

Preparation and structure of stable dispersions of uniform TiO₂ nanoparticles

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A set of narrow fractions of anatase TiO₂ nanocrystals was isolated by the stepped coagulation of polydisperse hydrosols using strong acids as coagulators. The sols and gels prepared from the fractions were studied by LAXS, SAXS, turbidimetry, dynamic light scattering, and other methods. The shape of uniform titania nanocrystals in the fractions was determined to be plate-like; thickness of the platelets was 2–3 nm and their lateral sizes differed considerably in the fractions. A rapid partial coagulation and slow sol separation processes were observed after the addition of HCl and KCl to the sols. The rapid coagulation threshold was shown to depend essentially on nanoparticles size; the rate of the slow process depended strongly on the electrolyte concentration. Some stable concentrated dispersions of nanometer periodicity were formed from the narrow titania fractions.

Key words: *titania; nanocrystals; hydrosol; fractionation; coagulation*

1. Introduction

Highly ordered titania nanostructures of nanometer periodicity are very promising materials [1, 2]. Their properties depend on the size and shape of nanocrystals, as well on the type of superlattice. These structures can be obtained from titania nanodisperse hydrosols. It is necessary to prepare sols of uniform (monodisperse) nanocrystals and then to conduct sol-gel-xerogel transformations under the control of structural changes.

The fractionation method has been developed, allowing one to isolate uniform titania nanocrystals from hydrosols [3, 4]. From the fractions, stable sols and gels of various dispersity can be prepared. This work concerns the preparation and study of these dispersions.

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2. Experimental

Nanodisperse TiO₂ hydrosols stabilized by HCl and HNO₃ were used for fractionation. The initial sols were synthesized by hydrolysis of Ti alkoxides and chloride and contained mainly the anatase nanoparticles with brookite impurity [5]. The fractionation was effected by the stepped sol coagulation using the same acid that stabilized the initial sol [3, 4].

The hydrodynamic particle radius R_{HD} was measured by the dynamic light scattering (DLS) method [3]. The optical density D , turbidity spectra, and coagulation thresholds C_c of the sols were studied by UV-vis spectroscopy [4]. TiO₂ weight concentration in the sols was determined by the gravimetric analysis. TiO₂ volume concentration ϕ was calculated from TiO₂ weight concentration and the anatase density equal to 3.84 g/cm³.

The X-Rays diffraction patterns of titania xerogels were recorded with a diffractometer DRON-3 [4]. Mean sizes of primary anatase crystals L_{hkl} along different directions were calculated by the Scherer formula

$$L_{hkl} = \frac{\lambda}{\Delta \cos \theta}$$

where θ is the diffraction angle, λ – the wavelength, $\Delta = (\Delta_1^2 - \Delta_2^2)^{1/2}$ – the true half-width of reflection, Δ_1 – measured halfwidth, Δ_2 – instrumental peak broadening determined from a standard sample.

The SAXS measurements of the sols were carried out using a KRM-1 diffractometer [4]. The scattering coordinate was measured in terms of the scattering vector modulus $s = 4\pi \sin \theta / \lambda$ in the range of s from 0.07 to 4.26 nm⁻¹. The preliminary treatment of the initial scattering curves (smoothing, normalization) was made with the SYRENA software [6].

3. Results and discussion

3.1. Properties of the TiO₂ hydrosols

Nanodisperse sols of anatase particles are stable in the acidic medium at 0.5 < pH < 2.5 [5]. Positive charge and the surface hydrophilic layer stabilize the particles. These sols have an absorbance peak with a maximum at $\lambda \approx 214$ nm. In the visible range at $\lambda > 450$ nm and at $\phi = \text{const}$, the sols reveal the Rayleigh scattering:

$$I \propto V \lambda^{-4}$$

where I is the intensity of the scattering light, V – the particle volume. The turbidimetry is thus an effective method for studying stabilization and destabilization of sols.

