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Fiber Optic Sensor Application for Nanoparticle Size Measurement in Chemical Reactors

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Different kinds of fiber optic sensors (FOS) for nanoparticle size measurements during their growth in chemical reactors are discussed. It was shown that in reactor without mixing a single-mode FOS can be applied for real-time size measurements, and in the presence of turbulence (in reactor with active mixing) capillary FOS should be preferred.

Keywords: Correlation spectroscopy, Dynamic light scattering, Nanoparticles, Chemical reactor, Fiber-optic sensor, Capillary light guide.

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1. INTRODUCTION

Interest to the investigations devoted to different methods for obtaining nanoparticles and study of their chemical and physical properties has increased during last years. This is conditioned by the fact that with the decrease in the size, properties of particles can differ from the properties of macroscopic materials or separate atoms of the given substance. The possibility to obtain nanoparticles with different parameters allows to use them widely in engineering, medicine, electronics and different branches of industry. The size which can be exactly determined using methods of correlation spectroscopy is one of the main characteristics of nanoparticles defining their properties.

2. BASIS OF THE MEASUREMENT METHOD

At propagation of laser radiation through liquid which contains suspended disperse particles, radiation scattering on fluctuations of particle concentration induced by the Brownian motion occurs. For the experimental determination of these fluctuations it is necessary to minimize the scattering volume [1] using the optical scheme represented in Fig. 1.

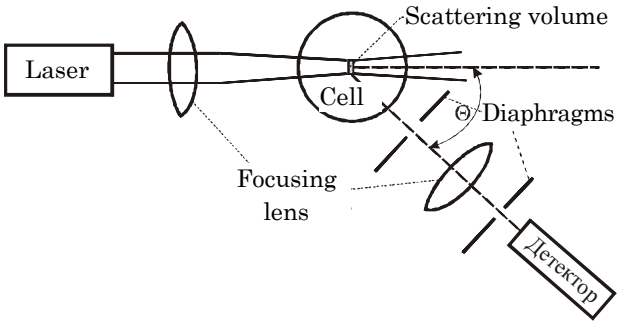

Fig. 1 – Optical scheme of the experimental plant

Autocorrelation function (ACF) of intensity fluctuations contains information about all dynamic processes occurring in the studied medium

$$G^{(2)}(\tau) = \langle I(0)I(\tau)\rangle = \lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T} I(t')I(\tau+t')dt' , \quad (1)$$

where τ is the time delay; I is the intensity of scattered light in time moments t, $t+\tau$.

In the case of monodisperse scattering medium (spherical isotropic particles), experimental ACF will be the following [2]:

$$G^{(2)}(\tau) = a + b\exp(-2D_T q^2\tau) , \quad (2)$$

where a is the constant component; b is the constant depending on the spatial and temporal averaging of the scattering signal; D_T is the particle diffusion coefficient; $q = (4\pi n/\lambda)\sin(\theta/2)$ is the modulus of the wave scattering vector (n is the refractive index of liquid; λ is the wavelength of laser radiation; θ is the scattering angle).

Determining time of the e-fold decrease in ACF, one can calculate the diffusion coefficient which is interconnected with hydrodynamic radius of spherical particles by the Stokes-Einstein formula [2]

$$D_T = \frac{kT}{6\pi\eta R_h} , \quad (3)$$

where k is the Boltzmann constant; T is the temperature; η is the medium viscosity; R_h is the hydrodynamic radius of a particle.

3. MEASUREMENTS IN CHEMICAL REACTORS

In spite of the fact that synthesis of nanoparticles in chemical reactors [3] is the simplest and widespread, control of the particle size during the process of their growth is complicated because of the optical opacity of chemical reactor walls. Therefore, in order to completely automate the measurement process, it is necessary to replace the optical scheme by the FOS.

3.1 Chemical reactor without mixing

FOS represents the combination of two light guides, whose optical axes of both ends are placed in one plane

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perpendicular to each other (Fig. 2). One of light guides acts as the radiation source bringing it to the studied medium away from laser, another one – as the inlet of the scattering signal receiver transmitting light coming on its aperture to the photoelectronic multiplier (PEM). FOS (by its sensitive part) is placed directly into chemical reactor. Scattering volume obtained by FOS coincides in the order of magnitude with that obtained by using the ordinary optical scheme.

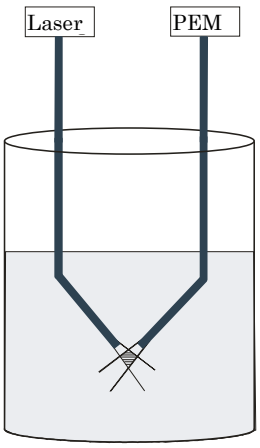

Fig. 2 – Fiber optic sensor (FOS)

Sensors were produced of monomode (core diameter is 5 μm; numerical aperture is $\alpha = 0{,}1$) and multimode (diameter is 100 μm; $\alpha = 0{,}3$) fiber. To define the optimal configuration of FOS, we have measured the ACF of light scattered by monodisperse spherical particles (latex of the radius of 100 nm in water and titanium oxide of the radius of 18 nm in propanol-2) (Fig. 3a).

