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Low – temperature sol – gel synthesis of crystalline materials

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Sol-gel chemistry has opened new era of modern materials science by enabling production of ceramic materials at near-room temperature. Thousands of papers have been published since, and new hybrid materials and composites widely used in our everyday life have been obtained. From a chemical point of view, these materials actually have compositions identical with their high-temperature ceramic analogs, but there is a drastic difference in structure and phase composition. In the majority of cases, oxide systems produced using sol-gel method possess an amorphous structure and huge surface area with narrow micro/mesopore size distribution. At the same time, a great variety of oxides and mixed oxide systems with quite a number of по-моему, это лишнее слово: и так понятно, что модификации разные polymorphic modifications and, consequently, properties can only be produced by high-temperature treatment. Investigation of mechanisms and methods of crystallization for such systems in the colloidal state at temperatures less than 100 °C would significantly contribute to developing new materials obtained by low-temperature sol-gel synthesis. Taking into account millions of different thermosensitive organic, inorganic, and bioorganic substances, which could be used in producing hybrids and composites, potential of low-temperature sol-gel technology is immense. In fact, it is a 'second wind' for developing classical sol-gel technology with its more than a hundred-year history. The present review describes fundamental principles of crystallization of oxide sol-gel systems in solution and gives examples of applications of composites produced by low-temperature sol-gel synthesis.

1. Motivation.

Metal oxides are one of the most intensively studied and promising classes of modern materials numbering hundreds of various compounds. Counting the quantity of possible solid solutions and mixed oxide systems produced on their basis is barely possible. At the same time, application of these systems is significantly limited by the methods of their production . As a rule, these imply high-temperature treatment required for formation of crystals in the course of solid-phase topochemical reactions. Taking into account the multimillion-large number of various organic substances, finding conditions for synthesis of such crystalline systems in solution at temperatures less than 100°C would, of course, result in emergence of new materials with unique properties and practical applications. Despite the fact that fundamental principles are to be developed, the main motivation is practical:

- ✓ The number of simple oxides is limited. However, the variability of mixed oxides and solid solutions on their basis is practically infinite. When considering these compounds as a potential source of new materials, a low-temperature conception may turn out to be fruitful.
- ✓ Turning any high-temperature process into a low-temperature one is always preferable due to both lower power consumption and more practical application.
- ✓ The scope of organic and thermosensitive compounds is immense, as well as that of oxide systems; merging both enlarges dramatically the scope of hybrid materials.
- ✓ An organic dopant can either deliver a required property to the matrix – oxide or provide a multiple increase in that already exhibited.

Despite almost a hundred-year[1] history of sol-gel synthesis, developing methods of producing crystalline sols of metal oxides remains a rather difficult problem.

In our works, we have materialized many of these predictions: new materials for electronics and spintronics, photocatalysis, biomedicine, textile, and more emerged.

2. The methodology

2.1. Terminology

The classical interpretation of the term “sol-gel synthesis” does not concretize whether the state of the product is amorphous or crystalline. The term “low-temperature sol-gel synthesis” introduced in the present review only concerns the production of crystalline materials and imposes the following requirements on the system:

- ✓ The presence of pronounced crystalline phase with an amorphous content of no more than 10 %;
- ✓ High sedimentation stability of a sol and its capability of polycondensation and gelation;
- ✓ Crystallization processes are carried out at a temperature of no more than 100°C and atmospheric pressure.

2.2. Proof of Conception

Developing methods of sol-gel synthesis as one of soft chemistry sections started with studying phase transitions of silicon-organic species in aqueous and aqueous-alcoholic solutions[2-5]. Formation of colloidal nanoparticles as a sol was instantly accompanied by polycondensation of disperse phases resulting in a stable gel state[6]. This approach was very promising for many important and spectacular applications in such domains as, for example, stabilization of organic dyes[7], entrapment of enzymes[8] and proteins[9] for prolonged and improved activity[10], and creation of “impossible” organic catalysts for complex one-pot acid-base and redox transformations[11]. The possibility of entrapping various species into in highly porous silica matrix became a revolutionary stage of development for this method[12]. Results obtained by researchers in the 60-90s of the 20th century[13-16] allowed silica-based sol-gel materials to gain significant popularity, including real industrial applications. However, at present, the vigorous trend in studying silica-based materials shows an obvious deceleration. It is due to the fact that the silica matrix itself is highly inert to various physical and chemical processes owing to its amorphous structure. As a consequence, it is not active itself and cannot increase the activity of an entrapped component.

Despite the fact that there are no data on low-temperature crystallization of a silica sol so far, there exist a large number of oxides and mixed oxide systems (see Section 3) that have been successfully synthesized in solution at a temperature less than 100°C. Below, we will try to prove the possibility of this phase transition theoretically and show the practicability of this approach visually. The Development of methods aimed at obtaining new sol-gel materials displaying their own activity in various processes is determined by chances to successfully adjust the crystalline structure formed in the course of synthesis. It is quite obvious that unique properties of a material are not only provided by the presence of developed, ordered (но я не уверен) structure, as is the case for silica, but also by the presence of the long-range order, that is, crystal structure. Taking into account the formation of these sol-gel materials from solutions at low temperatures is initiated, as a rule, by irreversible reactions of hydrolysis and alcoholysis, the particles formed at an initial stage appear to be rather amorphized (more than 90 %)[17]. In this case, it is possible to represent the structure of the particles produced by a soft chemistry method as a nucleus and a cover, where in the center is a crystal germ shrouded in a "fur coat" of ligands and intermediate products, see Fig. 1.

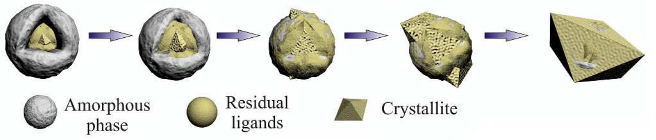


Figure 1. Visualization of growth of a crystal nucleus covered with an amorphous coating.

Three main stages of a process of crystallizing particles from a solution can be distinguished[18-20]: turning the system into a metastable state, emergence of crystals (formation of germs) and growth of crystals. It means that in order to achieve the maximum degree of crystallinity of hydrosols, one needs to carefully control the two processes: 1) nucleation and 2) growth of the formed crystal nuclei. Thus, the transition of the system to a metastable state is the key factor determining the possibility of beginning the crystallization of a new phase, formed from theoretically homogeneous liquid medium. In case of reactions molecular precursors hydrolisis yielding ultradisperse phases, the size of heterophase fluctuation in the bulk of the formed product will be responsible for the emergence of a metastable state. Despite the fact that the formation of a nanoparticle as a new phase in a homogeneous solution is related to reduction of the chemical potential of a substance (formation of intramolecular and intermolecular bonds), the change in free energy (or the thermodynamic potential) for the system may be positive. This is due to the fact that at initial stages of phase formation, an important role is played by the interface possessing the excess positive surface energy. Fig. 2A shows the change in free energy vs. the size of the formed crystal nucleus as a new phase. A maximum is distinctly observed at a certain critical value of the radius r_{crit}. Thus, for $r < r_{crit}$, an increase in the size of a germ of a new phase results in an increase in free energy, increasing the entropy factor and destabilizing the system. For $r > r_{crit}$, the growth of the crystallization center becomes a thermodynamically favorable process, at the expense of reducing free surface energy, providing a spontaneous start of the two subsequent stages (nucleation and growth of crystals)[18]. The mechanism of the further behavior of the system is perfectly illustrated and proved in the theory of LaMer[18], Fig. 2B. When the concentration of the molecular precursor in solution approaches a critical level, required for formation of nuclei, C_{crit}, the system is involved into the initial stage of nucleation. But this process quickly reaches a saturation maximum due to the equilibrium between the level of delivery of "building" ions and the "norm" of their consumption in the construction of the crystal framework, Fig. 1.

