

MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

Formation of Se⁰ Nanoparticles in an Aqueous
Cationic Polyelectrolyte

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Received December 23, 2002

Abstract—The nanostructures formed by reduction of Se(IV) in the selenite–ascorbate redox system in an aqueous solution of supermacromolecular polycation, poly[trimethyl(methacryloyloxyethyl)ammonium] methyl sulfate, were studied by static and dynamic optical scattering and flow birefringence.

Formation of uncharged metal nanoparticles of 1–100 nm size, which have energy-saturated surface and exhibit certain anomalies in physicochemical properties, is extensively studied [1].

However, such metal nanoparticles are unstable in aqueous solutions in the absence of stabilizing agents. One of the most promising procedures for preparing stable metal nanoparticles is reduction of their ionic species in polymer solutions. In the course of the pseudo-template synthesis, macromolecules and forming nanoparticles recognize each other, which allows control of the nanoparticle size by varying the structure and molecular weight of the polymer [2].

Such polymer-stabilized nanoparticles are of particular importance as highly selective catalytic systems and adsorption matrices for immunoassay, and, due to the rapid development of the biological nanotechnologies, as active components of drugs and transport systems for biologically active compounds [3–5].

However, much less attention was given to non-metal nanoparticles, especially those of amorphous selenium(0) (nano-a-Se⁰), which, in contrast to metal nanoparticles, can be described as an inorganic polymer containing predominantly the Se₆ and Se₈ ring fragments bound by the Se–Se covalent bonds [6]. Nano-a-Se⁰ exhibits unique photoelectric and semiconductor properties and X-ray sensitivity; it is used as highly sensitive biological sensor for immunoassay [7] and chromatographically mobile affine reagent [8].

Moreover, selenium is an imperative element for normal vital activity, it exhibits antioxidative, antimutagenic, immunostimulating, and detoxication activity [9]. Therefore, selenium and its compounds are of particular interest as potential drugs.

As shown in [10], the reduction of sodium selenite with glutathione in aqueous solution of bovine serum albumin (BSA) yields red nano-a-Se⁰, which is weakly toxic but retains the biologically active properties typical for ionic selenium species. It was found that these nano-a-Se⁰ particles are predominantly stabilized by adsorption processes, in which the noncovalent (poorly understood at present) interactions of the BSA macromolecules with nanoparticles play the decisive role.

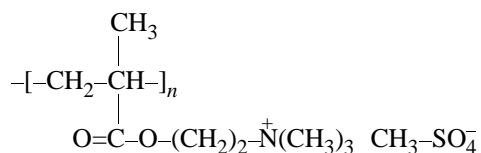
To reveal the nature of these interactions and their contribution to stabilization of nano-a-Se⁰, we studied formation of selenium(0) nanoparticles in the presence of a synthetic polybase and analyzed the morphological characteristics of the resulting adsorbates by various optical methods.

EXPERIMENTAL

In our work we studied nanoparticles of a-Se⁰ prepared by reduction of selenious acid (SA) with ascorbic acid in the presence of a polymer and without it.

The reagent purity was no less than 99.99%. The reduction kinetics was studied at the SA concentration of 1.7 mM at 20°C on a Specord M40 spectrophotometer (λ 320 nm).

As a polymeric stabilizer we used supermacromolecular poly[trimethyl(methacryloyloxyethyl)ammonium] methyl sulfate [polybase (PB)] with M_w 9×10^6 and intrinsic viscosity in 1 M NaNO₃ $[\eta]^{21} = 4.5$ dl g⁻¹:



The nanocomposites of PB and elemental Se in the 90 : 10 weight ratio were prepared by reduction of Se(IV) in solutions with a selenium concentration of 0.01%.

The variation of the apparent viscosity of PB solution with time in the course of SA reduction was monitored on a Brookfield rheoviscometer at a rotor rotation rate of 12 rpm.

The relative viscosity η_r was determined on an Ostwald capillary viscometer with a water outflow time of 120 ± 0.2 s at 21°C.

Using the flow birefringence (FBR) procedure [11], we evaluated the molecular dispersity of the resulting adsorbates in solutions using the gradient dependence of the FBR value Δn .

The FBR value Δn was determined in relation to the gradient of the rotor rotation rate g and PB concentration c at fixed concentration of selenium. We used a titanium dynamo-optimeter equipped with an internal rotor (4 cm high, with a 0.3 mm gap between the rotor and stator). All the measurements were carried out in the temperature-controlled solutions at 21°C to exclude changes in the viscosity and optical density due to the temperature gradient. The experimental setup was calibrated using phenylethyl alcohol with high FBR ($\Delta n/g$ 17×10^{-12}) and the polystyrene-bromoform system. The error in the FBR determination $[n] = \lim_{g \rightarrow 0, c \rightarrow 0} (\Delta n/gc\eta_0)$ (η_0 is the solvent viscosity) did not exceed 10%. The measurements were performed at $g < g_k$, where g_k is the velocity gradient at which the flow becomes turbulent.

