Small angle neutron scattering and small angle X-ray scattering studies of platinum-loaded carbon foams

P U SASTRY*, V K ASWAL and A G WAGH
Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
*Corresponding author. E-mail: psastry@barc.gov.in

Abstract. The morphology of carbon nanofoam samples comprising platinum nanoparticles dispersed in the matrix was characterized by small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS) techniques. Results show that the structure of pores of carbon matrix exhibits a mass (pore) fractal nature and the average radius of the platinum particles is about 2.5 nm. The fractal dimension as well as the size distribution parameters of platinum particles varies markedly with the platinum content and annealing temperature. Transmission electron micrographs of the samples corroborate the SANS and SAXS results.

**Keywords.** Fractal; small angle scattering; nanoparticles.

PACS Nos 61.43.Hv; 61.05.fg; 61.05.cf; 61.46.Df

1. Introduction

Porous carbon materials loaded with the noble metal have a wide range of applications such as support for catalysts and in fuel cells [1,2]. Mostly, the properties used in such applications depend on the pore structure of the host as well as size distribution of the metal clusters. In this study, we have investigated the morphology of the carbon aerogels (or carbon foams) incorporated with platinum nanoparticles by SAXS and SANS.

2. Experiment

The samples used in this study were obtained from RRCAT, Indore, India [3]. They were annealed at various temperatures, viz., pure carbon sample (S0), two samples (S1, S2) annealed at 400°C containing 11% and 15% by weight of Pt and one sample (S3) containing about 12% Pt by weight but annealed at 900°C. Initial investigations were done on SANS using the instrument at Dhruva reactor, BARC, India. The data were collected in the wave vector transfer magnitude Q range of

P U Sastry, V K Aswal and A G Wagh
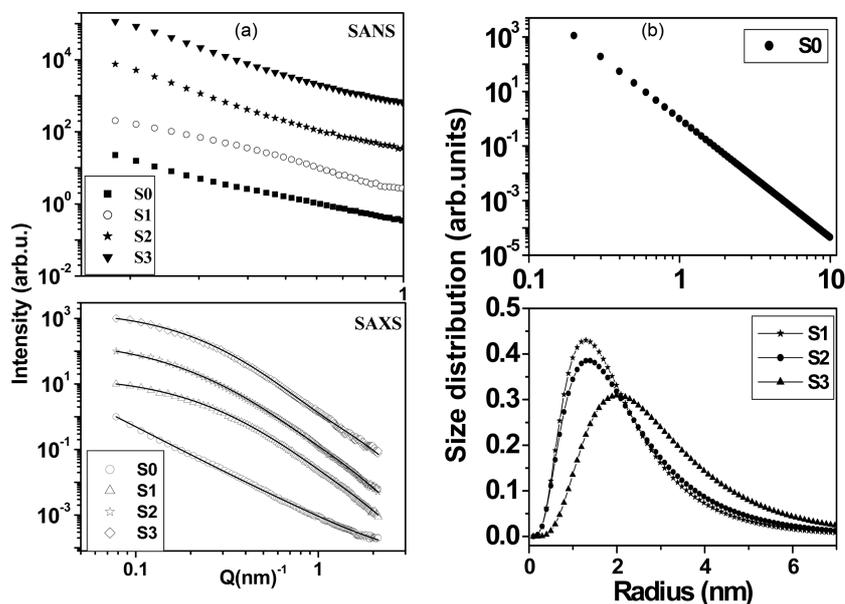
Figure 1. (a) SANS and SAXS profiles of pure carbon matrix (S0) and platinum-loaded-carbon samples (S1–S3). (b) Size distribution of pores in S0 and of platinum particles in S1–S3, as obtained from SAXS.

0.018 to 0.35 Å^{-1}. SAXS data were recorded using Rigaku make 12 KW rotating anode X-ray generator. Scattered X-ray intensity $I(q)$ was recorded as a function of scattering vector q ($=4\pi\sin\theta/\lambda$) with X-rays of wavelength (λ) of CuK$_\alpha$ and scintillation detector. The intensities were corrected for sample absorption and smearing effects of collimating slits [4].

3. Results and discussion

The results of SANS are displayed in figure 1 plotted on log–log scale. For the sample without platinum the profile is a straight line whereas the profiles of the samples containing platinum show a hump-like feature over the line profile. The latter may indicate the presence of platinum–platinum particles in the carbon matrix as also showed by TEM (showed for S3 in figure 2). SAXS profiles, plotted on log–log scale, show similar features and the scattering from platinum (high-Z element) is revealed with better clarity

The line profile of the scattering intensity of S0 extending over more than a decade of q-range follows a power law: $I(q) = I_0 q^{-\alpha}$ indicating fractal nature of the structure. For mass fractals $\alpha \leq 3$ and fractal dimension $D_{\mathrm{m}} = \alpha$ whereas for scattering from rough pore–mass interfaces, $\alpha > 3$ and the (surface) fractal dimension $D_{\mathrm{s}} = 6 - \alpha$. In porous solids, mass fractals are often called pore fractals since the scattering laws are identical upon interchanging the positions of pores and solids by Babinet's principle of reciprocity.
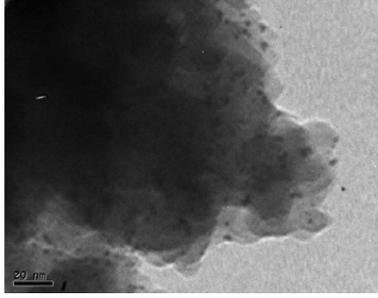
Figure 2. TEM picture of sample S3.