It is seen from Fig. 3a that ACF obtained using the monomode FOS and ordinary optical scheme coincide. Therefore, fiber optic sensor should be produced of monomode fiber. Using monomode FOS, measurements of the nanoparticle sizes in sol-helium reactor [4] were carried out in the real-time mode. A number of kinetic growth curves of nanoparticles which correspond to different molar concentrations of titanium as the dependence of the second moment [3] $\mu_2 = \int m^2 F(m) dm$ (where m is the particle mass; $F(m)$ is the particle mass distribution function) versus the time are represented in Fig. 3b. Increase in the hydrodynamic size of nanoparticles from 2 nm to 10 nm took place during observed time delays from the beginning of solution deposition in reactor.

Application of monomode FOS allowed to control with high accuracy the growth process of nanoparticles in the real time scale in chemical reactor without mixing at different concentrations of titanium.

3.2 Chemical reactor with mixing

Since for reaction implementation it is necessary to thoroughly mix solutions of initial reactants, chemical reactor usually contains machine mixer [5, 6] in order to increase the operating efficiency. The latter leads to the appearance of turbulent fluid motion in the studied medium, and in this case, values of the measured particle radius differ from the real one and depend on both the Reynolds number $\mathrm{Re} = ND^2\rho/\eta$ (N is the rotation rate; D is the diameter of mixing arm; ρ is the liquid density; η is the dynamic viscosity of liquid) (Fig. 4a, b) and the position of monomode FOS inside reactor (see Fig. 4c). This is conditioned by the interaction of scattering particles located in one vortex induced by macroscopic stochastic motion of liquid. Therefore, statistics of the scattered radiation considerably differs from the Gaussian one.

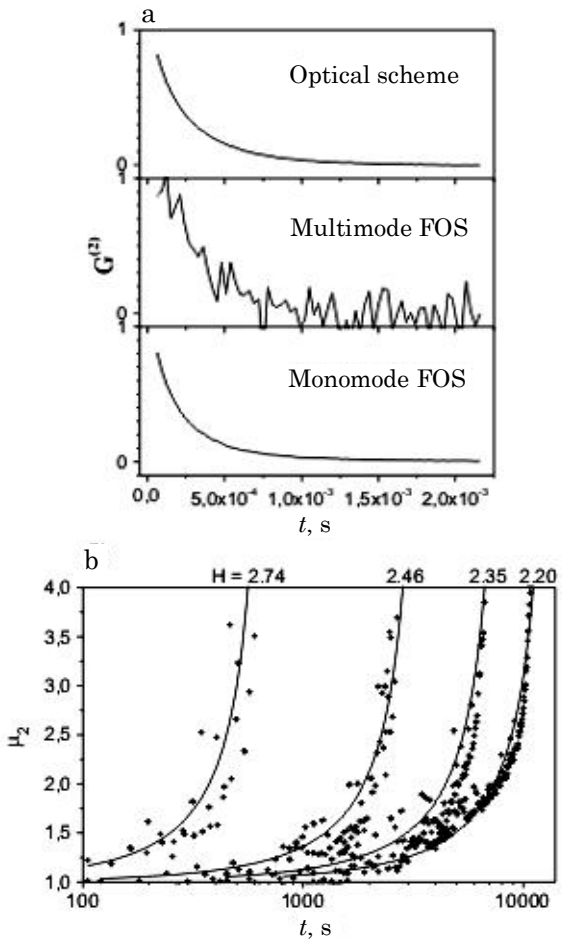

Fig. 3 – a) ACF of the scattered light (TiO_2 particles of the radius of 18 nm); b) kinetic growth curves of nanoparticles at different hydrolytic ratios

The authors of [6] use correlation which allows to recalculate the measured particle radius to the real one depending on the Reynolds number and FOS location in reactor. In the present work, in order to measure the nanoparticle size we propose to eliminate turbulence in the scattered volume using capillary FOS.

Capillary light guide (CLG) is the light guide where liquid, which fills cavity in the tube-shaped reflecting cladding [7, 8], acts as a core. Capillary FOS represents system consisting of three light guides: two monomode light fibers located perpendicular to each other and one capillary light guide (Fig. 5). One of monomode fibers as well as in usual FOS is the conductor of coherent radiation from laser, and the second fiber acts as a receiver of scattered radiation with its further transmission to the PEM. CLG with the core diameter of 150 μm (produced of TEFLON AF 2400 with the refractive index of 1,29 that provides the light guide properties) can be considered in this case as the closed cell with a slowly flowing liquid.