In the general case ($dn/dc \neq 0$, where dn/dc is an increment of the solution refraction index, which comprised 0.155 and 0.214 for PB-H₂O and PB-Se⁰-H₂O systems, respectively), the experimental $[n]$ value includes three effects: $[n] = [n]_e + [n]_{fs} + [n]_f$, where $[n]_e$ is the intrinsic anisotropy and $[n]_{fs}$ and $[n]_f$ are the micro- and macroform effects, respectively [11]. The total segmental anisotropy $[n]_e + [n]_{fs}$ is determined by the equilibrium rigidity of the polymer chain A and by the structure of a polymer unit, whereas $[n]_f$ is related to the asymmetry of the macromolecule (or particle) p by the following expression:

$$[n]_f = [(n_s^2 + 2)/3]^2 [M_w (dn/dc)^2 f(p)] / (30\pi RT n_s) \\ = \text{const} M_0 (dn/dc)^2 f(p),$$

where M_w is the molecular weight of the adsorbate macromolecule; n_s , refractive index of the solvent; T , absolute temperature; R , universal gas constant; and

$f(p)$, tabulated function of the ratio of axes of a rigid (impermeable for solvent) ellipsoid approximating a particle [11].

Thus, for macromolecular flexible-chain and moderately rigid-chain polymers ($A < 5$ nm) with insignificant optical anisotropy and low molecular weight of the monomeric unit, $[n] \sim [n]_f$, which allows direct determination of the parameter p from the experimental FBR values [11].

Using the elastic (static) light scattering method [12], we evaluated the molecular weight M_w and the size R_g of nanoparticles in question, and also their affinity for water solvent (from the second virial coefficient A_2). The amount of macromolecules adsorbed on the selenium nanoparticle surface was determined from the ratios of M_w for PB and its adsorbates. The reduced intensity of the solution scattering R_θ was determined using a Fica photogoniometer. The wavelength of the incident vertically polarized light was 546.1 nm. The measurements were performed at the scattering angles $\theta = 30^\circ - 150^\circ$. The solutions and solvents were purified by centrifuging at 15×10^3 rpm for 1.0–1.5 h. The refractive index increments dn/dc were determined with an IRF-23 refractometer.

The experimental data on the light scattering were treated with the Zimm procedure by double extrapolation (to $c = 0$, $\theta = 0$) of the dependences of Kc/R_θ on $\sin^2(\theta/2) + kc$ (K is the calibration constant, and k is a numerical constant).

The average hydrodynamic parameters of the particles R_H were determined by the quasi-elastic (dynamic) light scattering method [13]. The parameter ρ^* characterizing the nanostructure conformation [14–17] was determined from the experimental ratio of R_g and R_H for the PB-Se⁰ adsorbate.

The optical section of the unit for measurements of the dynamic light scattering was equipped with an ALV-SP goniometer (Germany) and an He-Ne laser (λ 632.8 nm, 20 mW). The correlation function of the scattered light intensity was evaluated with a 288-channel Photo Cor-FC correlator (Anteks Joint-Stock Company, Russia). The experimental data were treated by the Tikhonov's methods of cumulants and normalization using appropriate software.

In reduction of SA with ascorbic acid, the first-order rate constant with respect to SA was $1.56 \times 10^{-3} \text{ s}^{-1}$, and it increased to $2.1 \times 10^{-3} \text{ s}^{-1}$ in the presence of PB. Without PB, the resulting Se⁰ nanoparticles were unstable and formed aggregates in 3–4 days, which then precipitated. In the presence of

the polymer stabilizer, the nano-a-Se⁰ particles were aggregation-stable for at least 6 months.

The apparent viscosity of the PB solution remained constant for 1 day, comprising about 200 cPs, and then it sharply decreased to 30 cPs, which suggests that the total number of the particles in the solution decreased owing to the adsorption of macromolecules on the surface of selenium nanoparticles. As seen from the comparison of the intrinsic viscosity of the initial PB and PB-nano-a-Se⁰ adsorbate, the estimated $[\eta]$ value decreased from 55 to 12 dl g⁻¹. At the same time, M_w for the adsorbate determined from the data of the static light scattering was 100×10^6 , i.e., it increased by a factor of 11 as compared to the free PB macromolecules.

The second virial coefficient A_2 for this system is very small (0.1×10^{-4} cm³ mol g⁻¹); it shows that the thermodynamic state of solution is close to ideal.

