Size spectroscopy of porous glasses and porous glasses with metal nanoparticles using UV–VIS and X-ray radiation

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UV–VIS and X-rays radiation were used for porous silica (PS) and porous silica with Ag nanoparticles investigations. It has been shown that XRD experiment gives information about the correlation function of heterogeneity in PS. Well-known plasmon resonance in UV spectral region was applied for the concentration and mean diameter of the metal particles determination.

Keywords: porous silica, X-ray diffraction (XRD), plasmon, silver nanoparticles.

1. Introduction

Electromagnetic interactions with non-homogeneous substances are powerful techniques for the structure and quality investigations of such species of solid state [1–4]. These methods are sensitive and nondestructive and have wide range of time (frequencies) and dimensions (wave vectors) applications. Porous glasses (porous silica) are not an exception. IR spectroscopy has been used for detail measuring and qualifying the properties of adsorption centers (OH-groups) in PS [5–7]. An ellipsometric technique has been used for transitional layer investigation [8]. UV–VIS absorption spectroscopy of the plasmon oscillations is an effective method for metal nanoparticles investigations [4–6]. Our goal here is to show the efficiency of the X-ray diffraction (XRD) method for PS structure investigation, possibility of the quantitative (UV–VIS) measurement of a mean diameter and concentration of the spherical metal nanoparticles in PS.

2. XRD measurement of porous structure

A method of small angles scattering of X-rays is employed by some investigators for surface heterogeneity probing of, for example, porous and fine-dispersed materials [9]. But there are a lot of difficulties in experimental data interpretation.

2.1. Experimental

There are a lot of methods for measuring the porous sizes distributions, porosity, fractal dimensions that describe inhomogeneous features of the PS [10]. Electromagnetic interactions, in particular Rayleigh scattering, is a very convenient method. But a rather rigid approximation ($ka \ll 1$, where k – wave vector, a – peculiar size of heterogeneity) does not permit us to get reliable and detailed information about PS structure. It is more preferable to use the electromagnetic wavelength λ that is much less than a ($\lambda \ll a$). So it must be less than 1 nm. Commercial setup has been used for XRD measurements (Rigaku/XRD). The angle precision $\Delta \Theta < 1°$, $\lambda = 0.154$ nm CuK_{α} spectral lines source. The dependence of X-ray intensity was measured upon the angle of incidence for "mirror angle" scattering scheme (Fig. 1).

Two curves (Fig. 2) have the same "resonance" angle $2\Theta_0 = 22°$, but different half-height angle width and amplitudes. Pore diameter corresponds to the most probable diameter that was measured with BET nitrogen method (BELSORP 28SA).
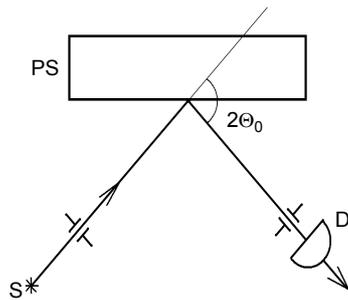

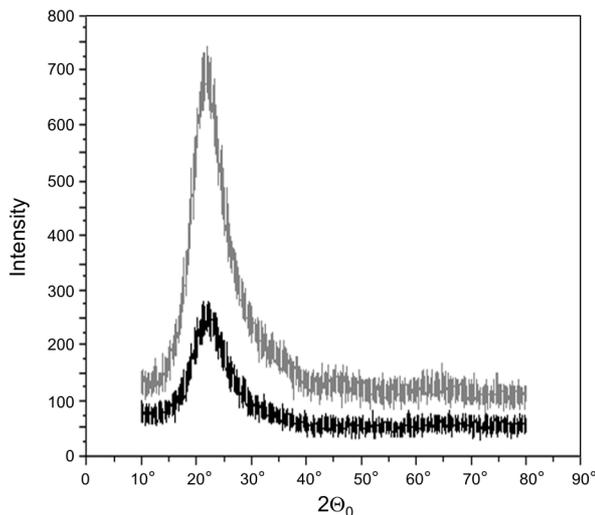Fig. 1. XRD scheme: PS – sample, S – source CuK_{α}, D – detector.

Fig. 2. Experimental angle dependences of the intensity of X-ray for two PS samples with pores diameters: 5.4 nm (lower curve), 6.8 nm (upper curve).

