FRACTIONATION OF NANOCRYSTALLINE TiO_2 BY COAGULATION OF HYDROSOLS

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ABSTRACT

From the polydisperse TiO_2 hydrosols contained plate-like anatase nanocrystals the narrow nanocrystal fractions have been isolated. The anatase platelets in the fractions have been shown to have similar thickness ~2 nm and different lateral sizes in the range of 4-29 nm. The gels and xerogels ordered in nanometer scale have been prepared from the isolated fractions. The structure of gels has been shown to depend crucially on acid concentration in the dispersion medium. Destabilization of diluted TiO_2 sol by some electrolytes and the slow increase of sol turbidity have been studied. It has been found that the rate of the slow turbidity increase rises strongly with electrolyte concentration and has a minimum at some pH-values. The results obtained enable to improve the fractionation procedure and to develop highly ordered TiO_2 nanomaterials.

INTRODUCTION

Uniform (in size, shape, and phase composition) oxide nanocrystals can be used as building blocks for the preparation of highly ordered materials of nanometer periodicity [1]. These materials may be formed by drying the liquid dispersions of uniform nanocrystals. It is obviously that such dispersions are exclusive objects to study the effects of different parameters on structure and properties. So it is very important to develop methods of preparation of the uniform nanocrystals and their stable dispersions.

We developed the procedure of fractionation of TiO_2 nanocrystals based on the coagulation of polydisperse hydrosols by strong acids [2, 3]. The fractionation is possible due to the reversibility of the rapid coagulation and to the existence of a strong dependency of a threshold of the rapid coagulation C_c on particle size. To obtain more narrow TiO_2 fractions it is necessary to study the peculiarities of interaction of the sols with electrolytes in more detail.

In the paper we describe the preparation of narrow TiO_2 fractions of different dispersity from polydisperse hydrosols, the preparation of the ordered concentrated dispersions from the fractions, and also some new experimental results on destabilization of the TiO_2 sols by electrolytes.

EXPERIMENTAL

Initial polydisperse TiO_2 hydrosols synthesized from Ti tetrabutoxide and tetrachloride were stabilized by HCl and HNO_3 and contained mainly the anatase polymorph nanoparticles [2-4]. A mean hydrodynamic radius of particles R_h in the sols was in the range of 7-10 nm.

R_h was measured by DLS using photon-correlation spectrometer; optical density D and coagulation thresholds C_c were determined by UV-visible spectroscopy in a 30-mm wide cell [2-3]. TiO_2 weight concentration in the dispersions was determined by the gravimetric analysis.

The fractionation was conducted by the stepped coagulation using the same acid, which stabilized the initial sol. From the precipitated fractions at first the stable 5-15% sols of different dispersity were prepared. Then, after determination of TiO_2 content and pH, the sols were diluted or concentrated [3]. Gels were obtained either by evaporating the concentrated sols in the air or by coagulation of the sols by HCl additives. Xerogels were prepared by drying the sols and gels in the air at room temperature till constant weight.

All stable dilute and concentrated dispersions prepared were studied in some weeks after preparation.

The X-Rays experiments in small and wide angles of scattering are described in detail in [3]. Diffraction patterns of the fractions in wide angles were obtained for dried sols. A mean size of primary anatase nanocrystals L_{101} was calculated from a peak halfwidth by the Scherer equation.

The SAXS measurements of the sols were carried in capillaries, while the gels were investigated in a flat cuvette. 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) as well as the calculation of the correlation function of the scattering particles and of the pair distribution function within a single particle was made with SYRENA software complex [5]. Particle radius of gyration R_g was calculated from the innermost part of the SAXS curve (Guinier approximation [6]) and from Fourier transformation of the SAXS curve [5], then the values obtained were averaged.

RESULTS AND DISCUSSION

FRACTIONATION

Five anatase TiO_2 fractions of different dispersity were obtained by the stepped coagulation of the initial hydrosol by HNO_3. The coagulation thresholds C_c of these fractions ranged in an interval 0.7-1.9 M HNO_3, the R_h values - from 4 to 12 nm, and the L_{101} values - from 3 to 6 nm (see Table).

Table. The characteristics of five nanocrystalline TiO_2 fractions stabilized by HNO_3. Samples 1-5 were studied in 1 month after preparation, sample 5a in 2 years.