In this study, the magnitude of α for S0 is found to be about 2.7 from SANS and 2.6 from SAXS suggesting that the structure of pure sample is of mass fractal in nature. The scattering profile can be represented by the equation [5]

$$I(q) = CP_1^2(q)S(q), \tag{1}$$

where $P_1(q)$ is the form factor of the basic unit of the fractal aggregate and $S(q)$ is the structure factor of the scattering centres. For basic units of spherical shape with radius r_0, $P_1(q)$ is given by

$$P_1(q, r_0) = 3[\sin(qr_0) - qr_0\cos(qr_0)]/(qr_0)^3. \tag{2}$$

The structure factor for mass fractal system is given by [6]

$$\begin{aligned} S(q) = 1 + [d\Gamma(d-1)/\{(qr_0)^d[1 + 1/(q^2\xi^2)]^{(d-1)/2}\}] \\ \times \sin[(d-1)\tan^{-1}(q\xi)], \end{aligned} \tag{3}$$

where ξ and $2r_0$ are the upper and lower cut-offs of the fractal whereas d is the fractal dimension D_{m} as mentioned above.

The parameters obtained by fitting the SAXS data are given in table 1. The pore size distribution $\rho(r)$, varies as a power of fractal dimension $\rho(r) \sim r^{-(7-\alpha)}$. Figure 1 gives the pore size distribution for sample S0.

The SAXS data of samples S1–S3 were fitted to $I_p(q)$ by treating them as carbon foam coexisting with platinum particles.

$$I_p(q) = C_1 P_1^2(q)S(q) + C_2\left(\int P_2^2(q, R)D(R)R^6 \mathrm{d}R\right), \tag{4}$$

where $P_2(q, R)$ is the form factor of the particles with radius R, C_1 and C_2 are constants which depend on the electron density contrast between the scatterers and the matrix. The size of platinum particles were estimated using log-normal distribution given by

$$D(R) = 1/(\sqrt{2\pi})\sigma R\exp(-[\ln(R/R_0)]^2)/(2\sigma^2), \tag{5}$$

where σ is the variance and R_0 is the geometric mean of the distribution.

Figure 1 shows the size distributions and the fitted parameters are given in table 1. In the table, $\langle R \rangle$ represents the average radius of the particles and the width of the distribution is given by the parameter S which is $[\langle R^2 \rangle - \langle R \rangle^2]^{1/2}$.

P U Sastry, V K Aswal and A G Wagh

Table 1. Structural parameters of the pure and Pt-doped carbon foam samples.

Sample	$\langle R \rangle$ (nm)	S (nm)	D_{m}	r_0 (nm)
S0	–	–	2.65	0.5
S1	2.25	1.32	1.6	1.75
S2	2.44	1.7	1.8	1.9
S3	3.18	1.89	1.9	1.4

Results show that the average platinum particle radii obtained from SAXS are in the range 2.2–3.2 (± 0.03) nm. The order of magnitudes of the particle radii obtained from SAXS is in close agreement with values showed by TEM images. It may be noticed that the average size of the platinum particles and the width of the distribution, representing the extent of polydispersity is noticed to be larger for S3 which may be due to higher annealing temperature. As the sample is annealed at high temperature, there seems to be rearrangement of particle assembly leading to growth (or clustering) of particles. This is reflected in the observed changes in size as well as size distributions, particularly in S3 which was annealed at higher temperature. The fractal dimension of the carbon matrix is reduced significantly due to the introduction of platinum particles but the mass (pore) fractal nature is retained. The change in mass fractal dimension after inclusion of platinum is most likely due to change in pore structure after annealing at high temperatures and inclusion of at least some of the platinum into the pores. The value of upper limit ξ is found to be in the range $>$(110–130) nm. Similarly, the value of r_0, the lower limit of the fractal is enhanced considerably from the pure sample S0. The findings of this study would be useful in the applications of the samples.

Acknowledgements

References

[1] J Marie, S Berthon-Fabry, P Achard, M Chatenet, A Pradourat and E Chainet, *J. Non-Cryst. Solids* **350**, 88 (2004)
[2] F J Maldonado-Hodar, C Moreno-Castilla and P F Perez-Codenas, *Appl. Catalysis* **B54**, 217 (2004)
[3] R K Khardekar and N G Borisenko, *International Conference, 3rd Moscow Workshop on Targets and Applications* (Moscow, Russia, 2007)
[4] P W Schmidt and R Height, *Acta Crystallogr.* **13**, 480 (1960)
[5] A Guinier and G Fournet, *Small angle X-rays* (Wiley, New York, 1955)
[6] T Freltoft, J K Jems and S K Sinha, *Phys. Rev.* **B33**, 269 (1986)
[7] P W Schmidt, *J. Appl. Crystallogr.* **15**, 567 (1982)