We apply a short wave approximation ($ka \gg 1$) for theoretical interpretation of the measurements [1, 2].

2.2. Results and discussion

It is evident that the interaction of the electromagnetic waves with heterogeneous structures is the most typical for wavelength less or equal to the scale of the heterogeneity. The most advanced results were obtained in optics and acoustics [1, 4]. We have no mirror reflection in such approximation. We take into account large variations of parameter $q_z\sigma_\zeta$, where $\bar{q} = k(\bar{n}_s - \bar{n}_i)$, while $\bar{n}_{s,i}$ – unit vectors for the scattering and incident waves accordingly, q_z – orthogonal to the surface component of vector $\bar{q}$, σ_ζ – variation of the height of the surface inhomogeneity. At the same time Fraunhofer approximation is satisfied $k\sigma_\zeta^2/L \ll 1$, where L – distance to the observation point. If we take into consideration the stipulation that $D \gg l_\zeta$ (l_ζ – correlation radius, D – diameter of the X-ray bunch), then we approve non-coherent nature of the scattering. So it is characterized by the section of the scattering (per square unit) σ [1].

In the case of mirror reflection the author of the article [2] calculated exact formula for the isotropic field of heterogeneity with the normal distribution $K_\zeta(\rho) = {} = \exp[-\rho^2/2l_\zeta^2]$:

$$\sigma = \frac{|R|^2 q_z^2 l_\zeta^2}{8\pi} \left[E_i\left(q_z^2 \sigma_\zeta^2\right) - C - 2\ln\left(q_z \sigma_\zeta\right) \right] \exp\left(-q_z^2 \sigma_\zeta^2\right) \tag{1}$$

where $E_i(z)$ – exponential integration function, $C \approx 0.577$, $q_z = 2k\sin\Theta_0$.

The $2\Theta_0$ dependence of σ is shown in Fig. 3. The main conclusions are: i) location of the peak is affected by $q_z\sigma_\zeta$ parameter; ii) amplitude of the peak depends upon $q_z l_\zeta$. One can find location of the peak $\sin\Theta_0^{\max} = (\sqrt{2}\,k\sigma_\zeta)^{-1}$. Taking into account $\Theta_0 \approx 11°$, $\lambda \approx 0.154$ nm, one can find $\sigma_\zeta = 0.09$ nm. This value corresponds to the case when $q_z\sigma_\zeta = 1.40$.
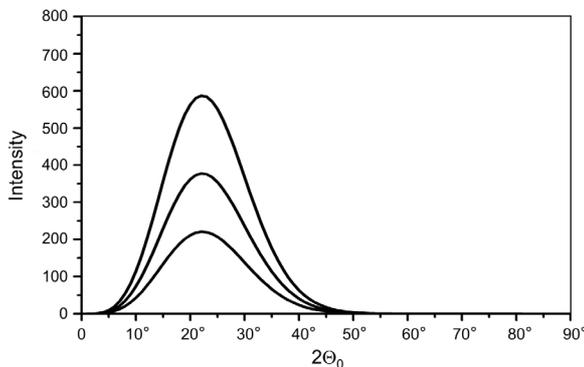

Fig. 3. Theoretical angle dependences of the intensity of X-ray for different $q_z l_\zeta$: 130, 170, 212 (from bottom to top); $q_z\sigma_\zeta = 1.40$.

The ratio of the amplitudes in Fig. 2 is 2.83, so $l_{\zeta_1}/l_{\zeta_2} = \sqrt{2.83} \approx 1.68$. It is in fair correspondence with the ratio of the most probable pore diameters 6.8 nm/5.4 nm = 1.26, which were measured by nitrogen condensation method. If we suppose that correlation radius l_s is proportional to the mean pores diameter $\langle d \rangle$, then ratio $\langle d_1 \rangle / \langle d_2 \rangle \approx 1.32$ (compare with 1.68 for l_ζ).

Concluding this chapter we can say that XRD experiments are a rather effective technique for measuring correlation parameters of the PS surface, which are connected with the pore diameter distribution.

