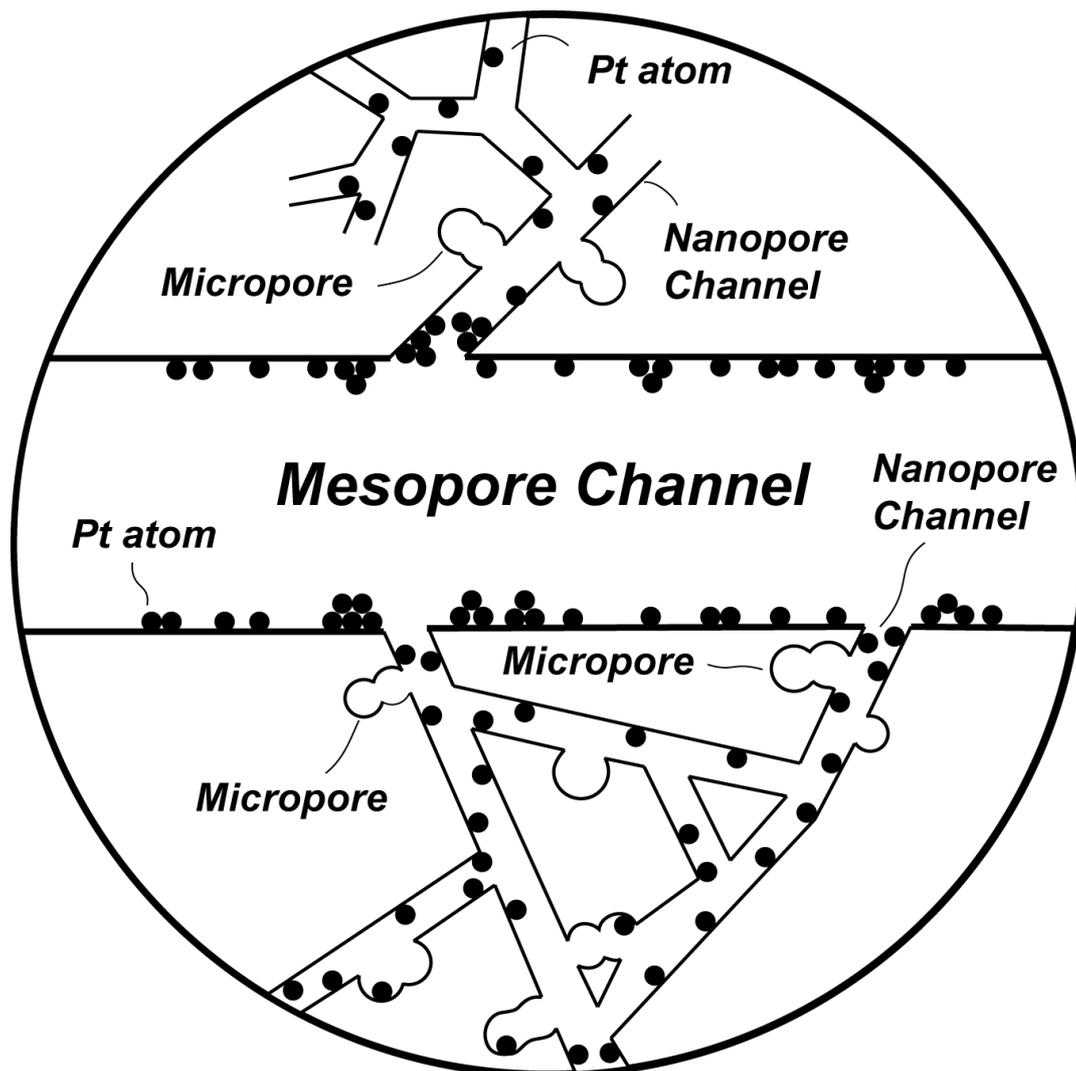
Figure 6   A typical "guess" of the activated carbon porous structure.
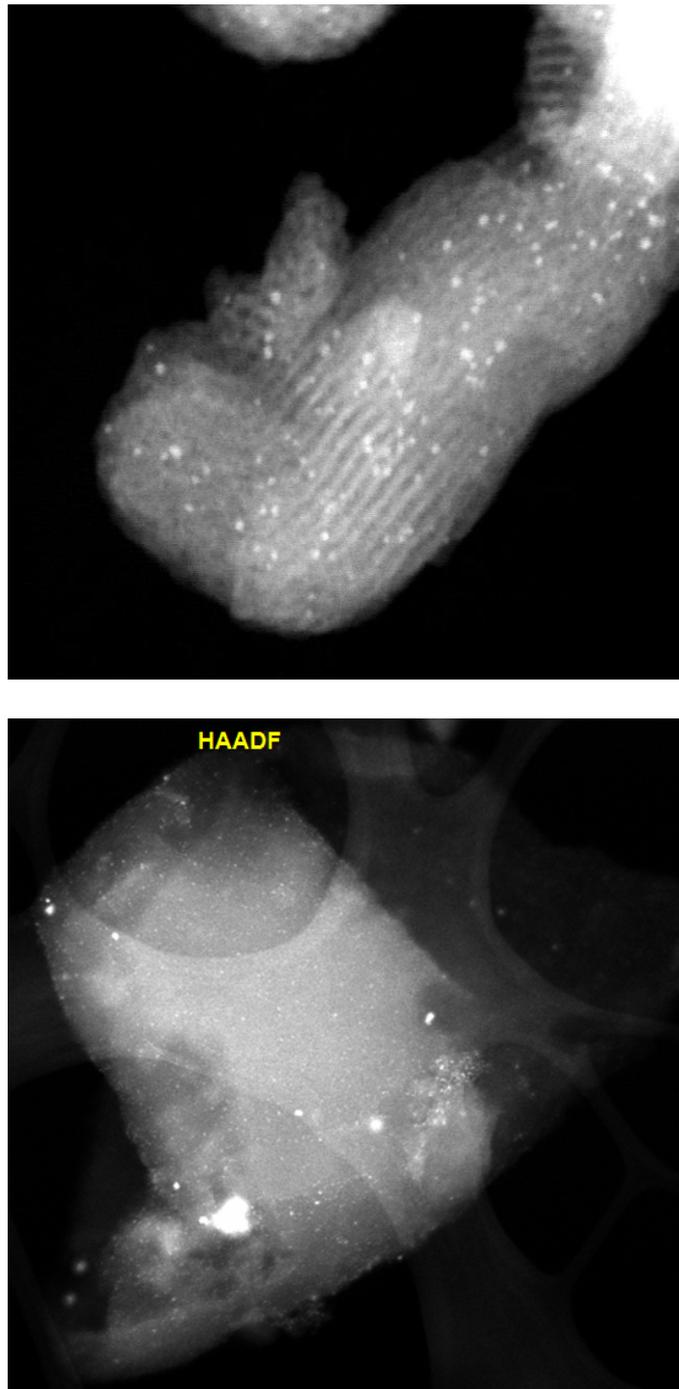
Figure 7 Comparison of porus materials: (left) A HAADF STEM image of Silica MCM mesopores with embedded PdRu nano particles. (right) A ACB-Pt sample. MCM sample shows clear sign of ordered pores and is viable for STEM 3D tomography measurement. Our ACB-Pt sample, irrespective magnification, showed no clear sign of pore structure.

