

Hybrid inorganic-organic nano- and microcomposites based on silica sols and synthetic polyelectrolytes

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Abstract. Interaction between anionic (and cationic) colloidal particles of silica having the particles diameters 12 and 22 nm with synthetic cationic (and anionic) polyelectrolytes of various nature and structure was studied by potentiometric, conductimetric spectroturbidimetric and viscometric methods in aqueous solution. It was shown that the complexation of silica nanoparticles with linear polyelectrolytes leads to formation of mostly stoichiometric interpolyelectrolyte complexes (IPEC) which precipitate from aqueous solution. Casting of water-soluble IPEC followed by thermal treatment gives thin composite films insoluble in water while 'layer by layer' (LbL) deposition of polyelectrolyte components onto silica sols leads to formation of multilayered nano- and microcomposites. The possible mechanism of formation of LbL multilayers consisting of silica sol (SiO₂) 'cores' and polyethyleneimine-polyacrylic acid (PEI-PAA) 'shells' was suggested. It was found that in diluted aqueous solution the radius of gyration, R_g and hydrodynamic radius, R_h^{mean} of LbL particles are independent on LbL concentration and smaller than 100 nm. The zeta potential values of LbL particles are arranged between -10 and -30 mV. The average size of LbL particles estimated by scanning electron microscopy (SEM) is in the range of 200–500 nm. Thermal treatment of LbL multilayers followed by etching of (SiO₂) 'core' by HF leads to formation of a series of spherical nanocavities and blob-like microcavities.

Keywords: nanomaterials, silica nanoparticles, linear polyelectrolytes, interpolyelectrolyte complexes

1. Introduction

Hybrid inorganic-organic nanocomposites comprising inorganic nanoparticles and functional polymers are novel and unique class of nanomaterials that synergistically combine and enhance the best properties of inorganic and organic polymers [1–4]. The potential application fields of such hybrids can include specialty coatings, membranes, sensors, biomaterials, drug delivery systems, catalysts etc. The most common principle concepts of incorporation of inorganic nanoparticles into polymer matrix and the resulting properties of such

materials have been reviewed by authors [5–7]. Classification of polymer/silicate nanocomposites based on synthetic techniques was suggested in [8]. Although titanium [9, 10] and aluminum [11] oxides have been utilized as the inorganic components interacting with functional polymers, the colloid silica due to easy preparation by sol-gel technology [12] is one of the promising inorganic polymeric materials that interacts with polyelectrolytes and forms, so called interpolyelectrolyte complexes (IPEC) – products of interaction of two oppositely charged polyelectrolytes [13–17]. Mech-

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anisms of formation, structure and properties of IPECs based on synthetic polyelectrolytes have been thoroughly investigated by Bixler and Michaelis [18], Tsuchida and Abe [19], Kabanov [17], Zezin and Kabanov [20], Bekturov and Bimendina [21], Philipp *et al.* [22]. Polyelectrolyte complex formation between strong polyanion and cationic nanogels was studied by Ogawa *et al.* [23]. Recently [24] the multilayered nanomaterials were developed on the basis of hydrogen-bonded complexes of polyacrylic acid and methylcellulose. Ultrathin membranes with participation of colloidal particles and cationic polyelectrolytes [25], layered double hydroxide and anionic polyelectrolytes [26], and colloidal biocatalysts consisting of polystyrene-based colloid particles coated with glucose oxidase and hoseradish peroxidase [27] as well as polyelectrolyte composite films [28] and nanotubes [29] were assembled *via* the LbL self-assembling. Hybrid ternary organic-inorganic films consisting of chitosan, poly(monomethyl)itaconate and silica nanoparticles were designed by Martinez *et al.* [30] and further the same authors [31] embedded the semiconductor CdS nanoparticles into organic-inorganic hybrid by *in situ* technique. Thus the understanding of the basic principles of fabrication of composite inorganic-organic nano- and micro-materials where one component phase is nanoparticle is a challenging task [32].

The present communication deals with studying of the formation and characterization of hybrid inorganic-organic nano- and microcomposites as a result of interpolyelectrolyte complexation between silica nanoparticles and linear polyelectrolytes.

2. Experimental

2.1. Materials

Colloidal particles of silica are commercial products purchased from Ludox (Grace GmbH & Co. KG, Worms, Germany) were abbreviated as HS-40, AS-40 and CL in dependence of surface charge, nature of counterions, particle size and surface area. Table 1 represents some physico-chemical characteristics of anionic and cationic nanoparticles of silica.