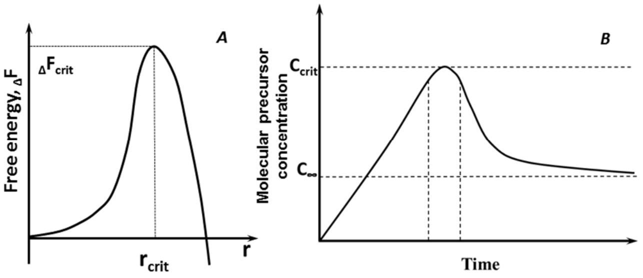


Figure 2. A) The change in free energy vs. the size of the formed crystal nucleus. B) Illustration of the LaMer[18] theory depending on the change in the concentration of the molecular precursor in solution with time.

Thus, the theoretical proof of performing low-temperature crystallization of oxide materials in aqueous solutions using the sol-gel chemistry method is quite persuasive. A key question in this case is the selection of optimal conditions that provide specified parameters. In practice, this question is, very individual and realized empirically in most cases. In the present review, we will only consider the most appropriate examples, including those performed by our scientific group.

2.3. Ways to increase crystallinity in a solution

A general approach to increasing the crystallite sizes and the degree of crystallinity is promoting diffusion of ions to the crystallization center.[17,24] In case aqueous solutions, the boiling methods are most popular[17].They initiate the thermal dehydration of a highly hydrated cover with its gradual decomposition, , see Fig. 1. Application of this approach was considered by several scientific groups dealing with crystallization of sol-gel materials at low temperatures[21-27]. The use of biocatalytic processes can be another interesting method of growth of crystallites under neutral pH conditions[28], with application of biological precursors[23]. It is shown that in this case[28] , the biodestruction of the amorphous cover containing intermediate products of transition metal complexes is performed in the course of an enzymatic reaction, transforming stable amorphous areas into ionic configurations. As a result, this also promotes the formation of nanocrystalline phases in aqueous solutions. Removal of organic ligands and curing of the defects can be achieved even by increasing the polarity of the medium and facilitating protolytic mechanisms by creating extreme pH. Thus, fully crystalline particles of $BaTiO_3$ can easily be produced at 90 °C by introducing titanium alkoxides into aqueous solution of the strong base $Ba(OH)_2$[29]. The same effect is achieved by the reported techniques for improvement the crystallinity of TiO_2 by peptization. Indeed, "re-dissolving" in HNO_3 the XRD amorphous precipitate from hydrolysis of titanium alkoxides provides a stable sol consisting of uniform anatase nanoparticles[24,30-33]. Among other ways of activating (not the least important and gaining popularity at present) the crystallization are external physical factors (ultrasound, microwaves, UV) under atmospheric pressure[26, 35]. General mechanisms for effects of pH of a medium and external physical factors on the growth of crystalline phase will be considered below.

We would like to highlight the two approaches (chemical and physical activation) and to consider these in more detail, see Fig. 3. The attention is payed to the prospects of the present approaches not only from the viewpoint of successful crystallization of oxides and their derivatives in aqueous solutions, but also to demonstrate successful stabilization of the crystalline sols, capable of participating in the further stages of polycondensation and sol-gel process.

2.4. Effect of acidic peptization on the formation of crystalline sols.

Sol formation consists of the hydrolysis and condensation reactions, which are catalyzed in the presence of an acid. The hydrolysis reaction leads to the formation of original nuclei or basic units, while the condensation reaction leads to the particle growth as predicted by the LaMer theory, the strength of the acid and its concentration affecting the crystallization of amorphous shell of the crystal-shell particles formed during condensation. In particular, the effect of the concentration ratio $[Me^{n+}]/[H^+]$ ratio, temperature and type of precursor is reported in by Liu et al.[35] particle growth, as predicted by the LaMer theory[18], fig. 2B. The addition of an acid to amorphous hydroxide $MeO(OH)_n$ shell was found to result in breaking oxo- bonds and the protonation of the surface of crystalline particles. A decrease in particle sizes also results in stimulation of crystallization processes[19], an increase in nucleation rather than growth of the formed crystals being the rate-limiting step.

In Fig. 3 we compare the size of the anatase crystals vs. the concentration ratio $(Ti]/[H^+])$ and protonating agent strength $(\log(K_{d(acid)})$. To obtain the data, four acids with various dissociation degree in aqueous solution were used. More oxobonds can be broken among titanium atoms by using a stronger acid, which can affect the nucleation and the crystal growth of TiO_2, leading to bigger crystallites as well as colloid particles of TiO_2. It was expected that this could beneficially influence the size of final colloidal particles, in particular, the size of the crystalline core. This method allows not only to form highly photoactive crystalline particles as sol colloid, but also to obtain nano-dispersed powder capable of resuspension in aqeous solution giving initial colloid state.

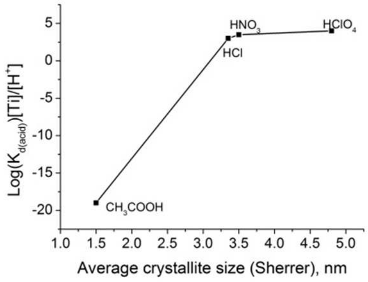


Figure 3. Effect of acidic peptizers on the growth of TiO_2 crystallites in aqueous solutions.

2.5. Physical activation of colloidal particles and growth of crystals.

Physically- and mechanically-assisted synthesis is appealing because it can dramatically reduce reaction time, improve product yield, and enhance material properties when compared to conventional synthesis routes[36-38]. While conventional heating is limited by thermal conduction from the vessel walls, physical fields (ultrasonic, electric fields, microwaves, ultraviolet etc.) can quickly and uniformly heat a solution by directly coupling to molecules within the solution through polarization or conduction. Polarization is the process of dipole formation from bound charges and aligning polar molecules along an oscillating electric field. Conduction is the motion of free charge carriers and ions in response to an electric field.

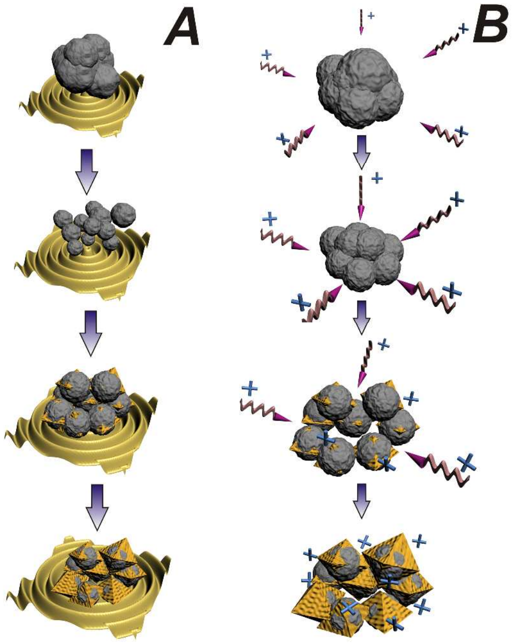


Figure 4. Comparative visualization of the mechanism of growth of crystals formed under the influence of (A) physical and (B) acidic peptization.