Fraction	C_c	a	b	c	R_g	R_h	L_{101}
	M HNO_3		nm		nm	nm	nm
1	1.6-1.9	15	4.3	1.7	4.3	4	2.9
2	1.3-1.6	16	4.8	1.7	4.9	5	3.9
3	1.0-1.3	21	5.4	1.7	6.2	6	4.1
4	0.8-1.0	24	7.4	2.0	7.2	7	4.5
5	0.7-0.8	28	8.3	2.0	8.4	12	5.6
5a	0.7-0.8	29	9.9	1.8	9.0	14	5.6

Then the five 1% sols stabilized by HNO_3 with pH 1 were prepared from the fractions and studied by SAXS. Figure 1 shows the scattering curves. Their analysis allowed to determine the gyration radius R_g and a shape of nanoparticles in the fractions (see Table).

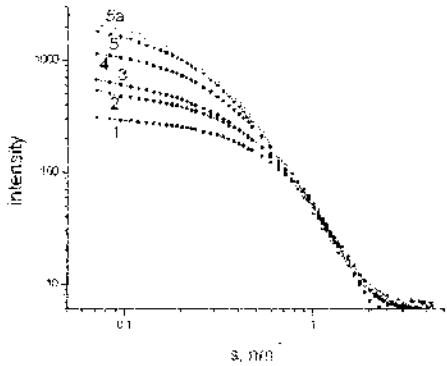

Figure 1. SAXS curves of the five TiO_2 fractions isolated from the polydisperse sol. Curves 5 and 5a refer to the same sol measured in 1 month and 2 years correspondingly.

To determine a shape of nanoparticles the correlation functions of the scattering particles $\gamma(r)$ and the pair distance distribution functions within a single scattering particle $\Gamma(r) = (\gamma(r) * r)$ and $p(r) = (\gamma(r) * r^2)$ were calculated [5]. For example the p(r) functions are presented in Figure 2. It was established that the pair distribution functions were fitted well with the appropriate functions for the particles with a prism-like shape rather than for the globular-like or rod-like particles. Under the assumption of prism-like particles scattering, the characteristic sizes of a prism **a**, **b** and **c** were calculated.

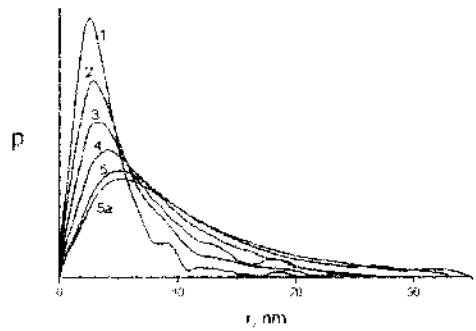

Figure 2. p(R) functions calculated from the curves presented in Figure 1.

The Table shows that in all fractions studied the anatase nanoparticles are plate-like and the platelets have minimum constant size **c** close to 2 nm. The other two sizes of the platelets, **a** and **b**, in different fractions range from 4 to 29 nm. It is also seen that the higher coagulation threshold C_c the lower particles sizes **a**, **b**, R_g, R_s, and $L_{(01)}$.

ORDERED TiO_2 DISPERSIONS

Gels and solid xerogels stabilized by HCl were prepared from narrow TiO_2 fractions and studied by SAXS. The analysis of the results revealed that some samples have rather ordered structure at nanometer scale. The scattering curves of these samples have a broad maximum which position corresponds to a long period in the range of 6-30 nm. It was established that the character of ordering of the sols and gels depends crucially on HCl concentration C in the dispersion medium.

In Figure 3 the scattering curves of three gels contained uniform plate-like anatase TiO_2 nanocrystals are presented (curves 1-3). These gels have HCl concentration C equal to 0.2, 0.8, and 1.6 M, correspondingly, and relatively close concentration of TiO_2 (57-67 w.%) and R_s values (6-8 nm). We can see that the scattering curves of these dispersions differ qualitatively.

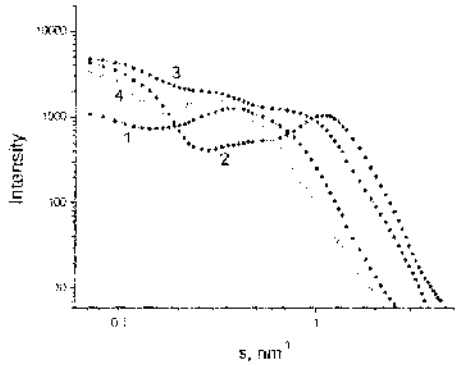

Figure 3. SAXS curves of the gels with HCl concentration C 0.2 (1), 0.8 (2) and 1.6 M (3) and xerogel (4), prepared from narrow anatase TiO_2 fractions.

Curve 4 in Figure 3 corresponds to a xerogel obtained by slow drying one of the gels in the air. This glass-like solid sample contains 85 w.% TiO_2. The distinct maximum on the scattering curve reveals that this material is also relatively ordering.