Table 1. Physico-chemical characteristics of colloidal silica nanoparticles

Characteristics	Type of colloidal particles		
	HS-40	AS-40	CL
Surface charge	–	–	+
Counterion	Na ⁺	NH ₄ ⁺	Cl [–]
SiO ₂ [wt%]	40	40	30
Na ₂ O [wt%]	0.41	0.05–0.08	–
Particles size [nm]	12	22	12
Surface area [m ² /g]	240	140	240
pH (25°C)	9.7	9.1	4.5

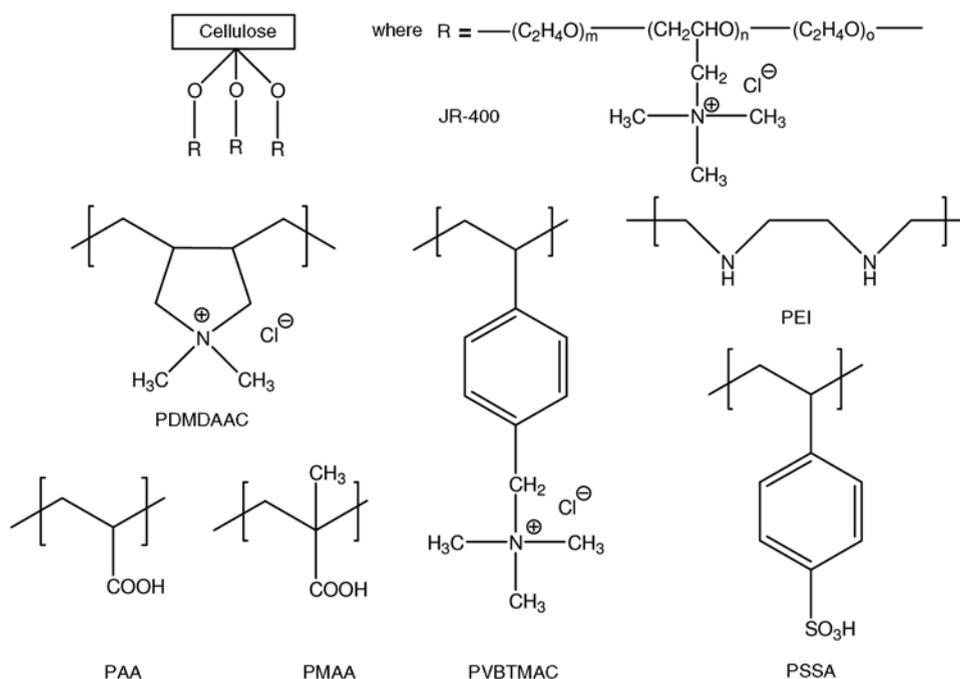


Figure 1. Structural formulas of linear polyelectrolytes

Table 2. Some of physico-chemical characteristics of linear polyelectrolytes

Characteristics	Linear polyelectrolytes						
	JR-400	PDMDAAC	PVBTMAC	PEI	PSSA	PAA	PMAA
Surface charge	+	+	+	+	–	–	–
Counterion	Cl [–]	Cl [–]	Cl [–]	OH [–]	H ⁺	H ⁺	H ⁺
M·10 ^{–3} [Dalton]	100–3000	219	100	25	500	450	250
pH (25°C)	5,66	4,90	5,48	8,37	8,01	3,00	3,40

As linear cationic and anionic polyelectrolytes the quaternized ammonium salts of cellulose derivatives (JR-400) [33], poly-N,N-dimethyl-N,N-diallammonium chloride (PDMDAAC), poly-N-vinylbenzyl-N,N,N-trimethylammonium chloride (PVBTMAC), polyethyleneimine (PEI), polystyrenesulfonic acid (PSSA), polyacrylic (PAA) and polymethacrylic (PMAA) acids purchased from Polysciences, Inc. (Warrington, PA, USA) were used. Structural formulas of water-soluble polyelectrolytes and some of their physico-chemical characteristics are represented in Figure 1 and Table 2. In addition to linear polyelectrolytes, microgel of PDMDAAC with average diameters of particles 1–3 μm was used.

2.2. Methods

Potentiometric and conductimetric titrations were carried out with the help of combined pH/Conductometer ‘Mettler-Toledo MPC-227’ (Schweiz, Switzerland) at room temperature. Turbidity of solutions was measured by photoelectrocolorimeter ‘FEK-56’ (Moscow, Russia) at $\lambda = 340$ nm and room temperature. Viscometric measurements were carried out on Ubbelohde viscometer at 298 ± 0.1 K. Optical microscope of LOMO (Saint-Petersburg, Russia) was used for observation of thin powders and multilayered films structures.