3. Plasmon resonance measurements of the diameter and concentration of the metal nanoparticles in PS

Optical investigations of the metal colloid particles are more than 100 years old. The basic results for the spherical particles were obtained by Mie (1908). The task becomes much more difficult when we try to take into account the particle size distribution. This is the so-called "non-correct mathematical problem". This problem was solved for lidar detection of aerosol pollution in atmosphere. We took another way: firstly we produced monodisperse distributed metal nanoparticles and then applied to them plasmon resonance method.

3.1. Experimental

We utilized PS as a reducing agent and matrix for metal nanoparticles growth. The metal precursor ($AgNO_3$) was spread inside the pores by soaking the PS in aqueous solution of the precursor, followed by drying the PS in air or not high vacuum (0.1 torr). Reductive growth of the metal clusters in the pores started during drying process and its rate was significantly accelerated upon heating of the PS in the water vapor atmosphere under permanent pressure [11]. Typical weight concentration of $AgNO_3$

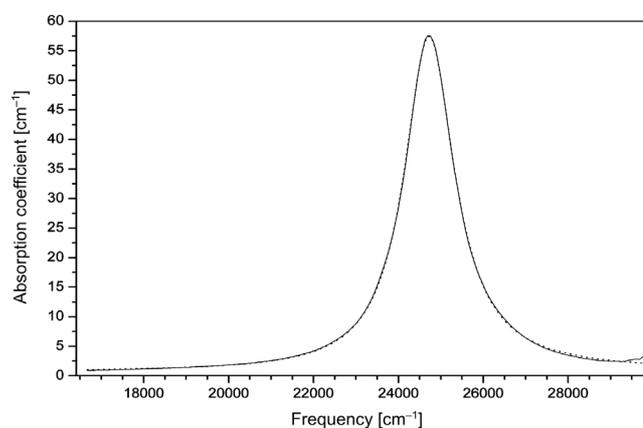Fig. 4. Frequency dependence of the absorption coefficient for PS:Ag sample; $d = (10.19 \pm 0.05)$ nm, $f = 3 \times 10^{-5}$, $d_{pore} = 13$ nm.

in aqueous solution was 0.1–1%. Concentration and diameter of the particles were proportional to the time and temperature of the heating accordingly. Duration of the process varied from 30 to 120 min, temperature 500–700°C. One can see an excellent coincidence of theoretical and experimental dependences (Fig. 4), that indicates that the distribution of the particles is a quasi-monodisperse one. Such result was obtained by additional treatment of the PS:Ag with aqueous solution of HNO_3 acid and drying. Correlation coefficient overreached 0.999. Measurements were carried out with C-115-M1 UV–VIS spectrometer, which was upgraded by implementation of two channels accessory and digital processing. That provides accuracy 0.2% in transmittance measurements.

3.2. Results and discussion

Surface plasmon oscillations in spherical metal nanoparticles have two different peculiarities as compared to volume one. Firstly, it can be excited by transverse electromagnetic field. Secondly, surface plasmon frequency is $\omega_{sp} = \omega_{vp}/\sqrt{2}$, where ω_{vp} – plasmon frequency for volume. So we have to do measurements, for instance, for Ag metal in near UV-visible region ($\lambda_{sp} \approx 400$ nm) instead of UV ($\lambda_{vp} \approx 280$ nm). Heating of PS:Ag sample in the water vapor atmosphere to high temperature (700°C) leads to partial pyrolysis of H_2O within the nanosize pores (and nanoparticles) [11]. So we have rival reactions: oxidation and reduction. In their turn these reactions depend upon pore walls in silica and particles surfaces. PS:Ag nanoparticles sample is the so-called "chemical nanoreactor". Based on the experimental data, we can suppose that the volume-feeling factor $f \ll 1$ and neglect dipol–dipol interaction between metal nanoparticles. One can write [4, 5]

$$K = \frac{18\pi f \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_2}{(2\varepsilon_m + \varepsilon_1)^2 + \varepsilon_2^2} \qquad (2)$$

where K – absorption coefficient, ε_m – mean dielectric constant of PS matrix, $\varepsilon = \varepsilon_1 + i\varepsilon_2$ – complex dielectric constant of the metal, $\varepsilon_1 = \varepsilon_0 - \omega_p^2/\omega^2$, $\varepsilon_2 = \omega_p^2/\omega^3 \tau_{eff}$, $\omega_p^4 = 4\pi N e^2 / m$.