Thus, it is possible to provide significant activation of colloidal phases both by disaggregating agglomerates by an increase in ion mobility for initiating the accelerated processes of crystallization, Fig. 4.

For example, using microwave-assisted sol-gel route, the crystalline colloids of ZnO[39], ZrO_2[40], TiO_2[26,41], SiO_2[42], WO_3[43], AlF_3[44], MgO[45] have been obtained, as well as some mixed oxides like $BaTiO_3$[46,47], etc[48]. Using ultrasonic treatment, the crystalline particles of TiO_2[34],[49], AlOOH[27], ZrO_2[50] and some mixed oxides $Pb(Zr,Ti)O_3$[51] were synthesized at room temperature. However, although the existing approaches in most cases lead to an increase in crystallinity, theydo not allow to perform the formation of stable colloidal systems at neutral pH values. For this purpose, stabilizers are usually used or solvents with different polarity are selected. At the same time, there is only a small number of papers, which report original methods of the formation of highly crystalline sol-gel systems in aqueous solutions at neutral pH promising for biochemical engineering and electronics[27,34]. For isnstance, our group has succeeded in employing a low-temperature ultrasonic-assisted method to prepare nanocrystalline TiO_2[31] and AlOOH[27] sol-gel materials directly from hydrolysis products of alkoxide precursors in an aqueous medium with no addition of modifying agents.

2.6. Peculiarities of sol-gel transition for nanocrystalline particales.

As was mentioned before, the crystallization of colloid particles inevitable leads to the formation of the core-shell structures. The further behaviour of the particle is defined by the composition and size of the amorphous shell. It is well known that the key parameters for inorganic polymer growth are thermodynamic characteristics of the particle state (such as surface energy, the sign of the surface potential, crystallographic energy of interaction within the crystal etc.) as well as the external parameters (temperature, PH, medium etc.)

Obviously, the main role in the further partical growth, their aggregation and formation of inorganic frame (gel) is given to residual ligands acting as interface to the surrounding solution.

The role of controlled hydrolysis has already been determined, whereas the reaction control by polycondensation between the amorphous shells of the crystalline particles in solution will define the possibility of the low-temperature sol-gel transition.

The role of ligands in the formation of the primary particles was found to be in facilitation of the hydrolysis-polycondensation and also stabilization of the emerging particles in solution against aggregation through enhanced interaction with the solvent molecules The direct kinetic data show that the speeds of hydrolysis and polycondensation objectively increase when chelating heteroligands are introduced in the precursors.[17] It can be said in a simplified manner that the ligands act as surfactants in stabilization of the particles and quantitative evaluation of this role has been reported.[42] These particles are both individual molecular species as well as colloid particles stabilized in solution by interactions between the ligands and the solvent by the forces typical for colloid systems. This finding led to proposal to denote them as Micelles Templated by Self-Assembly of Ligands (MTSALs).[17]

3. Scopes of nanocrystalline objects for low-temperature sol-gel synthesis.

A large number of papers are devoted to producing crystalline ceramic oxides from aqueous solutions at low temperatures. Among them (in order of increasing atomic number of metal) are Al_2O_3[52], AlOOH[27], TiO_2[53-59], V_2O_5[61], MnO_2[62], Mn_3O_4[63], β-FeOOH/α-Fe_2O_3[64], Fe_3O_4[65], CoO[66], Co_3O_4[67], NiO[68-70], $NiFe_2O_4$[71], Cu_2O [72,73], CuO[74], ZnO[75-81], ZrO_2[82], AgO[83], Ag_2O[83], CdO[84,85], Cd_2SnO_4[86], In_2O_3[87], SnO_2[88,89], $LnMO_3$ (Ln = La, Nd; M = Cr, Mn, Fe, Co) [90,91], $LaNbO_x$[92], CeO_2[+x93], Tl_2O_3[94],α-PbO_2[95] and many others not presented here.

Using already perfected methods of chemical and physical peptization, production of stable sols is, as a rule, not a problem for practically all of the presented systems. In this review, we will only dwell upon crystalline sols, which are most intensively studied and used since these are stable in a wide range of temperatures and pH values.

3.1. Alumina.

Aluminum oxides and hydroxides total to dozens of various polymorphic modifications. In a single γ-Al_2O_3 → α-Al_2O_3 process 9 transition modifications of alumina have been found (δ, ε, η, θ, ι, κ, π, ρ, χ)[96]. Annual production of alumina amounts to more than 100 million tons, and, of course, one of the main directions of its use is catalysis. The presence of acid-base centers, high specific surface area, economical availability and relative stability determine its use in the major processes of oil refining and organic synthesis as the support of catalytically active phases[97-103]. Apart from its immense role in catalysis, crystalline aluminum hydroxide also finds application as a fire retardant filler for polymer applications[104]. It decomposes at about 100-300°C, absorbing a considerable amount of heat and giving off water vapor. In addition to behaving as a fire retardant, it is very effective as a smoke suppressant in a wide range of polymers, especially in polyesters, acrylics, ethylene vinyl acetate, epoxies, PVC and rubber[104]. Aluminum hydroxides are indispensable for pharmaceutics owing to their high activity as antacids and adjuvants[27,105]. Boehmite is the only aluminum hydroxide approved by FDA for parenteral injections.

Four polymorphs of aluminum hydroxide exist, all based on the common combination of one aluminum atom and three hydroxide molecules into different crystalline arrangements that determine the appearance and properties of the compound. The four combinations are: gibbsite[106] (γ-$Al(OH)_3$, bayerite[107] (β-$Al(OH)_3$, nordstrandite and doyleite both designated as $Al(OH)_3$. Two oxyhydroxides are also available: boehmite (γ-AlOOH) and diaspore α-AlOOH. Each of the presented hydroxides and oxyhydroxides has its own unique structure and a set of functional properties. The literature provides thousands of different examples of preparing the sols of both monohydroxides (gibbsite[106], bayerite[107]) and trihydroxide[108], but only few papers on entrapping organic molecules into a matrix of crystalline aluminum hydroxide are available[27,105,109-110].

In Section 4.2, we will consider various examples of entrapping organic molecules in detail and provide evidence for prospects of developing this direction.

Three classes of alumina precursors are typically used for preparation of crystalline sols (1) aluminum alkoxides, (2) inorganic alumina salts, (3) aluminum oxide hydroxide (boehmite) or aluminum hydroxide (bayerite), either in the form of a gel or as a dispersed nanopowder. The hydrolysis of aluminum alkoxides was first described by Yoldas in 1973[111]. In this work, it was shown that depending on the reaction temperature the hydrolysis and polycondensation can result in boehmite or amorphous aluminum monohydroxide. A preparation method for porous, transparent aluminum oxide films from aluminum alkoxide sols was also described[112]. This opened a new route in alumina sol-gel chemistry. Aluminum alkoxides are very reactive, so that the addition of chelating agents to control both the hydrolysis and polycondensation rate is often required[113]. Aluminum isopropoxide and aluminum sec-butoxide were both used to obtain high-surface-area monolithic gels with crystalline structure[114].

It is well known that aluminum salts hydrolyze and condensate into aluminum oxide hydroxide gels under basic conditions[115]. However, aqueous aluminum salt solutions are acidic due to partial aluminum hydroxocomplex hydrolysis, as shown by the following equation[116].

$$[Al(H_2O)_6]^{3+} + nH_2O = [Al(OH)_n(H_2O)_{6-n}]^{(3-n)+} + nH_3O^+$$

Increasing pH shifts the equilibrium to the right. During basification, Al^{3+} ions undergo several intermediates[117] and the subsequent condensation (via olation and oxolation) results in formation of polynuclear hydroxides or oxo-hydroxides, eventually leading to sol-gel transition. Focus has been put on controlling the hydrolysis by gradual and homogenous increase of pH.