Dynamic and static light scattering experiments were conducted with a Brookhaven Instruments (NY, USA) BI-200SM goniometer, a BI-Turbo-Corr digital auto/crosscorrelator, and a BI-Cross-Corr detector, including two BI-DS1 detectors. A Sapphire 488-100 CDRH laser from Coherent GmbH operating at the wavelength of $\lambda_0 = 488$ nm (vertically polarized) and the power adjusting from 10 to 50 mW was a light source. The scattering angles were varied in the range of $\theta = 30$ – 150° . In the DLS experiments, pseudo cross-correlation functions of the scattered light intensity, $G_2(t)$, were collected with the self-beating method [34].

The time average intensity of the scattered light, I_θ , was recorded simultaneously. The intensities measured in counts of photons per second, cps, were normalised with respect to the Rayleigh ratio of toluene. The temperature of the samples was controlled by means of a Lauda RC 6C thermostated water bath. For light scattering experiments the selected concentrations of LbL samples were $C_p = 0.121, 0.605,$ and 12.1 mg/ml. Aqueous solutions were passed through the hydrophilic Millex-HV 0.45 μm pore size and 13 mm in diameter filters prior to measurements to remove dust particles.

Zeta-potential measurements were performed with a Nano-ZS Zetasizer ZEN3600 from Malvern Instruments (Malvern, UK) equipped with 4 mW He-Ne laser operating at $\lambda_0 = 633$ nm. Nano-ZS Zetasizer is based on the back scattering data detection ($\theta = 173^\circ$). M3-PALS technique and Smoluchowski analysis is used to measure the zeta-potential. Size & Zeta-potential-DTS1060 folded capillary cell was employed for the simultaneous size and zeta-potential measurements. Temperature was stabilized with a Peltier temperature control.

SEM pictures were obtained for freeze-dried LbL samples using Hitachi S-4800 (Tokyo, Japan) instrument. Freeze-drying solution was deposited on a grid for SEM and quickly frozen under liquid nitrogen. The grid then was placed in vacuum to remove water.

2.3. Preparation of thin powders, composite films and layer-by-layer compositions of IPEC

Bidistilled water was used for preparation of colloidal particles and polyelectrolyte solutions. Aqueous solutions of polyelectrolytes (0.01 mol/l) were added dropwise to the aqueous solution of colloidal silica (0.01 mol/l) under stirring. The precipitated IPEC particles were separated from supernatant by preparative centrifuge ‘T-62’ (Warsaw,

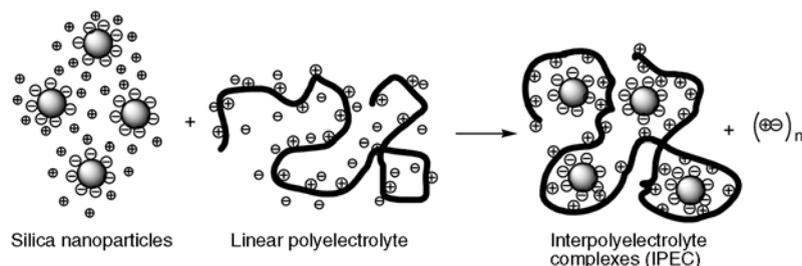


Figure 2. Scheme of IPEC formation between silica sols and linear polyelectrolytes

Poland) at 5000 rpm. They were then washed with acetone several times. After drying for one day in vacuum oven, the IPEC particles were obtained in the form of thin powder.

Since the IPEC obtained by mixing of aqueous solutions of HS-40 and JR-400 preserved in aqueous solution, by casting the equimolar mixture of HS-40 and JR-400 onto Teflon surface the thin films were fabricated. After thermal treatment of thin films at 100°C for one day they became insoluble but swellable in water. The LbL assembly process developed for planar solid substrates was adapted for silica sols. At first the dilute aqueous solutions of silica sols, PEI and PAA with concentration of $C = 10^{-3}$ mol/l were prepared. To 1 ml of AS-40 1 ml of PEI was added under stirring during 5 min. Then 1 mL of PAA was added to 2 ml mixture of AS-40 and PEI. Sequential addition of PAA and PEI to AS-40/PEI was continuously repeated 10 times under constant stirring time 5 min for each stage. The obtained solution consisting of SiO₂ ‘core’ and PEI-PAA ‘shell’ was abbreviated as (SiO₂)/(PEI-PAA)₁₀ (where 10 correspond to number of PEI-PAA multilayers). One drop of opalescent solution of (SiO₂)/(PEI-PAA)₁₀ was deposited onto the glass surface, dried in air and then heated in oven at 100°C during 6 h. Etching of SiO₂ from (SiO₂)/(PEI-PAA)₁₀ compositions was provided by dipping the glass surface into 0.01 mol/l HF during 1 min and rinsing with bidistilled water. This procedure was repeated the required times. Finally the multilayered coatings were dried in air.