Let us define τ_{eff}:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau} + \frac{2v_F}{d} \qquad (3)$$

τ – Drude relaxation time, d – diameter of the nanoparticles, v_F – Fermi velocity (for Ag is approximately 1.4×10^8 cm/s).

Let us find the coefficient of absorption for resonant frequency ω_{sp}, when $2\varepsilon_m + \varepsilon_1(\omega_{sp}) = 0$

$$K_0(\omega_{sp}) = \frac{9f \varepsilon_m^{3/2}}{c} \frac{\omega_{sp}^4}{\omega_p^2} \tau_{eff}. \qquad (4)$$

If we add the formula for half-width ($\Delta\omega_{1/2}$) we will have two equations with measured parameters $\Delta\omega_{1/2}$, $K_0(\omega_{sp})$ and calculated parameters f, d. A parameter $\Delta\omega_{1/2}$ is usually found from equation $K(\omega_{sp} \pm \Delta\omega_{1/2}) = \frac{1}{2}K_0(\omega_{sp})$. This leads to a cubic algebraic equation. It can be simplified for $\Theta = \omega_{sp}\tau_{eff} > 3$. Though this assumption leads to a complicated expression, too. An adsorption curve is a nonsymmetrical one. The whole width $\delta_{1/2} = \delta_1 + \delta_2$ has a rather simple formula

$$\frac{1}{\delta_{1/2}} = \frac{\Theta^2 - 2}{\sqrt{\Theta^2 + 2}} \tag{5}$$

where $\delta_{1/2} = \frac{\Delta\omega_{1,2}}{\omega_{sp}}$, $1/\Theta = 1/\Theta_d + 1/\Theta_0$, $\Theta_d = \frac{\omega_{sp}d}{2v_F}$, $\Theta_0 = \omega_{sp}\tau$. Dependence $\frac{1}{\delta_{1/2}}(\Theta_d)$ is pictured in Fig. 5 for some value of Θ_0.

If we take into account the value for metal Ag $\tau \approx 2.5\times10^{-14}$ s [5], we will get $\Theta_0 = 117.5$, that does not correspond to the well-known data [5]. So we have to suppose that the relaxation time near the surface of the metal nanoparticles is far lesser. To fit Eqs. (3) and (5) with experimental data [5], we have to put $\tau = 4.2\times10^{-15}$ s ($\Theta_0 = 20$, Fig. 5). Small diameters of the particles (< 1 nm, $\Theta_d < 2$) have not been described by the classical Drude theory ever.

In addition to formula (5) we can introduce a new parameter $\Delta\delta_{1/2} = \delta_1 - \delta_2$, that characterizes an asymmetrical form of the curve $K(\omega)$

$$\Delta\delta_{1/2} = \frac{2}{\Theta^2 - 2}. \tag{6}$$

Thus, Eqs. (4) and (5) solve the problem. Firstly, we find

$$d = \frac{2v_F}{\omega_{sp}\delta_{1/2}} \qquad (\Theta_d \ll \Theta_0). \tag{7}$$

Then we use d to calculate f:

$$f = \frac{2}{9}\frac{\omega_p^2}{\omega_{sp}^4}\frac{cv_F}{d\varepsilon_m^{3/2}}K_0(\omega_{sp}). \tag{8}$$

We could apply different approximations to calculate ε_m, for example, Bruggeman [4], but it does not give fairly reliable result. So we find ε_m from a resonant condition $2\varepsilon_m + \varepsilon_1(\omega_{sp}) = 0$. The final formula for nanoparticles concentration N is:

$$N = \frac{4}{3\pi\varepsilon_m^{3/2}}\frac{\omega_p^2}{\omega_{sp}^4}\frac{cv_F}{d^4}K_0(\omega_{sp}). \tag{9}$$
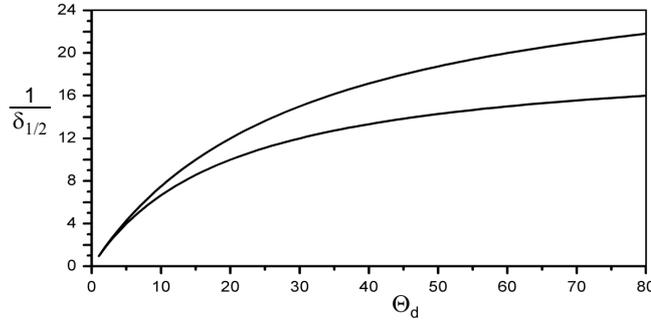
Fig. 5. Particle diameter dependence of the reference spectral width Θ_0 = 20, 30 (from bottom to top).