After sol synthesis, the anatase particles usually do not grow bigger but decrease and then stabilize [5]. Thus the aged sols can be divided into two groups – “equilibrium” and “nonequilibrium” sols. The former ones have stable particles which were shown to be the individual anatase nanocrystals. The particles in “nonequilibrium” sols are likely the aggregates of nanocrystals which slowly disintegrate. Some conditions accelerate their disintegration, in particular the acid concentration. It was found [5] that in the “equilibrium” sols synthesized and then aged at room temperature, R_{HD} is usually equal to 8–13 nm.

3.2. Fractionation of TiO₂ nanocrystals

For the purpose of fractionation, the “equilibrium” sols are used. Although they have relatively narrow particle size distribution, they are still polydisperse, and narrower fractions can be isolated. The method is based on the partial coagulation of the sols by electrolytes. To initiate the rapid partial coagulation, the electrolyte is introduced into the initial sol in a concentration exceeding the rapid coagulation threshold C_c . For fractionation, three conditions should be fulfilled. The first one is the existence of a strong dependence of the rapid coagulation threshold on particles size. That is, larger nanocrystals should coagulate at lower electrolyte concentrations. The second is the reversibility of the rapid coagulation. This means that if the electrolyte is removed from coagulates, they will be dissolved and transparent sols will be formed again. And the last condition is that the sols prepared from the fractions should be stable at long storage. These conditions are fulfilled if either HCl or HNO₃ is used as the coagulator.

By the stepped coagulation we succeeded to isolate five fractions of varying dispersity from the same sol. The initial sol was synthesized from Ti(OBu)₄ and stabilized by HNO₃. Table 1 shows HNO₃ concentrations at which the coagulation was conducted. From these fractions five sols were prepared stabilized by HNO₃ with pH 1.

Table 1. HNO₃ concentrations used for precipitation of the TiO₂ fractions, R_{HD} and L_{hkl} values of the fractions

Fraction No.	[HNO ₃] [mol/dm ³]	R_{HD} (±1) [nm]	L_{101} (±0.4) [nm]	L_{200} (±0.4) [nm]
1	0.5–0.8	16	5.6	4.6
2	0.8–1.0	13	4.5	3.6
3	1.0–1.2	9	4.1	3.5
4	1.2–1.5	7	3.9	3.4
5	1.5–1.8	5	2.9	3.3

Figure 1 shows the mean particle radius R_{HD} for the initial sol and its fractions measured at various Ti concentrations. The figure clearly reveals the varying dispersity of the fractions. The sols obtained were found to be very stable: their turbidity did not change during 1.5 year of observation.

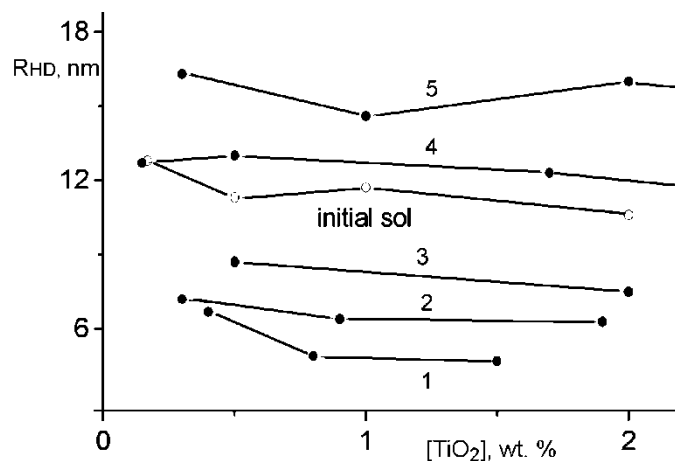


Fig. 1. Dependences of the mean hydrodynamic particle radius on TiO_2 concentration for the initial sol and its fractions. Numbering of fractions corresponds to that in Table 1

Figure 2 shows the diffraction patterns of the same fractions. All patterns are characteristic of the nanocrystalline anatase. Curve 5 has the broadest peaks, thus fraction 5 is composed of the smallest nanocrystals. Curve 1 represents the biggest ones.