Several examples of both chemical and physical peptization of crystalline nanoparticles of aluminum hydroxides exist[27,118-121]. Fig. 5 shows images of boehmite xerogels produced using treatment by acetic acid (Fig. 5a,c) and ultrasound (Fig. 5b,d). Despite a substantial difference in preparation, both samples demonstrate similar structure.

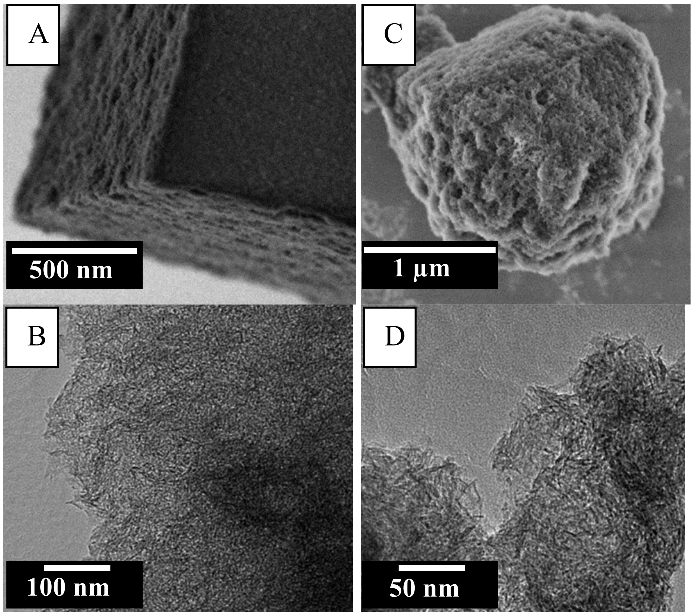


Fig. 5. SEM and TEM images of boehmite xerogels prepared with acetic acid (a,b) and ultrasound treatment (c,d).

3.2. Iron oxides.

Iron oxides play a crucial role in development of modern technology and materials science. A large number of different phases of iron oxides, hydroxides or oxy-hydroxides are well-known to date. Among those, the most studied are $Fe(OH)_3$, $Fe(OH)_2$, $Fe_5HO_8{\cdot}4H_2O$, Fe_3O_4, FeO, five polymorphs of FeOOH and four of Fe_2O_3[122, 123]. These oxides can be synthesized by all known wet chemical methods, but tailoring the particle size in nano range and morphology towards a particular application still remains a challenging task. Synthesis of iron oxides in the nano range for various applications has been an active area of research during the last two decades. In order to achieve required results, one has to carefully select the pH of a solution, concentration of reagents, temperature, procedure of mixing and oxidation rate [124]. Morphology of the formed particles also depends on several processes like nucleation, growth, aggregation and adsorption of impurities. At the same time, producing an iron oxide with selected particle size and morphology often fails, and for this purpose approaches to transition of one polymorphic modification of iron oxide to another are employed[125]. The sensitivity of the preparative method complicates both the reproducibility and scale-up of the process. Recently, several colloidal chemical synthetic procedures have been developed to produce mono-disperse nanoparticles of various materials. This includes the classical LaMer mechanism, Fig. 2B, wherein a short burst of nucleation from a supersaturated solution is followed by the slow growth of particles without any significant additional nucleation, thereby achieving a complete separation of the nucleation stage[18]. Here are some examples of sol-gel synthesis of iron oxides with different crystalline structure. Again, no calcination has been applied to achieve crystallinity.

The most popular method of preparing a sol of iron oxy-hydroxide employs the hydrolysis of the Fe^{3+} cations. However, aging of the sol prepared by pouring fresh ferric solutions into concentrated NaOH or KOH solutions has to take place at 60–80°C for a period of time ranging from a few days to several weeks[126]. In Ref.[127] , the sol-gel synthesis of α-Fe_2O_3 was carried out from condensed ferric hydroxide gels obtained from $FeCl_3$ solutions in NaOH. After aging the gel at 100°C for 8 days, mono-disperse pseudo-cubic α-Fe_2O_3 particles were obtained. The reaction proceeded through a two-step phase transformation from precipitated $Fe(OH)_3$ gel to a fibrous β-FeOOH and finally to α-Fe_2O_3. Oxidation of the Fe^{2+} ions in a solution at neutral pH values usually results in the formation of finer crystallites than those produced in alkaline Fe^{3+} solutions. Moreover, oxidation of the ferrous salt solutions by air bubbling yields one or several of the following products: goethite (α-FeOOH), lepidocrocite (γ-FeOOH), magnetite (Fe_3O_4) and hematite (α-Fe_2O_3). Crystallization of iron oxides also strongly depends on anions and cations being adsorbed on the surface of the formed particles. Furthermore, various phases formed during the oxidation of aqueous ferrous systems suggest that the oxidation rate, which can be influenced by pH, temperature and other additives (anions or cations), is the dominant factor in determining the hydrolysis product. Using the same precursors, α-FeOOH, γ-FeOOH, and Fe_3O_4 with different morphology can be obtained by adjusting the synthesis conditions[129]. Acicular goethite particles were obtained after aerial oxidation of iron(II) solutions at 20°C – 80°C in acidic conditions. Depending on the temperature, the length of the particles varied between 0.1 – 0.5 μm and the aspect ratio lay between 5 and 10. Poly-disperse microcrystals of magnetite were produced at neutral and basic pH at 90°C by the addition of KNO_3 to $FeCl_2$ and KOH solution[129].

Despite the fact that not all types of iron oxides have been obtained using sol-gel method, we actually believe that this is only a question of time and motivation, since very attractive mechanisms of chemical and physical peptization exist at present.

3.3. Titania.

Since the discovery of unique activity of $Pt_{cat}/TiO_{2(anode)}$ photocatalysts in oxidation of H_2O molecules to hydrogen and oxygen under the influence of sunlight the titania-based materials became one of the most studied to date[130, 131]. Numerous investigations have been performed to study and improve photoactivity of TiO_2[132-134]. For this purpose, a large number of various methods of production have been analyzed to realize the possibility of adjusting its properties in the course of synthesis and to achieve the maximum effect[17,24,25,26,34,134-137]. We would like to give prominence to the most important issue in this multitude. namely, controllable growth of TiO_2 crystalline phase from aqueous solutions of molecular precursors as the main method for increasing photoactivity of the materials produced on its basis. Moreover, synthesis of crystalline particles of TiO_2 phases at low temperatures (<100°C) eliminates the need for using high temperatures, which is extremely economically important. Thus, one can achieve efficiency not only by a decrease in applied energy, but also by reducing the time between production of a material and its final application. This commercial interest was instantly followed by a huge number of papers aiming at avoiding high-temperature or harsh chemical conditions and devoted to low-temperature formation of TiO_2 nanocrystals, which results in a number of certain benefits:

1) it allows to perform functional and structural modification with thermally unstable species, such as biomaterials[133], metal-organic frameworks (MOF)[138], dyes[139], organic LED, in situ by entrapping directly into inorganic polymer matrix, which was previously considered impossible in crystalline titania gel; 2) it enables adjusting the growth of crystallites, average particle size, as well as the degree of crystallinity; 3) it facilitates carrying out the processes of forming nanocomposites in polymer matrix, using polymer solutions as reaction media and performing the polymerization of monomers in the presence of the formed sol system to achieve a homogeneous distribution of particles. The main drawback of low-temperature methods is low crystallinity of obtained materials and, as a consequence, low photocatalytic activity of species. The key approach to provide a solution to this problem is the sol-gel method [17,24,25,26,34,135-137,140,141]. A low-temperature procedure for the synthesis of TiO_2 using a water-soluble titanium complex and enzymes was developed[28]. The formation of nanocrystalline and monodisperse TiO_2 from a water-soluble and stable precursor, ammonium oxo-lactato-titanate, $(NH_4)_8Ti_4O_4(lactate)_8{\bullet}4H_2O$ was also described[23]. Previously,

we have studied mechanisms of the growth of TiO_2 crystalline phase caused by chemical peptization in aqueous solutions[24]. Thermal dehydration of hydrolysis products of $TiCl_4$ to obtain a crystalline sol of anatase was investigated[22]. Ref.[25] reports an original method of obtaining a suspension of nanocrystalline TiO_2 powder using titanium methoxide as a precursor, which possesses an anomalously high specific surface area.

However, all similar investigations imply either chemical modification of the surface of the formed particles or chelation of the used precursors at the hydrolysis stage. Moreover, the use of aqueous solutions for producing a crystalline sol of TiO_2 is complicated by a high degree of hydrolysis for the used precursors. Most of those are inorganic salts, the use of which inevitably results in consequent purification stages for the materials obtained. The use of alkoxides in the hydrolysis process is complicated by residual terminal alkoxide groups in the structure of $TiO_{2-n}(OR)_{2n}$, which cannot be removed even with a large excess of water[35]. Above all, a complex effect of low-temperature conditions on the formation of crystalline titania, growth of crystalline phase and nucleation remains unclear.

A solution to these problems is the use of physical and chemical peptization activating the colloidal phases in nano-sized titania-based aqueous solutions, see Fig. 4. For example, B. Reeja-Jayan et al. were the first to perform microwave-assisted formation of TiO_2 nanocrystalline films on a flexible polymer substrate, which were suitable for use in electronics[26]. In our recent paper[142], we also report potential applications of low-temperature sol-gel methods for the formation of conducting coatings. Ref. [41] also reports a successful synthesis of TiO_2 particles by hydrolysis of tetraisopropyltitanate under ultrasonic irradiation. However, they used acetic acid as a dispersant, protonating the surface of the formed particles, which prevents formation of stable sol-gel systems.

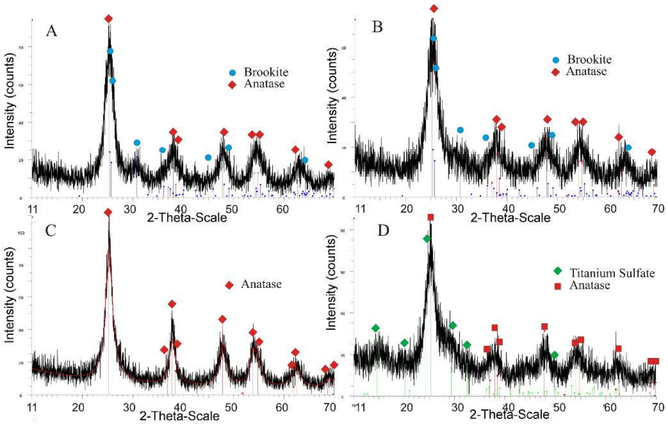


Figure6. X-Ray diffraction patterns of prepared TiO_2 samples using different protonating agents: (A) TiO_2 (HNO_3), (B) TiO_2 (HCl), (C) TiO_2 (Acet.), (D) TiO_2 (H_2SO_4)[24].

It is paradoxical, but according to previous results[17,24,25,26,31-34] the maximum growth of TiO_2 crystalline phase is attained using aqueous solutions, despite a high rate of hydrolysis for alkoxides under these conditions. In this case, pH will have a crucial effect on phase composition, and peptization will promote preservation of crystallinity and formation of stable sol-gel systems. Fig. 6 suggests that the use of strong acids, HNO_3 and HCl, leads to anatase-brookite crystallites, with almost equimolar ratio, see Fig. 6 (A, B). A decrease in acid strength illustrated by acetic acid results in crystallization of anatase TiO_2, Fig. 6 (C), which is analogous to the effect of ultrasonic and microwave treatment at neutral pH values.

Obtaining titania by sulfate method leads to forming a mixture of crystalline $Ti(SO_4)_2$ and anatase, Fig. 6 (D), sometimes called as thetta-phase[143]. Behavior of protonated particles in a solution and their ability to form aggregates in an aqueous medium depends on the value of the surface charge. A change in zeta potential of particles results in the formation of titania-based particles with different morphology. In case of a high protonating degree the particles with narrow size distribution, about 15 nm, see Fig. 7A, are formed;~~,~~ the use of acetic acid as a stabilizer promotes the formation of nanorods, Fig. 7B, and the formation of nanocrystalline titania sol under ultrasonic treatment leads to dense packing of particles with the size of about 15 nm. The absence of a strong surface charge in the latter case will also determine the possibility of gelation with the subsequent formation of a xerogel which undoubtedly increases the practical significance of this approach.

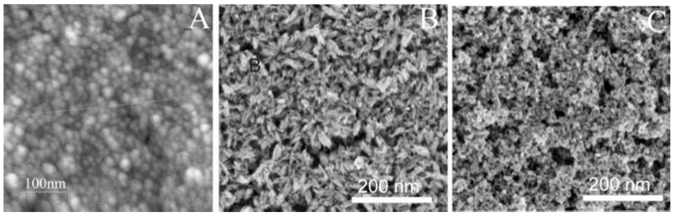


Figure 7. Morphology of the surface of dip-coating films produced from aqueous solutions of nanocrystalline TiO_2 sols prepared using A) HNO_3, B) Acetic acid as a peptization agent, C) ultrasonically activated TiO_2.

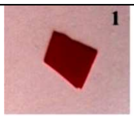
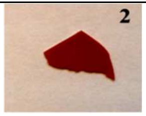
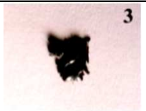
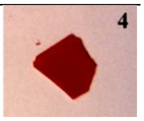
3.4. Mixed oxides.

Numerous oxides have been produced as polycrystalline thin films from aqueous solutions at low temperatures. Although most of the examples reported to date are single oxides, multicomponent films have been deposited, including doped single oxides (ZnO:Ni, Cu, Cd, Al, Sn; SnO_2:Sb; In_2O_3:Sn) solid solutions (spinel, ferrites; ZrO_2-Y_2O_3), and stoichiometric compounds ($CdSnO_4$; perovskites). From a practical point of view, the relative metal concentrations in solutions must be adjusted empirically to obtain a desired ratio of metals in the mixed oxides; different precipitation kinetics can make it difficult to achieve simultaneous and uniform precipitation of both components in the ratios desired for stoichiometric mixed oxides. Usually, oxides of high-valence (III–V) metal oxides can be prepared from acidic solutions, whereas low-valence (II–III) metal oxides have been deposited at neutral to basic pH. This reflects a fundamental difference in the precipitation chemistry of these metals, and affects the ability of multicomponent oxides being formed. The recepes to solve these problems may be found in the extensive literature on deposition of non-oxide films from aqueous solutions, or to the sol-gel literature where films of such mixed-oxide compounds as Pb(Zr, Ti)O_3, $BaTiO_3$ and $LiNbO_3$ have been successfully synthesized. These ways were based on direct interaction of components of a multiphase system, in which at least two types of solid ultradisperse particles generated from molecular predecessors are present. In this case, the formation of a nanocomposite will take place due to a deep intercomponental penetration of disperse phases at the nanolevel during the course of sol-gel reactions[31,33]. Such an approach in combination with chemical or physical peptization will obviously make it possible to realize a simple way to synthesize sols of crystalline mixed oxides at low temperatures directly.