3. Results and discussion

According to [13–16] the mechanism of interaction of silicate sols with linear polyelectrolytes can be considered as cooperative adsorption of negatively charged SiO₂ nanoparticles onto positively charged polyelectrolytes (Figure 2). The addition of a poly-

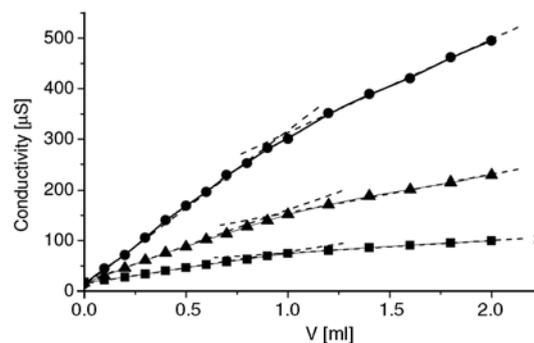


Figure 3. Conductimetric titration curves of colloidal dispersions of CL (1), AS-40 (2) and HS-40 (3) by PSSA (1), JR-400 (2) and PDMDAAC (3)

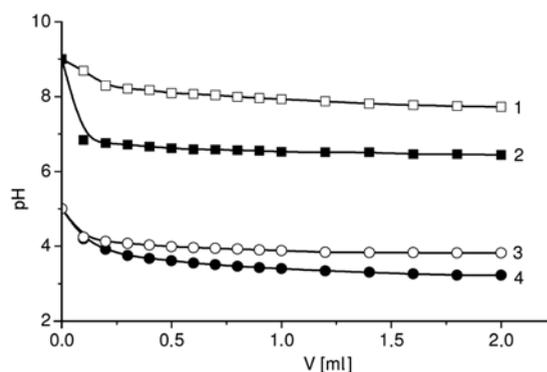


Figure 4. Potentiometric titration curves of HS-40 (1, 2) and CL (3, 4) by PDMDAAC (1), JR-400 (2), PAA (3) and PMAA (4)

cation to a solution of a silicate ions results in precipitation of IPEC.

Figures 3 and 4 illustrate the conductometric and potentiometric titration curves of silicate sols by linear polyelectrolytes. Compositions of IPEC found from the inflection points are equal or close to equimolar ratio of interacting components (Table 3). Increasing of the optical density and viscosity of systems indicates an aggregation of IPEC particles (Figure 5).

Photos of colloidal silica, polyelectrolyte solution, precipitated IPEC, and IPEC powders are shown in Figure 6.

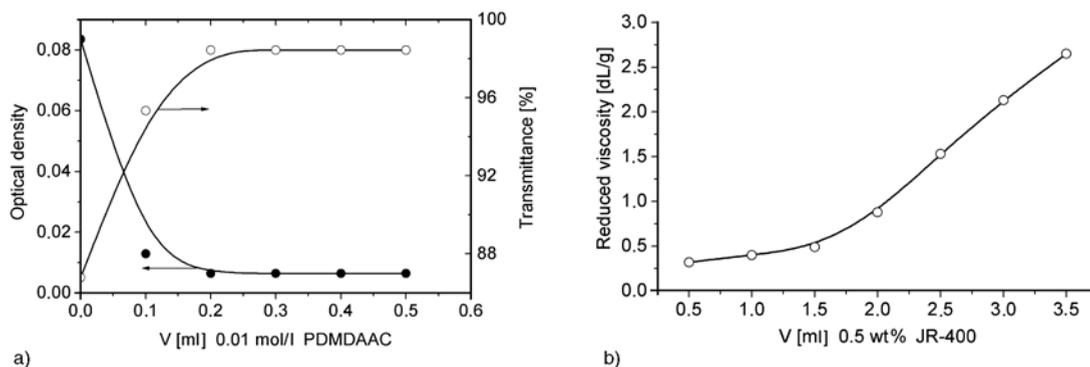


Figure 5. Spectroturbidimetric (a) and viscometric (b) titration curves of colloidal silica AS-40 by PVBTMAC (a) and JR-400 (b)

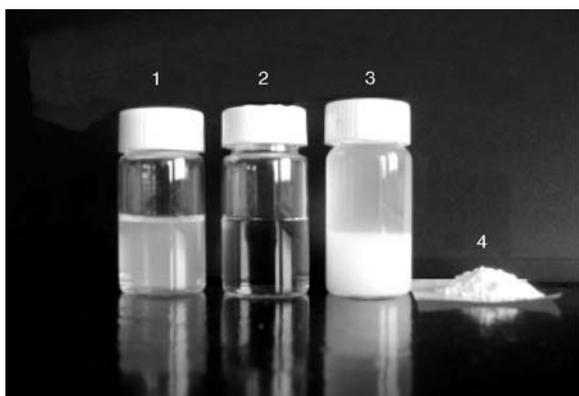


Figure 6. Photos of colloidal silica AS-40 (1), aqueous solution of JR-400 (2), precipitated IPEC (3), and IPEC thin powders (4)