The development of such approach will open the opportunity to prepare more ordered TiO_2 dispersions and nanomaterials of different structure.

DESTABILIZATION OF THE SOLS BY ELECTROLYTES

Kinetics of destabilization by HCl and KCl of the dilute sols prepared from the narrow fractions was studied as well. It was established that just after the electrolyte has been introduced into the sol the slow monotonic increase of turbidity occurs following by partial sedimentation.

At the first stage of this slow process, which can last for many months, the sols with a total concentration of electrolyte $C<C_c$ remain uniform. In contrast to the rapid coagulation taking place at $C>C_c$ and being entirely reversible, the slow process occurs both at low and high electrolyte concentrations and seems to be partially reversible.

Figure 4 shows the time dependencies of turbidity for five 0.4% sols stabilized by HCl after introducing additives of HCl (curve 1) or KCl (curves 2-5). All sols were prepared from the same narrow fraction characterized by R_h=6 nm. Sols with KCl additives have different pH values equal to 2.2 (curve 2) and 0.9 (curves 3-5); sol with HCl additive has pH~0. It was found that during the experiment the pH values of the samples did not change.

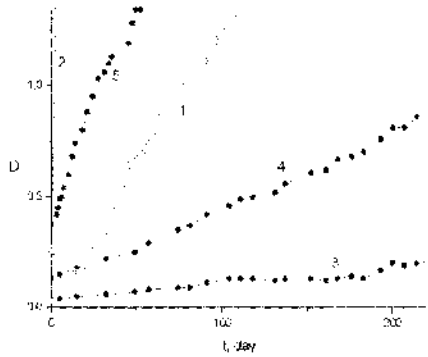

Figure 4. Kinetics of optical density of the 0.4 % sols with different electrolyte concentration and pH. 1 - 1.4 M HCl, pH~0; 2 - 0.8 M KCl, pH 2.2; 3 - 0.8 M KCl, pH 0.9; 4 - 1.1 M KCl, pH 0.9; 5 - 1.4 M KCl, pH 0.9.

From curves 3-5 in Figure 4 one can see that a rate of the turbidity increase rises strongly with electrolyte concentration at pH=const. Comparison of the curves 1-3 shows that the rate depends essentially also on pH: it is minimal in the sols with pH~1 and increases in orders of magnitude at pH ~0 and ~2.

The mechanism of these slow structural changes in the TiO_2 dispersions in presence of electrolytes is not clear yet. To understand it the additional experiments are necessary. The further investigation in this direction is very crucial in improving the fractionation procedure and in manipulation in nanoparticle size and shape.

CONCLUSIONS

1. From the polydisperse hydrosol contained plate-like anatase TiO_2 nanoparticles of 2 nm thick some fractions of platelets different in their lateral sizes have been isolated.
2. The gels and xerogels ordered in nanometer scale have been prepared from the narrow TiO_2 fractions. The structure of the gels has been shown to depend crucially on the acid content in the dispersion medium.

3. Study of the destabilization of the TiO_2 sols by HCl and KCl has revealed that the rate of the slow increase of turbidity rises strongly with electrolyte concentration and has a minimum at pH equal to ~1.

REFERENCES

[1]M. Niederberger and H. Cölfen. Oriented attachment and mesocrystals: Non-classical crystallization mechanisms based on nanoparticle assembly. *Phys. Chem. Chem. Phys.*, **8**, 3271–87 (2006).

[2]O.B. Pavlova-Verevkina, Yu.A. Shevchuk and V.V. Nazarov, Coagulation peculiarities and fractionation of nanodispersed titanium dioxide hydrosol. *Colloid Journal*, **65**, No. 4, 474-77 (2003).

[3]O.B. Pavlova-Verevkina, S.N. Chvalun, E.D. Politova, V.V. Nazarov, L.A. Ozerina and A.N. Ozerin, Study of the stable nanocrystalline TiO_2 hydrosol and its fractions. *Journal of Sol-Gel Science and Technology*, **35**, 91-97 (2005).

[4]O.B. Pavlova-Verevkina, N.V. Kul'kova, E.D. Politova, Yu.A. Shevchuk and V.V. Nazarov, Preparation of thermostable highly dispersed titanium dioxide from stable hydrosols. *Colloid journal*, **65**, No 2., 226-29 (2003).

[5]L.A. Feigin and D.I. Svergun, *Structure Analysis by Small-Angle X-ray and Neutron Scattering*. Plenum Press, New-York (1987).

[6]A.Guinier and G. Fournet, *Small Angle Scattering of X-rays*, Wiley, New York (1955).