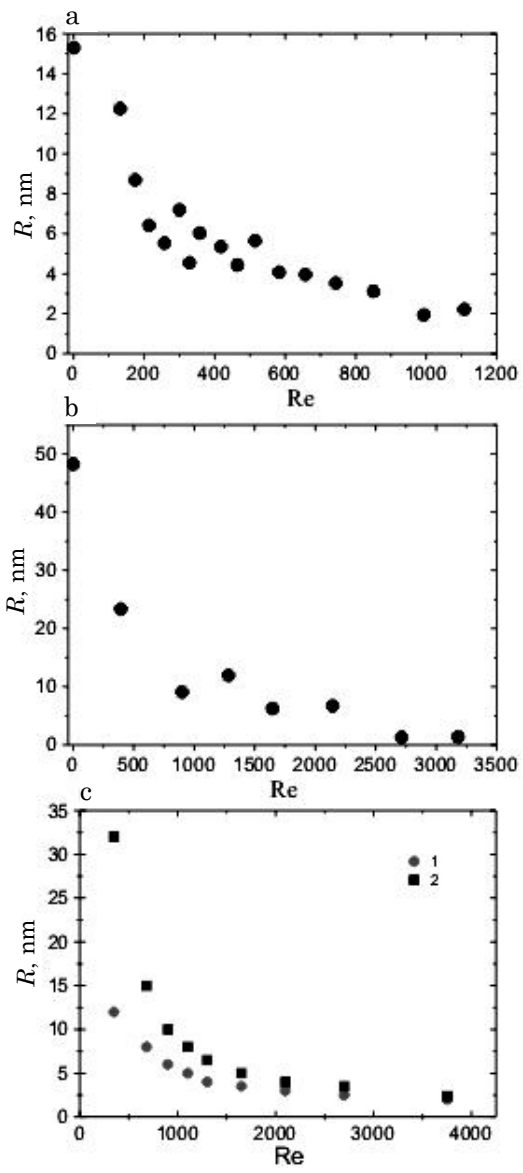

Fig. 4 – Dependence of the measured particle radius: a) and b) on the Reynolds number (a – titanium oxide, 18 nm; b – latex, 50 nm); c) on the FOS location (1 – in the symmetry plane of mixer; 2 – 3 cm away from the symmetry plane of mixer)

Thus, from one end of CLG the studied liquid is injected into its core from chemical reactor using micropump. Measurements of the radius of particles located in liquid are performed during slow motion of liquid in CLG (Fig. 6 where for comparison we present the ACF obtained using optical scheme with large accumulation time of scattering signal).

Then, liquid returns into chemical reactor through another end of CLG, and total automatization of the measurement process in the real time-scale is achieved at continuous liquid flow. When velocity field of liquid motion in LG is stationary and uniform, the results of measurements of the nanoparticle size do not depend on the velocity of liquid motion [9].

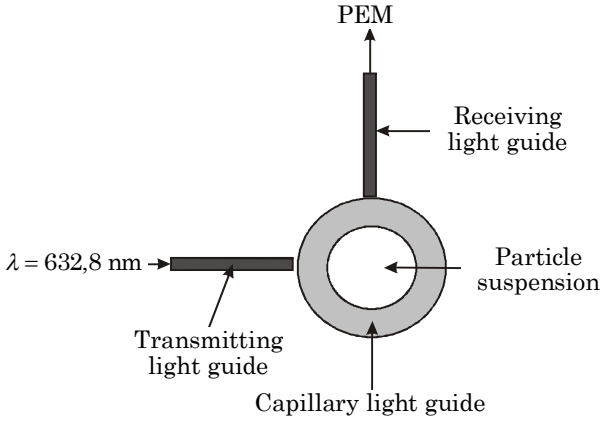

Fig. 5 – Capillary fiber optic sensor

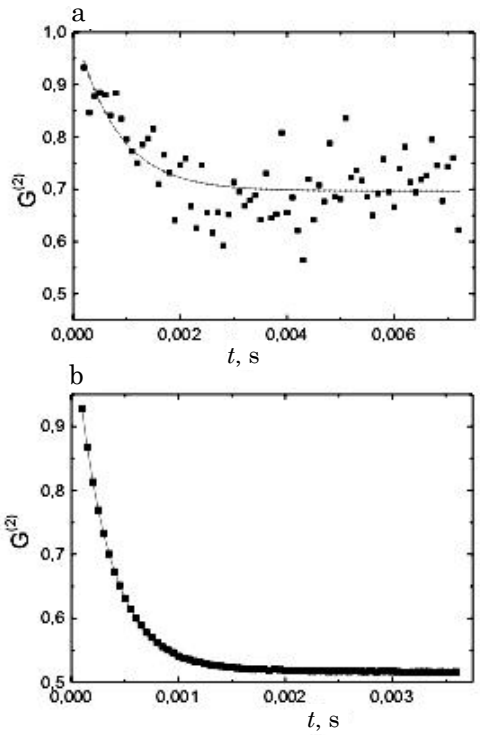

Fig. 6 – ACF of intensity fluctuations measured using a) capillary FOS; b) traditional optical scheme

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