Table 3. Compositions of IPEC determined from the inflection points of conductimetric and potentiometric titration curves

Polyelectrolytes	Composition of IPEC [mol/mol]		
	AS-40	HS-40	CL
JR-400	1 : 1.15	1 : 1	–
PDMDAAC	1 : 1.04	1 : 1.33	–
PVBTMAC	1 : 1.12	1 : 1	–
PEI	1 : 1.05	1 : 1	–
PSSA	–	–	1 : 1.2
PAA	–	–	1 : 1.1
PMAA	–	–	1 : 1
PDMDAAC microgel	1 : 1	1 : 1	–

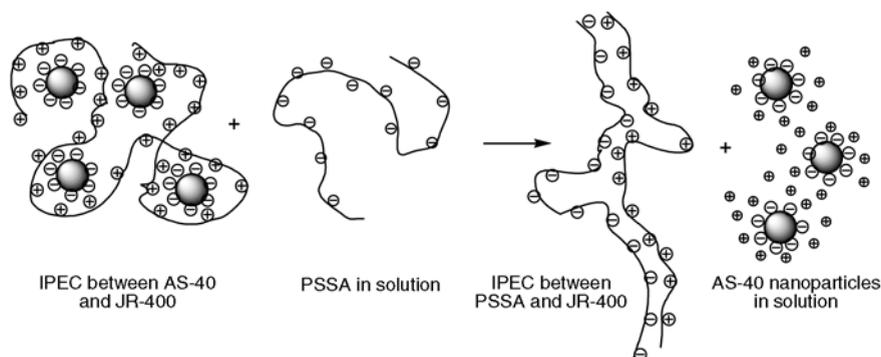


Figure 7. Release of silica sols from the IPEC as a result of competition reaction between IPEC and PSSA

Table 4. Dimensions of the (SiO₂)/(PEI-PAA)₁₀ LbL complex particles in water

LbL C _p [mg/ml]	Zimm		Guinier		CONTIN
	R _g ^Z [nm]	R _g ^Z /R _h ^{mean}	R _g ^G [nm]	R _g ^G /R _h ^{mean}	R _h ^{mean} [nm]
C _p → 0	72.4	0.76	88.8	0.92	96.4
0.121	70.7	0.74	82.9	0.87	95.7
0.605	72.2	0.73	83.1	0.84	99.3
12.1	74.5	0.81	89.6	0.97	92.4

SiO₂ particles are displaced by PSSA can schematically be represented by the following Figure 7.

Thus IPEC formation between silica sols and cationic polyelectrolytes and interpolyelectrolyte competition reactions with participation of strong polyelectrolytes can serve as preparative and technological basis for extraction and purification of SiO₂ nanoparticles.

The data of light scattering experiments for LbL consisting of (SiO₂)/(PEI-PAA)₁₀ are collected in Table 4. The main conclusion from these results is that the radius of gyration, R_g and hydrodynamic radius, R_h^{mean} of LbL particles calculated by using of Zimm and Guinier methods and of an inverse Laplace program CONTIN are independent on LbL concentration and smaller than 100 nm.