For example, we have studied[33] the formation of crystalline $CoTiO_3$ depending on stoichiometric ratios of reactants and subsequent annealing temperature. Synthesis of reactants proceeded in a single stage by mixing two solutions. The first solution was obtained by peptization of pyrochroite in highly acidic aqueous medium upon stirring and heating to 70°C, and the second one was prepared by mixing isopropyl alcohol and titanium isopropylate (C = 0.05 M). Stirring of the resultant solution was carried out for 4 hours at 80°C. Then the effect of stoichiometric ratios of components on the structure of the formed products was studied. Table 1 lists molar ratios of reagents for every experiment and results of the experiments.

Table 1

Stoichiometric ratios of components for every experiment

Experiment No.	**1**	**2**	**3**	**4**
$Ti(OC_3H_7)_4$ mol	0.027	0.027	0.027	0.027
$[Co(OH_2)](OH)_2$ mol	0.002	0.008	0.011	0.013
HNO_3 mol	0.012	0.012	0.012	0.012
H_2O mol	2.778	2.778	2.778	2.778
Temperature of formation for $CoTiO_3$	900 °C	900 °C	80 °C	530 °C
Image of the formed product	 1	 2	 3	 4

Visual data of thermal analysis for systems 1, 3, and 4, see Fig. 8, demonstrate that only under certain conditions, Sample 3, the formation of a single-phase system, which does not undergo phase transitions during heating, is observed. This conclusion is confirmed by the absence of characteristic thermal effects in the region of 450°C from the DTA and TG analysis. The most essential result is presented in Fig. 9c . It is shown that annealing the hydrated cobalt-ilmenite-type crystallites does not lead to phase and polymorphic transformations in a material, except for removal of the adsorbed and chemically bonded water. This conclusion confirms the possibility of forming the $CoTiO_3$ prestructures as a result of performing a low-temperature sol-gel synthesis without subjecting a material to a subsequent heat treatment.

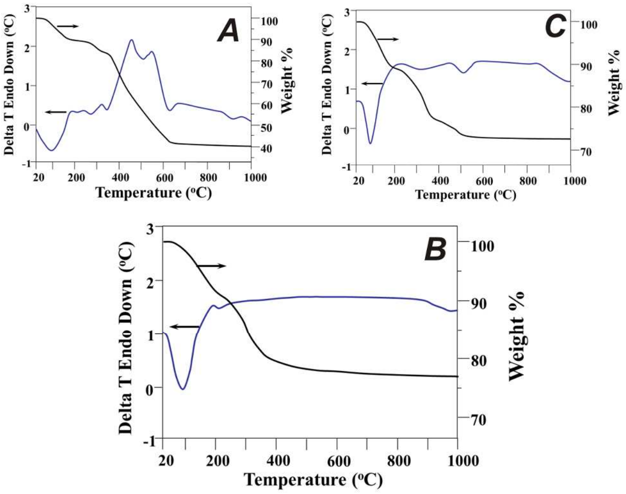


Figure 8. Thermal analysis of samples obtained according to experimental conditions of experiments: a) 1; b) 3; c) 4.

A number of articles on producing sol-gel mixed oxides possessing a high degree of crystallinity and, as a consequence, high functional characteristics is continuously increasing now. In our papers[31,33] , we have proved the possibility of obtaining crystalline mixed oxides using sol-gel chemistry for several systems without annealing stage.

4. Properties and application.

Development of low-temperature methods of producing crystalline phases of metal oxides from solutions will allow to extend the areas of their practical application substantially. Modern materials science numbers about 0.5 million of inorganic substances, the most part of which are thermally stable, whereas there are more than 27 million possible organic substances. Selection of optimal conditions for sol-gel synthesis of crystalline phases of inorganic oxides opens new possibilities for producing organo-inorganic hybrids with unique properties, the majority of which are still expected to be produced and studied. In this section, we will present some examples, which perfectly combine boundless possibilities of low-temperature sol-gel synthesis of crystalline oxide systems.

4.1. Electronics.

Among conductive ceramic materials, the most popular transparent films are ITO and FTO ceramics. High optical transparency and low film resistance have resulted in its wide application in many areas[144-147]. However, these are completely unsuitable for flexible devices because of their brittle nature. Moreover, a rapid increase in the price of indium and the absence of methods for obtaining similar systems at room temperature and atmospheric pressure with a minimum set of equipment motivated us to create a new class of transparent, conductive and flexible systems with good adhesion. This was achieved by entrapment of silver nanowires within sol-gel materials[142]. We will dwell here only upon the samples which showed excellent combination of transparency/conductivity and both of these samples were prepared with *crystalline* hydrosols –

boehmite (AlOOH) and anatase (TiO_2). A very simple procedure has been applied for the preparation of the films: mixing AgNWs and hydrosols at different ratios with a subsequent spraying on a substrate. In contrast to the other transparent conductive oxides, this method can be mastered by any living person. It is interesting to note that for crystalline matrices, the greatest electrostability of films with an optimum set of transparency and conductivity was observed, which reveals a crucial role of nanocrystals in improving operational characteristics of the samples.

SEM images of such films are shown in Fig. 9. In that work, four key parameters of these films were determined: conductivity comparable to ITO analog, excellent electrostability, high flexibility and exceptional adhesion to the substrate. Results obtained in the present work[142] are of great interest not only from the point of view of producing promising materials for flexible electronics, but also because they are actually precursors for creating absolutely new devices. Entrapping an organic dopant into a crystalline sol-gel matrix will allow to obtain new sensors for bioapplication (due to biocompatibility of boehmite and silver), as well as electrochromic coatings, solar cell elements, accumulators and supercondensers (due to crystalline anatase in the AgNW@TiO_2 composite).

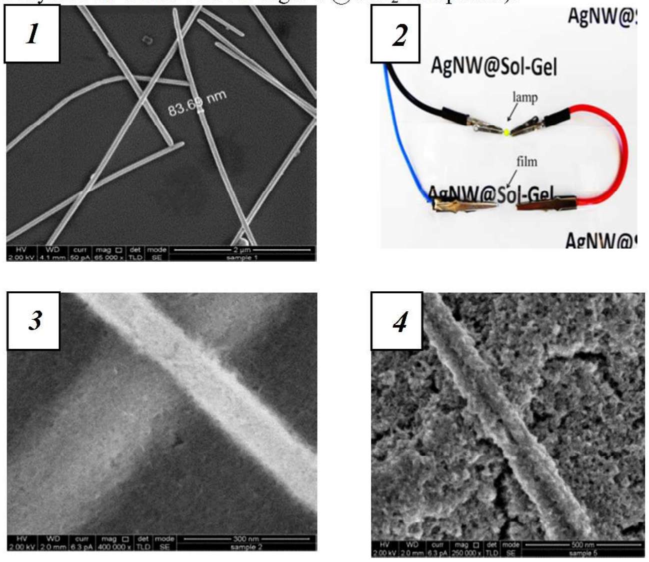


Figure 9. The SEM images of free (1) and entrapped AgNWs: AgNW@Al_2O_3 (3), AgNW@TiO_2(4). Demonstration of AgNW@Al_2O_3 as a transparent and conductive film – the LED bulb is lit (2).