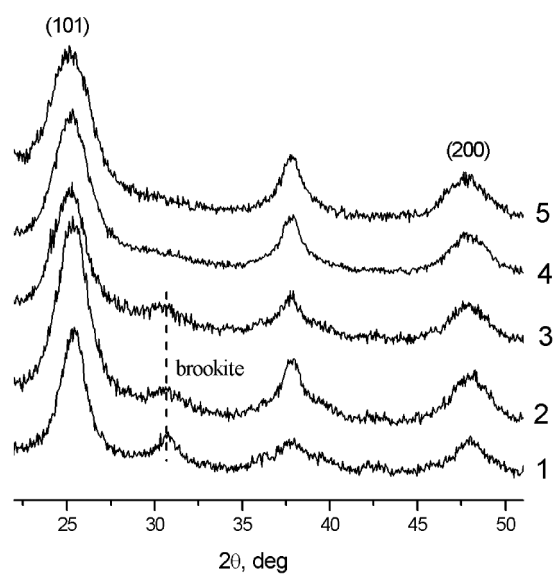


Fig. 2. Diffraction patterns of the TiO_2 fractions

The sizes L_{101} and L_{200} of anatase crystals as well as R_{HD} values in the fractions are shown in Table 1. One can see that in the series of the five fractions, these sizes

change consecutively and larger nanocrystals coagulate at lower acid concentrations. Because the initial sol contained the brookite impurity, the brookite phase is also present in the isolated fractions. However, brookite is present only in three coarser fractions (1–3). Thus the fractionation method allows us also to purify anatase nanocrystals of brookite impurity or, on the contrary, to concentrate the brookite nanocrystals.

For many titania applications (in particular for the catalysis) it is necessary to remove water and acid from xerogels by thermal treatment. Figure 3 shows the diffraction patterns of the fractions after their annealing at 500 °C for 2 h. It can be seen that after annealing, the anatase nanocrystals grew in all fractions and in the coarsest fraction 1 the large rutile crystals appeared. This experiment reveals that to obtain uniform anhydrous TiO₂ with high surface area one should use sols of pure anatase.

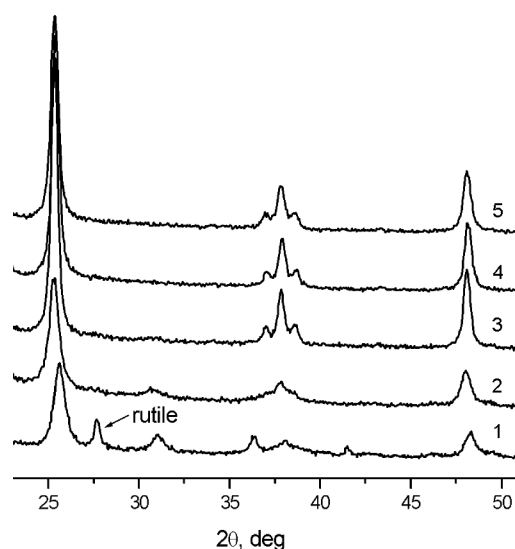


Fig. 3. Diffraction patterns of TiO₂ fractions after annealing at 500 °C for 2 h

The fractions were also compared by SAXS. Figure 4 shows the scattering curves of the diluted sols prepared from fractions 1 and 5. Their analysis [4] allowed us to determine not only the particle gyration radius R_g but also the particle shape.

Table 2. R_g and characteristic sizes of TiO₂ platelets for fractions 1 and 5 determined by SAXS

Parameter	Fraction 5	Fraction 1
R_g (± 0.2), nm	7.6	10
Characteristic size, nm ³	2×7×20	3×18×35

It was established that the anatase particles in these fractions are platelets. Their thickness was 2–3 nm and their lateral sizes differed considerably. The characteristic sizes of the platelets, as well as the R_g values, are given in Table 2.