In aqueous solutions, the average hydrodynamic radius R_H for free PO macromolecules is 540 nm, whereas for selenium nanoparticles prepared in the absence of polymeric stabilizer it comprises 170 nm. The size of the PB-Se⁰ adsorbate, evaluated from the dynamic and static light scattering data, is considerably smaller [R_g (rms radius of inertia) 70 nm, R_H 70 nm]. In this case, $\rho^* = R_g/R_H = 1$, which suggests almost ideal spherical shape of the adsorbate formed [14–17].

To determine the radius of the core selenium nanoparticles in the adsorbate, the aqueous PB-Se⁰ solution was lyophilically dried, and the dry product was pelletized and studied by small-angle X-ray diffraction analysis. It was found that the radius of the spherical Se⁰ particle was about 15 nm, i.e., it was smaller by nearly an order of magnitude than that of the particles prepared without polymeric stabilizer. Thus, in aqueous solution the thickness of the polymeric coating on the Se⁰ nanoparticles is about 55 nm, i.e., macromolecules are strongly compacted upon adsorption.

The data on the optical properties of PB suggest that in aqueous solutions it is an impermeable strongly asymmetric swollen ball with asymmetry $p > 2$ [18].

On passing from the PB-H₂O system to the PB-Se⁰-H₂O system, the optical anisotropy decreased from 10000 to 6000 cm⁴ s² g⁻², which is probably due to the changes in the macromolecule conformation.

It should be noted that, in the entire concentration (c) range studied, the PB-H₂O and PB-Se⁰-H₂O systems retain the molecular-dispersion state of solutions.

This is confirmed by the $\Delta n = f(g)$ dependences: at $g < g_k$, for any c , these dependences are well approximated by straight lines passing through the origin.

In the $[n] \sim [n]_f$ approximation for the PB-Se⁰-H₂O system, our calculations of the parameter p showed nonspherical conformation of the nanostructure; $p = 2.1$, which corresponds to the conformation of the Gaussian ball [11]. However, the absence of the concentration dependence of the reduced optical anisotropy in the PB-Se⁰-H₂O system indicates that the parameter p tends to 1, i.e., the conformation tends to spherical [11]. Since, even in the case of such rigid macromolecule as DNA, the shape of macromolecule adsorbates on metal nanoparticles is close to spherical [19], the $[n] \sim [n]_f$ approximation for the PB-Se⁰-H₂O system is inadequate. In this case, a major contribution to the observed optical anisotropy is made by the segmental optical anisotropy probably related to high hydrophobicity of the PB monomer unit [20], and specifically the hydrophobic interactions of non-polar macromolecule fragments with nano-Se⁰ are responsible for adsorption.

Assuming nearly spherical conformation of the nanostructure, its packing coefficient k can be described by the following equation [21]:

$$k = NM_w^* \Sigma_i \Delta V_i / v^* M_0, \quad (2)$$

where $\Sigma_i \Delta V_i = 253 \text{ \AA}^3$ [21] is the van der Waals volume of the monomeric unit, which is the sum of the van der Waals volume increments of the separate atoms in this unit; M_w^* , molecular weight of the particle; N , number of the adsorbed polymer macromolecules; M_0 , molecular weight of the monomeric unit; and v^* , adsorbate volume [$4\pi/3(R^*)^3$].

The R^* value is the rms radius of inertia or the average hydrodynamic radius of an adsorbate, which are equal under the experimental conditions studied.

The parameter k was 0.7, which is typical for globular proteins (k 0.6–0.8). Thus, the adsorbate can be described as a compact approximately spherical nanostructure.

Our data are of particular interest for deeper understanding of the biological and catalytic processes occurring in the nature with participation of nanoparticles of elements. We found that such nanoparticles are adsorption matrices for biological polymers and chemical reagents, which provides high local concentrations of these compounds and can strongly accelerate biochemical and catalytic processes.

CONCLUSIONS

(1) Spherical particles of amorphous selenium about 15 nm in size were obtained by reduction of selenium(IV) in the presence of the selenite–ascorbate redox system in aqueous solution of a cationic polyelectrolyte.

(2) Sharp decrease in the intrinsic and apparent viscosity of the resulting polymer–Se⁰–water solution indicates that the thermodynamic properties of this system become close to ideal, which suggests formation of aggregation-stable macromolecule adsorbates on selenium nanoparticles.

(3) As shown by the molecular hydrodynamics and optical data, the resulting adsorbate can be described as a supermacromolecular close-packed ($k \approx 0.7$) spherical nanostructure of nearly 70 nm size, containing about 11 macromolecules whose hydrodynamic radius in the free state would be 540 nm.

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