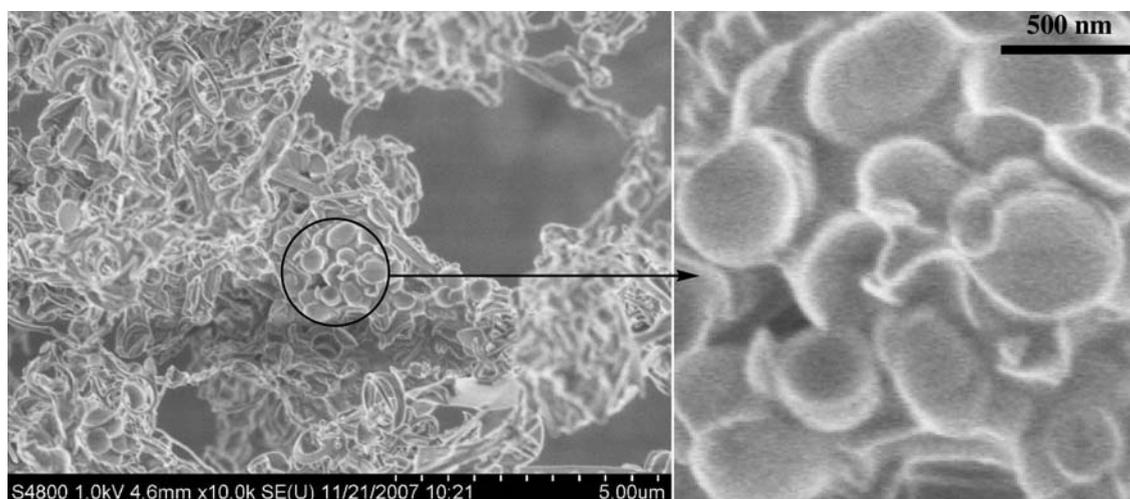
Following the LbL preparation procedure, the most expected conformation of (PEI-PAA)₁₀ shell layer is a swollen sphere (or a thick-walled sphere). The R_g/R_h ratios listed in Table 4 support this model. The Zimm's method is typically used for structures, density of which increases towards the centre of gravity, e.g. a polymer coil. In this respect the Guinier's method should give more reliable value of R_g. We tried to estimate the geometrical parameters of such a thick-walled sphere. In this model the

outer radius was taken as R₁ = R_h^{mean} = 96.4 nm, R_g = R_g^G = 88.8 nm, and the inner radius R₂ calculated from the Equation (1):

$$R_g^2 = \frac{3}{5} \cdot \frac{R_1^5 - R_2^5}{R_1^3 - R_2^3} \quad (1)$$

was equal to 80.0 nm.

It should be taken into account that measuring of the molar mass and R_g of (SiO₂)/(PEI-PAA)₁₀ by light scattering methods is not a straightforward task due to the difference in the refractive indexes of the polymers [35]. In this respect, the measured value of R_g might be somewhat underestimated, meaning that the actual wall thickness of the sphere is smaller. Feng *et al.* [36] fabricated hollow microcapsules having shells of polyelectrolyte complexes by polymerization of 4-vinylpyridine hydrochloride (VPy) in a solution containing surface-modified silica particles and poly(sodium 4-styrenesulfonate) (NaPSS), and followed by a core removal with HF. The continuous shells with a thickness of 5–15 nm on the silica particles were created by covalent linking of the NaPSS-PVPy complexes.

**Figure 8.** SEM picture of freeze-dried LbL particles of (SiO₂)/(PEI-PAA)₁₀. Arrow shows the enlarged area of circle

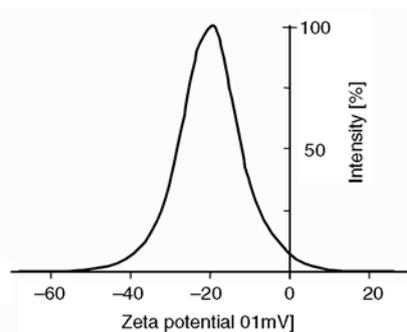


Figure 9. Zeta-potential measured for LbL of $(\text{SiO}_2)/(\text{PEI-PAA})_{10}$ with $C_p = 0.121$ mg/ml

SEM picture of freeze-dried $(\text{SiO}_2)/(\text{PEI-PAA})_{10}$ particles prepared from $C_p = 12.1$ mg/ml is depicted in Figure 8. In spite of the fact that during the freeze-drying process the ice crystals can damage the outer shells, the clones of ball-like particles are observed. The average size of such particles is in the range of 200–500 nm.

The zeta-potential of $(\text{SiO}_2)/(\text{PEI-PAA})_{10}$ is shown in Figure 9. The mean peak value of the zeta-potential distributions fluctuates between -10 and -30 mV depending on the LbL concentration,

which one could in principle be expected for salt-free aqueous solutions. The zeta-potential values and their sign agree well with the procedure of the complex preparation: the outer layer of the $(\text{PEI-PAA})_{10}$ complex consists of PAA.

Microphotographs of thermally treated $(\text{SiO}_2)/(\text{PEI-PAA})_{10}$ powder before and after etching of SiO_2 by HF are shown in Figure 10. Separate hollow spherical particles with different sizes and aggregated blob-like hollow particles bridged each other *via* hollow tubes are good seen. The mechanism of formation of LbL multilayers is probably multistage process (Figure 11). At first PEI chains may wrap one or several SiO_2 nanoparticles (Figure 11a). The added PAA chains are deposited onto SiO_2 -PEI particles via electrostatic interactions (Figure 11b). Sequential adsorption of PEI and PAA to a single SiO_2 and/or aggregated SiO_2 nanoparticles can produce a spherical and/or cylindrical $(\text{SiO}_2)/(\text{PEI-PAA})_{10}$ multilayers (Figure 11c, d). Here the dangled parts of PEI and PAA can participate in formation of IPEC particles and bridge the aggregated LbL particles (Figure 11d).