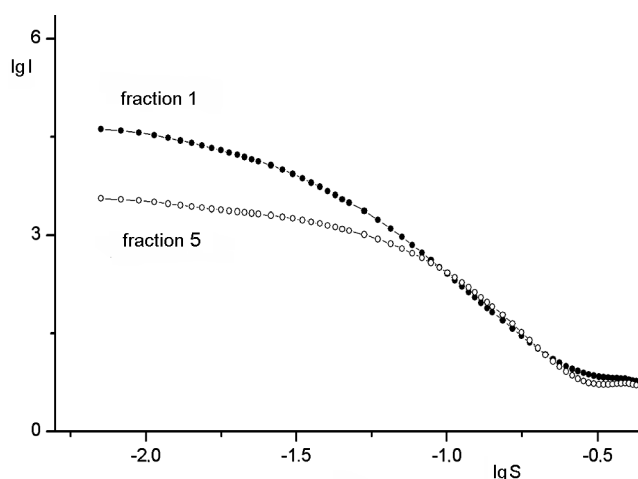


Fig. 4. SAXS curves of fractions 1 and 5

3.3. Destabilization of TiO_2 hydrosols by electrolytes

Since the fractionation method is based on the coagulation, the coagulation has been studied in more detail to improve the method. After introducing the electrolyte into the sol prepared from a fraction at least two different processes can occur – rapid partial coagulation and slow sol separation. The rapid coagulation occurs only above the threshold electrolyte concentration C_c , while the slow process takes place at both low and high electrolyte concentrations. The slow process appears at the beginning as monotonous growth of turbidity, and then the graduate sol separation appears. The rapid and the slow processes are studied separately.

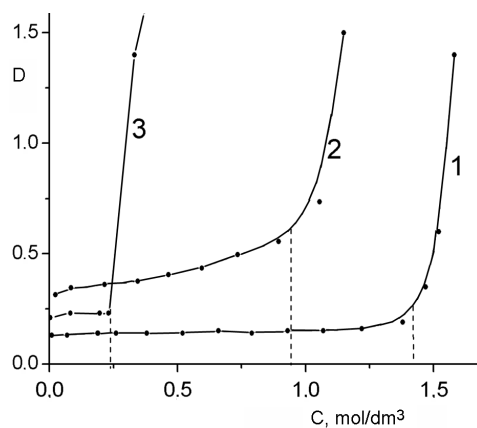


Fig. 5. Turbidity of the sols prepared from three fractions via HCl concentration.

R_{HD} of the initial sols are 5 (1), 8 (2) and 14 (3) nm.

The dashed lines represent rapid coagulation thresholds of the fractions

At first, the rapid coagulation was studied by turbidimetry. Figure 5 shows the rapid coagulation by HCl of three fractions with R_{HD} equal to 5, 8 and 14 nm. The turbidity was measured 2 min after adding acid additives to the initial sol. The inflection points on the turbidity dependences on HCl concentration are the rapid coagulation thresholds. It can be seen that C_c does depend strongly on the particle size. When KCl was used as the coagulator, the picture was rather similar, but C_c depended also on pH.

The complex of long-term experiments on the slow sol separation is in progress now. The nature and mechanism of this process is not clear yet. It may include the Ostwald ripening and slow coagulation. Its rate depends on electrolyte type and concentration, nanocrystals dispersity, medium pH. To understand the separation process, the impact of the factors mentioned and its reversibility should be studied. Figure 6 shows the first kinetic dependences obtained for a series of sols with KCl added.

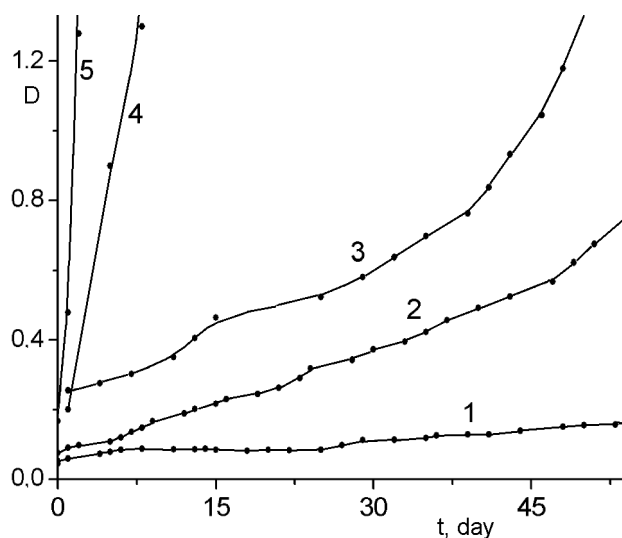


Fig. 6. Kinetics of the slow growth of turbidity of the sols with KCl concentration 0.25 (1), 0.5 (2), 0.7 (3), 1.1 (4) and 1.4 (5) mol/dm^3