S-4800 15.0kV 7.5mm x100k SE(M,LA0) 3/5/2008 09:48   500nm
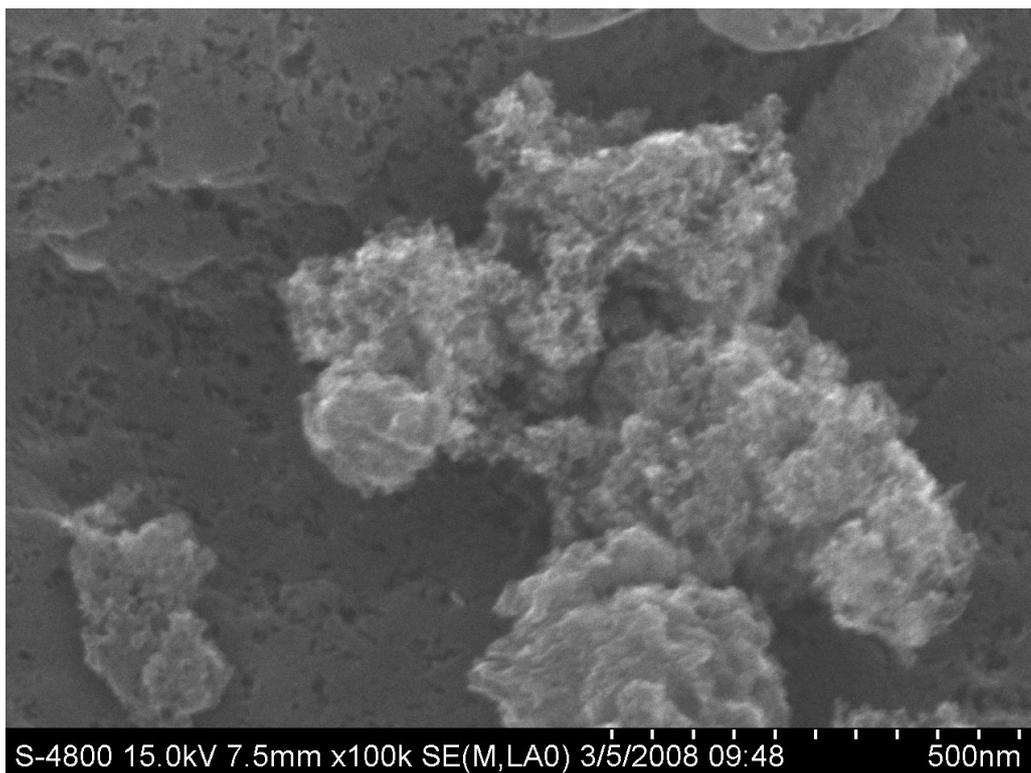
Figure 8 A typical SEM picture of the ACB-Pt sample. One can see pores are present on the surface.

In contrast, the ACB40-Pt sample has a very different morphology and the Pt exists in a form that is not readily shown as nanoparticles. It is quite possible that Pt forms even finer particles. Compared with the trend that measured hydrogen storage efficiency is higher for ACB40-Pt than ACB-Pt, it appears that the structure of ACB40-Pt is preferred in hydrogen storage. The post-processing of AC by oxidation has a significant impact on its property toward Pt impregnation and hence the hydrogen storage efficiency.

肆、參考文獻

1. P. Jain et al., J. Phys. Chem. C **111**, 1788 (2007)

2. L. F. Wang, and R. T. Yang, Energy Environ. Sci. **1**, 268 (2008).

3. Y. W. Li, and R. T. Yang, J. Am. Chem. Soc. **128**, 8136 (2006).

4. Y. W. Li, and R. T. Yang, J. Phys. Chem. C **111**, 11086 (2007).

5. FreedomCAR/DOE hydrogen storage technical targets,

   http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/freedomcar_targets_explanations.pdf.