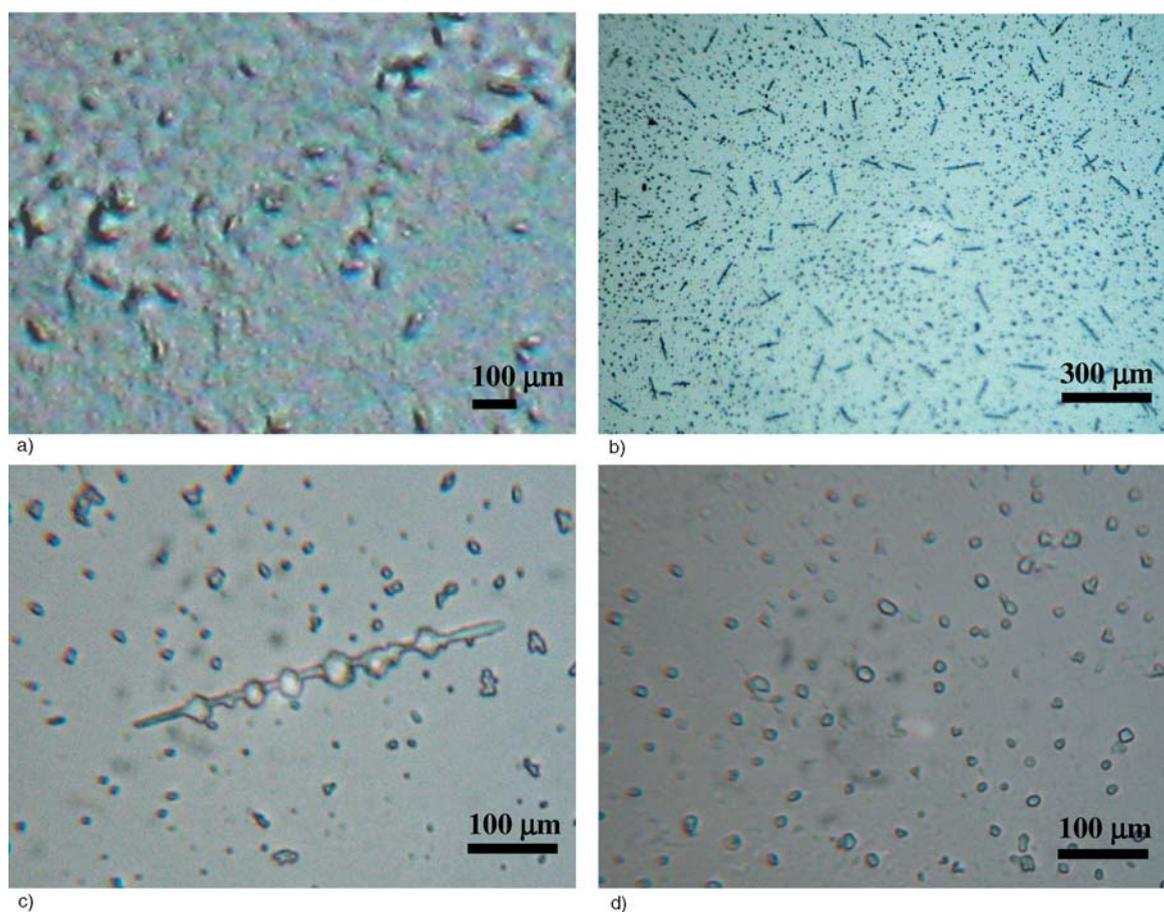


Figure 10. Microphotographs of $(\text{SiO}_2)/(\text{PEI-PAA})_{10}$ after thermal treatment (a) and after etching by HF (b, c, d)