Different amounts of KCl were introduced into the initial stable sol with an $R_{HD} = 5$ nm, pH 2.1, and low turbidity. KCl concentration in the sols varied from 0.25 to 1.4 mol/dm^3 , which was below C_c of the given fraction (1.6 mol/dm^3 KCl). After introducing the salt, slow clouding of the sols instantly began. From Figure 6 one can see that for a moderate initial period, the turbidity grew monotonously, the process rate increasing strongly with salt concentration. Then the process accelerated and later the sols separated slowly into two layers. The dispersion pH did not change during the whole experiment.

Preliminary DLS and SAXS measurements show that during the slow separation process the mean particle radii increase. First investigations of the reversibility of the

process reveal that the process is partially reversible. One can hope that further investigations of the peculiarities of sol destabilization by electrolytes will allow us to isolate even narrower fractions of titania nanocrystals.

3.4. Preparation of concentrated dispersions of uniform nanocrystals

We have succeeded in obtaining some stable concentrated dispersions (sols and gels) of nanometer periodicity from narrow fractions of anatase nanocrystals. The concentrated sols appeared to be stable only at a very narrow interval of pH close to 1. To prepare them, the dilute sols prepared from fractions and stabilized by HCl were ultrafiltrated and then evaporated in air. A series of sols with titania concentration ϕ from 1 to 21 vol. % and pH 1 was prepared from the fraction with $R_g = 5.5$ nm. The initial sol was obtained by electrolysis of TiCl_4 [7]. Its fractionation was done with HCl. The sols prepared were studied by SAXS. Some of the scattering curves obtained are shown in Fig. 7. From curve 1 corresponding to the diluted (1 vol. %) sol, the shape of nanoparticles in the fraction was determined. The particles found to be also plate-like, but the characteristic sizes of the platelets were $3 \times 14 \times 18 \text{ nm}^3$.

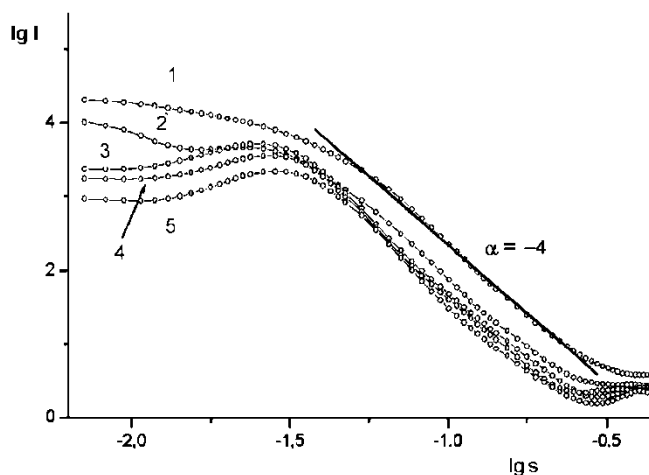


Fig. 7. SAXS curves of the sols with pH 1 and TiO_2 concentration 1(1), 12 (2), 15 (3), 18 (4) and 21 (5) vol. %

It can be seen from curves 2–5 in Fig. 7 that the scattering curves of the concentrated sols with $\phi = 12$ –21 vol. % have a maximum whose position depends on ϕ . The estimated long period L is equal to 21–29 nm.

Figure 8 shows the dependence $L(\phi)$ in the logarithmic scale. The slope of the straight line was found to be equal to 0.43 ± 0.05 . This value is essentially larger than the value 0.33 that is known to be characteristic of the isotropic liquids. Obviously, the plate-like shape of titania nanoparticles governs their slight orientation in plane.