In our experiments the estimated value of f (see Eq. (8)) is less than appropriate account evaluated from the whole quantity of Ag impregnated to the PS sample. That means that part of Ag was not subjected in the form of nanoparticles.

If technology does not provide monodisperse sizes distribution one has to consider this fact. We do that for the simplest step-type distribution function:

$$
F(d) = \begin{cases} \dfrac{1}{d_2 - d_1}, & d_1 < d < d_2 \\[2mm] 0, & d < d_1, d > d_2 \end{cases}.
\tag{10}
$$

We take Lorenz approximation for function (4). Thus we obtain the mean value of $\langle K(\omega) \rangle$:

$$
\langle K(\omega) \rangle = \frac{9\,\varepsilon_m^{3/2} f}{c}\,\frac{\omega^2}{\omega_p^2}\,\frac{v_F}{(d_2 - d_1)p^2}\,\ln\left[\left(1 + \frac{\omega^2 p^2}{4 v_F^2}\,d_2^2\right) \middle/ \left(1 + \frac{\omega^2 p^2}{4 v_F^2}\,d_1^2\right)\right]
\tag{11}
$$

where $p^2(\omega) = \left(\dfrac{\omega^2}{\omega_{sp}^2} - 1\right)^2$.

It is obvious that $\langle K(\omega_{sp}) \rangle = K_0(\omega_{sp})$, if we put mean value of $\tau_{eff} = (d_1 + d_2)/4 v_F$ in Eq. (4). Dependence (11) is pictured in Fig. 6. If $d_1 \to d_2$, then $\langle K(\omega) \rangle \to K(\langle \omega \rangle)$. We take into account the influence of the changes in d on the time of the relaxation τ_{eff}. At the same time resonant frequency ω_{sp} depends upon the parameter $|\bar{k} d|$, where $|\bar{k}| = 2\pi/\lambda$ – wave vector of the light [4]. But this dependence is due to the second power of the parameter $|\bar{k} d|^2 < 10^{-3}$. Hence we have a basis to neglect its impact on the resonance conditions. The same analysis was carried out for the Au nanoparticles in silica gel and Ag nanoparticles formed with different technology.
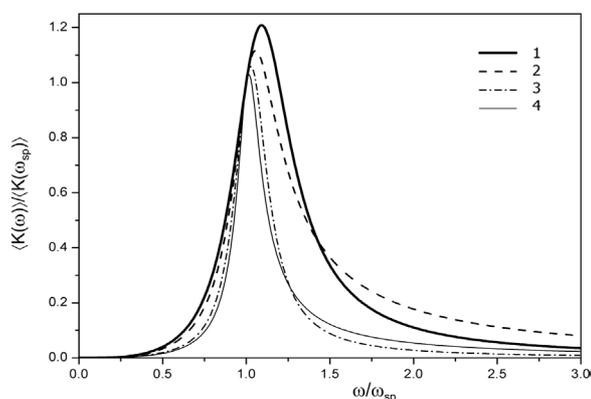
Fig. 6. Frequency dependences of the reference absorption coefficient for different values Θ_1 and Θ_2: 1.99 and 2.01 (curve 1), 0.01 and 3.99 (curve 2), 3.99 and 4.01 (curve 3), 0.01 and 7.99 (curve 4).

The extension of the range of coincidence of the experimental curve with theoretical one depends upon the width and the form of the function $F(d)$. For example, the correlation coefficient for the curve in Fig. 4 exceeds 0.999.

4. Conclusions

XRD method is rather an effective technique for measuring the heterogeneity of the PS. However, there are some difficulties when one compares the results of XRD with the results obtained by a capillary condensation method.

Well-known plasmon resonance in metal nanoparticles was used for the measuring of the mean diameter and concentration of particles. The natural demand to get reliable results is quasi-monodisperse particle size distribution.

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