4.2. Bioapplication.

A major obstacle in the introduction of bioactively-doped sol-gel based materials for medical applications has been the fact that the most widely studied sol-gel material, silica, despite being a GRAS material widely used as an additive in food and drug formulations, is still not approved by regulatory agencies for parenteral injections. In the works[27,109] , it was pointed to a potential solution of this problem by shifting the weight to alumina, which is approved by FDA and EMA for injections as the most common immunologic adjuvant. And again we have to address here to the ONLY crystalline phase of alumina to be used. Out of the six crystalline phases of alumina, the biologically active form of alumina used as an adjuvant in current vaccines is boehmite. Boehmite (AlOOH) adjuvants used in commercial vaccination for more than 70 years have gained widespread recognition and are considered to be safe for humans. Prospects of employing sol-gel boehmite as an alternative to existing alumina-based adjuvants consists not only in the possibility of entrapping bioactive molecules, but also in the possibility of widely adjusting the porous structure of the matrix carrier by initial conditions of synthesis.

An original approach was developed to obtaining the matrix (boehmite) itself using highly pure and biocompatible materials. This was considered impossible previously and required the use of acids or additional chelate molecules. Adding therapeutic enzymes to the crystalline hydrosol allows to substantially increase stabilization of an enzyme. The thermal stability was studied in detail, by the follow-up of kinetics, by differential scanning calorimetry and by circular dichroism. These techniques indicate that the entrapment shifts the temperatures of denaturation higher by 30–50°C. The authors have even shown that the boehmite matrix over a certain temperature range enhances the activity of the enzymes quite significantly with temperature, whereas free enzymes die out at these conditions. The DCS signals of temperature denaturation for free and entrapped acid phosphatase which is used for treatment of bone dysplasia are shown in Fig.10.

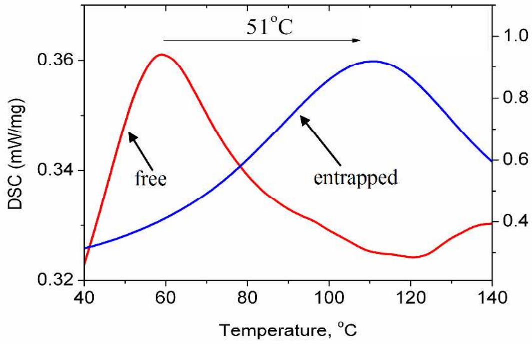


Figure 10. DSC analysis of free and entrapped acid phosphatase. An increase by 51°C in the denaturation temperature is observed for AcP@alumina (right curve) as compared to free AcP (left curve).

The similar observations were found also on horseradish peroxidase (HRP) used for release of toxic drugs in vivo from their pro-drugs and asparaginase (ASP) used for starving cancerous leukemia cells. Thus, when HRP or ASP are heated in solution to 75°C, their activity drops by 65% and 72%, respectively, but when entrapped it drops only by 1.2% and 1.9%, respectively.

The exceptional thermal stability in case of entrapment within alumina leads us to suggest that the rotational mobility of enzyme within alumina is restricted even to a higher degree than in silica providing the needed conditions for thermodynamic stability. This observation can be related to the crystalline nature of the alumina matrix. Amorphous silica is relatively soft compared to alumina, and during the heating the structure can still rearrange, providing more freedom leading eventually to earlier unfolding. The dense structure of crystalline boehmite nanorods of alumina keeps enzymes tighter, preventing easy unfolding[109].

Controlling the release rate for medications in crystalline sol-gel matrices provides large discretion due to the possibility of adjusting not only the size of particles, but also their shape. The results obtained, see Fig. 11, confirm the possibility of a slow release from crystal matrices. Cisplatin, an antineoplasmic medicine was used as a model drug in this study. Cisplatin was entrapped within alumina by adding the drug during the sol–gel manufacturing process. Furthermore, the research aim is the determination of the dynamics of cisplatin release from sol–gel processed alumina xerogels. Taking into account the volume of global market of biomaterials with slow drug release and controlled delivery, the present work is of major applied importance.

The kinetics of CSP release from the alumina into histidine buffer (pH=7.4) was measured and the results are presented in Figure 11. It is seen that the profile of cisplatin release from alumina is represented by gradual release. This behavior was found to fit the Weibull model. The 30% of total amount of CSP was released during 12 hours (Fig. 11a). The long release kinetics of CSP was studied as a function of time during two weeks (Fig. 11b). After 12 days assay, the studying systems showed similar trends of release. During the period, alumina showed 88% release of CSP.

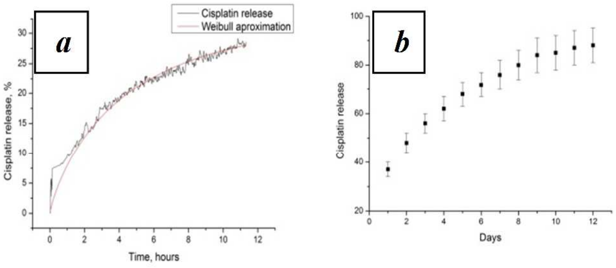


Figure 11. Short time (a) and long time (b) release profile of CSP from alumina and its fit to the Weibull model.

4.3. Magnetic properties.

Diluted magnetic semiconductors (DMS) are one of the most promising materials in spintronics[148, 149]. Among a number of materials belonging to DMS, the greatest interest is paid to the systems based on crystalline zinc and titanium oxides doped with the 3d metals, since the Curie point for such nanomagnetics is close to room temperature[150,151]. It is worth noting that at present methods of point physical manipulation are, as a rule, employed for producing DMS structures implying the use of high-vacuum equipment and high temperatures. Therefore, obtaining DMS nanocomposites with an organic matrix becomes impossible, so that using low-temperature sol-gel synthesis in this case also seems to be rather promising. Existing approaches to producing ZnO or TiO_2 DMS doped with the 3d metals represent various variants of classical sol-gel method employing various precursors and reductants of metal ions, action of UV irradiation, various catalysts of precursor hydrolysis, additives of polymers or surfactants to achieve homogeneity for a system of sols or gels[153,154]. Production of solid semiconductor oxide films doped with the 3d metals was the result of such syntheses. Such an approach implies thermal treatment of the product of sol-gel synthesis (temperatures up to 700°C), which affects the structure and properties of products, often resulting in undesirable effects – the formation of chemical compounds, a change in the degree of oxidation etc. This is confirmed by the results of numerous works on physics of diluted magnetic semiconductors. Originality of the studies performed by us comes from the fact that a new approach to synthesis of DMS has been developed for the first time, which allows to produce well-crystallized materials in liquid phase in the process of sol-gel synthesis without annealing stage.