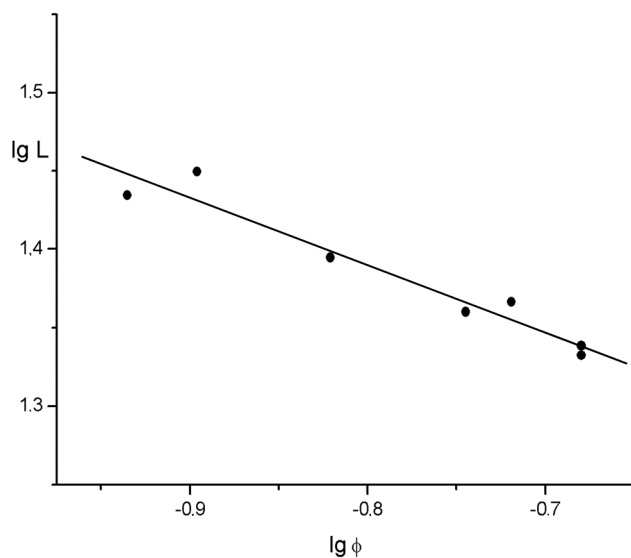


Fig. 8. Dependence of long period on volume concentration of the concentrated sols

Upon further concentrating the sol, at titania concentrations above 21–23 vol. %, the sols either gelate remaining uniform in volume or separate into two stable phases – dilute blue sol on top and viscous concentrated gel below. The consistence and structure of various titania gels were found to depend mostly on the content of acid in the dispersion medium.

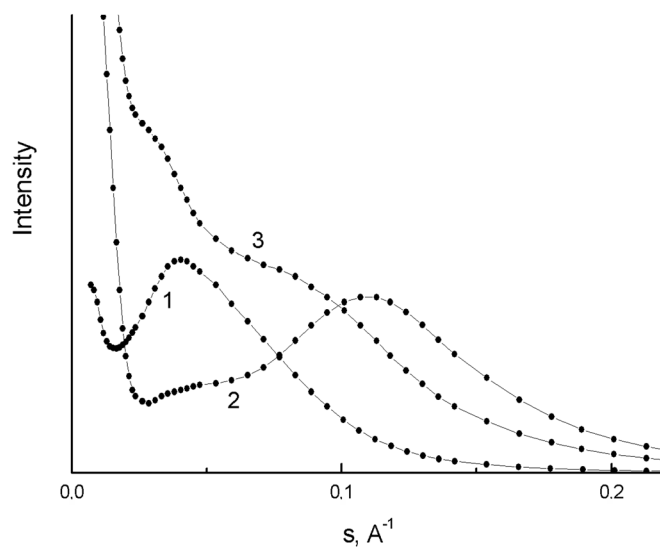


Fig. 9. SAXS curves of the gels with HCl concentration 0.2 (1), 0.6 (2) and 1.4 (3) mol/dm^3

Figure 9 shows scattering curves of three gels prepared by different methods. The gels were relatively similar in titania concentrations ($\phi = 24\text{--}30$ vol. %) and in dispersity ($R_g = 5\text{--}6$ nm) but differed in HCl concentration in the dispersion medium: 0.2, 0.6 and 1.4 mol/dm³. The latter concentration exceeded the coagulation threshold for this fraction ($C_c = 1.2$ mol/dm³ HCl). It can be seen that the three gels have qualitatively different structures characterized by nanometer periodicity. The long periods calculated from the maxima are in the interval 6–20 nm. Two of the curves have two maxima each. One could propose that the structure of some such ordered dispersions is close to liquid crystals. It should be emphasized that the ordered structures of nanometer periodicity were formed only from very narrow titania fractions but not from the initial polydisperse sols.

4. Conclusions

- A set of narrow fractions of anatase TiO₂ nanocrystals was isolated by the stepped coagulation of the polydisperse hydrosols using strong acids as the coagulator.
- After annealing, the fractions had different phase composition and dispersity.
- Stable hydrosols and ordered dispersions of nanometer periodicity were prepared from the fractions isolated.
- Electrolytes initiate rapid and slow separation of TiO₂ sols. The rapid coagulation threshold depends essentially on nanoparticles size; the rate of the slow process depends strongly on electrolyte concentration.
- Hydrosols of uniform TiO₂ nanoparticles can be precursors for preparation of novel highly ordered nanomaterials.

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