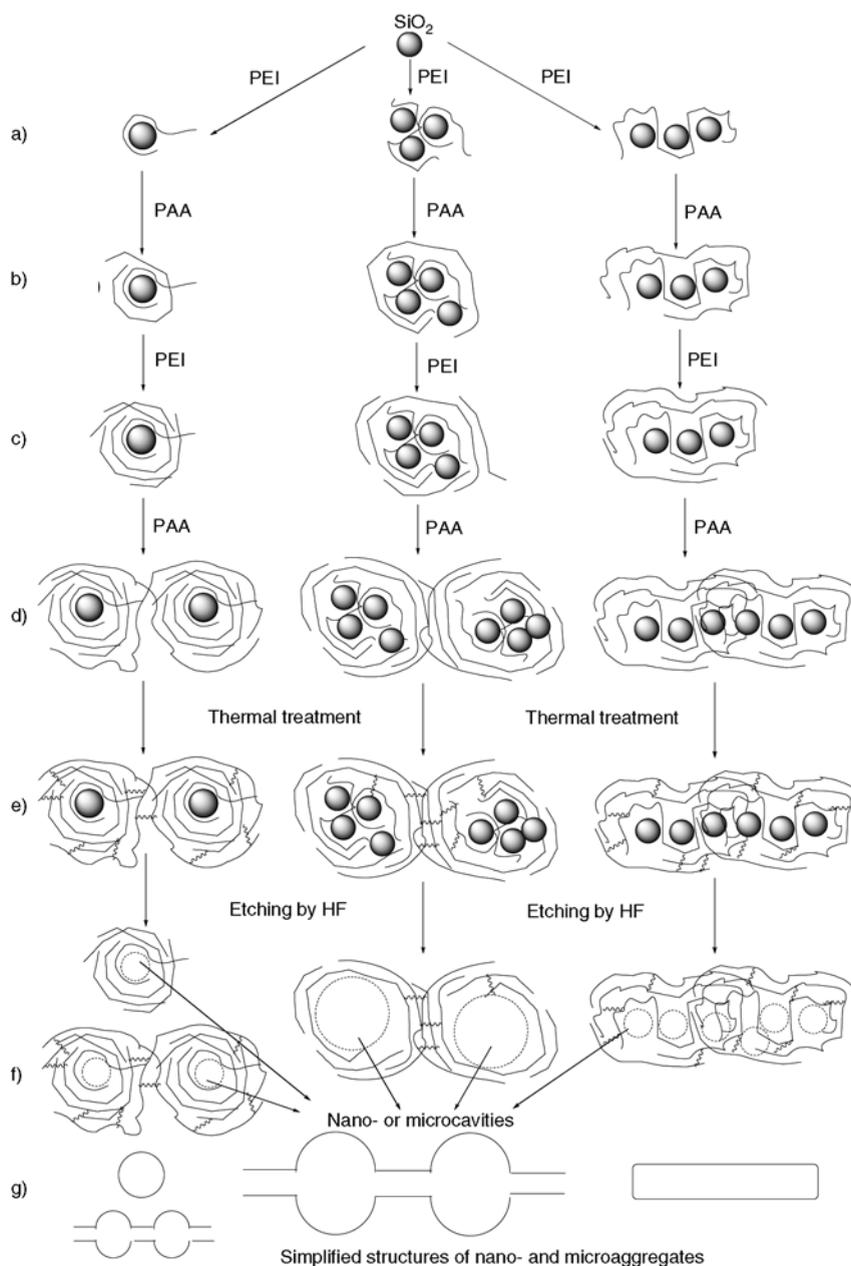


Figure 11. LbL multilayers assembled *via* interpolyelectrolyte reactions between silica sols and linear polyelectrolytes

The further thermal treatment of $(\text{SiO}_2)/(\text{PEI-PAA})_{10}$ multilayers or aggregates converts the ionic bonds $-\text{NH}_3^+ \text{ } ^-\text{OOC}-$ on ‘shell’ layers to covalent amide bonds $-\text{NH-OC}-$ analogous to amidization of PEI-PAA interpolyelectrolyte complexes (Figure 11e) [37]. Etching of SiO_2 ‘cores’ from LbL multilayers leads to formation of nano- and microcavities, sizes of which corresponds to single or aggregated SiO_2 particles (Figure 11f). The simplified nano- and microparticles of $(\text{SiO}_2)/(\text{PEI-PAA})_{10}$ can be represented as single or aggregated nanocavities, blob-like microparticles and even

nano- and microturbes (Figure 11g). In the course of LbL multilayers the growth of a various combinations of nano- and microparticles leading to different nano- and microstructures are possible.

4. Conclusions

Nano- and microsized hybrid inorganic-organic composites were assembled between colloidal silica sols and synthetic polyelectrolytes as a result of interpolyelectrolyte reactions. The composition of precipitated interpolyelectrolyte complex (IPEC)

particles is mostly stoichiometric. Preparation of thin IPEC powders and composite films is demonstrated. Competition interpolyelectrolyte reactions between IPEC and strong polyelectrolytes, in particular polystyrenesulfonic acid (PSSA), can have technological importance for extraction and purification of SiO₂ nanoparticles. The probable mechanism of formation of ‘layer-by-layer’ (LbL) multilayers is suggested. The LbL technique followed by thermal treatment of IPEC and etching of silica nanoparticles with HF leads to formation of various kinds of nano- and microcavities.

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