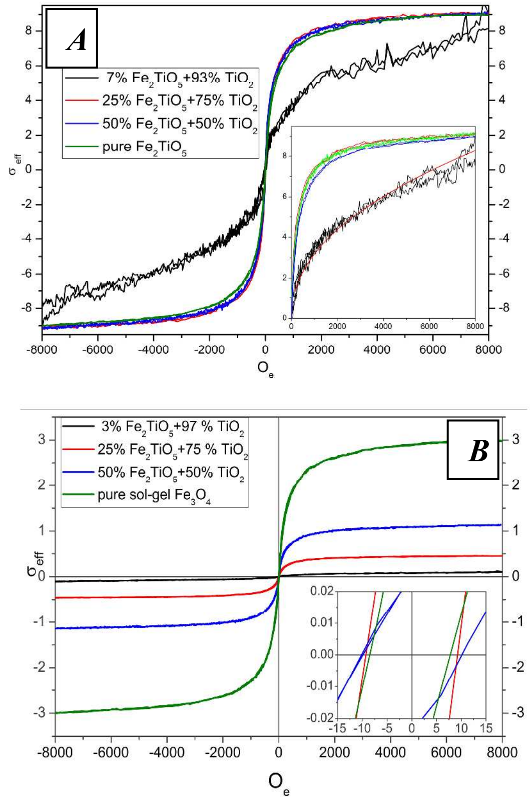


Figure 12. A) Effective magnetization of nanocomposites with the inorganic phase content of 50% in polyvinylpyrrolidone calculated for conditions of a uniform material vs. magnetic field intensity. PVP is used as a filler. B) Curves of magnetization for Fe_2TiO_5+TiO_2 composites in a PVP matrix calculated with respect to the magnetic phase content.

During realization of the project we have used a methodology based on the comparative analysis of magnetic and transport characteristics of materials possessing identical chemical composition, but different in their structure and the degree of oxidation of elements forming the basis of magnetic phases. Conditions leading to the formation of both magnetic and non-magnetic phases upon interaction of the system components have been simulated. It allowed to reveal the effect of the presence of non-magnetic phases emerging in the magnetic process on magnetic properties of the final products. Performed studies have shown that the conditions of sol-gel synthesis suggested by us allow to use low-temperature methods for producing DMS possessing ferromagnetic properties at room temperature. This success is, first of all, determined by crystallization of products from aqueous solutions with possibility of forming stable sol-gel systems. Fe_2TiO_5[30] produced in the process of low-temperature sol-gel synthesis is a solid solution of the Ti^{4+} ion isomorphically replaced by Fe^{3+} in a xerogel of titania crystallized in the structure of anatase, with the Fe/Ti stoichiometric ratio corresponding to pseudobrookite containing a number of the Fe^{2+} ions. Magnetic properties arise in this material due to an incomplete transition of Fe^{2+} to Fe^{3+} upon peptization of Fe_3O_4 nanoparticles in the medium of nitric acid. Apparently, architecture of the produced material is composed of nanoparticles constructed according to the nucleus-cover type. These heterostructures include nuclei of magnetite nanoparticles whose surface is wrapped in a Fe_2O_3 cover, in which the Fe^{3+} ions are isomorphically replaced by the Ti^{4+} ions.

Apparently, the phase volume of the cover of Fe_2O_3 with the Fe^{3+} ions isomorphically replaced by the Ti^{4+} ions is considerably greater than that of the Fe_3O_4 nucleus. Introducing additional quantities of titania upon producing materials similar to diluted magnetic semiconductors results in distribution of such particles over the material volume. The analysis of magnetization curves for some of the produced materials (Fig. 12A) has shown that all of them possess weak coercivity in weak fields, i.e. PVP-Fe_2TiO_5+TiO_2 nanocomposites possess ferrimagnetic properties.

Reducing magnetic characteristics to the relative magnetic phase content levels the characteristics of materials with high concentration of magnetic compounds, Fig. 13B. As Fig. 12B suggests, a 7% Fe_2TiO_5 content in the PVP matrix the magnetization parameters of the nanocomposite decrease as compared to the materials containing 25 and 50 % Fe_2TiO_5. Apparently. This is due to a decrease in the sizes of nanoparticles in the composite and a decrease in the volume of the magnetite nucleus in the structure of nanoparticles that comprise it. It may also be due to peculiarities of synthesis:while producing a 5% composite the synthesis of the magnetite sol is performed in diluted solutions, which results in the formation of ultrasmall magnetite particles, smaller than those produced in the synthesis of more concentrated magnetite suspensions.

4.4. Photovoltaic and photocatalytic activity

Nowadays, it is a great challenge to synthesize crystalline TiO_2 possessing high photoactivity[154] by using low-temperature methods without annealing stage. Its popularity as a photocatalyst is mainly due to its high chemical and thermal stability, as well as low toxicity and cost[155]. Application of titania strongly depends on its specific physico-chemical and semiconductor features[156]. The degree of crystallinity and the specific surface area are considered to be the main characteristics affecting photoactive properties. An increase in crystallinity results in prolongation of the rate of recombination of photoinjected electrons and holes, which increases reducing and oxidizing ability of the photocatalyst. An increase in the surface area leads to an enhancing adsorption ability for target molecules and, hence, results in acceleration of a catalytic process. However, both of these parameters are mutually exclusive and search for an optimum ratio is still going on [44]. High crystallinity is achieved upon annealing the samples at temperatures about 400°C and above. The same approach is, as a rule, used[158,159] also for obtaining materials with high photocatalytic properties. However, an increase in the degree of crystallinity results in collapse of the porous structure and a sharp decrease in specific surface area. Data listed below in Table 2 on comparison of morphological and photocatalytic properties evidently show that using low-temperature techniques of TiO_2 crystallization provides photodestruction effects analogous to those observed with the commercial product Degussa P-25, therewith maintaining high specific surface area and saving megawatts of energy expended in thermal treatment (annealing temperature 350 °C).

Highly photoactive titania-doped nanocrystals prepared by annealing-free approach.

However, pure TiO_2 absorbs only a rather insignificant part of solar spectrum due to its bandgap width. In this case, the most economically effective modifier the Fe^{3+} ions, which are characterized by the red absorption region. Besides, the Fe^{3+} ion is the only species having a 0.062±0.003 nm ionic radius similar to that of the Ti^{4+} ion. The Fe(III)-doped TiO_2 photocatalysts are considered among the most promising of those working under the effect of solar light. In particular, Kisch et al.[160] reported the ability of $Fe_2O_3 \cdot nTiO_2$ (n = 1, 2) based compounds to non-enzymatically bind nitrogen molecules to form ammonia in the presence of air moisture and solar light. Such nitrogen fixation is the second most important chemical process in nature next to photosynthesis. However, doping crystal lattice under the low-temperature sol-gel synthesis conditions is a difficult technical problem as compared to production of simple oxides. Mechanisms of low-temperature doping of anatase by a soft chemistry method were first reported in Ref.[30]. Such doping lead to a sharp increase in photoactivity under visible-light irradiation. Fig. 13 demonstrates the mechanism of the formation of Fe(III)-doped TiO_2 nanocrystals using nitric acid as an activator of ion mobility.

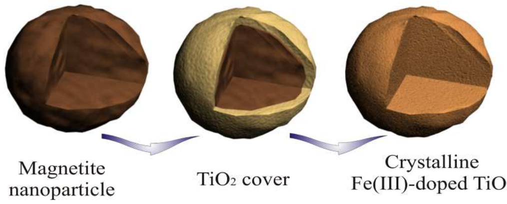


Figure 13. Visualization of the formation of Fe(III)-doped TiO_2 nanocrystals by a soft chemistry method.[30]

It was the first example of successfully performed synthesis of Fe(III)-doped titania by low-temperature sol-gel route without annealing. Results of assessing photocatalytic and photovoltaic activity, see Fig. 14, have revealed a drastic increase in photoactivity of Fe(III)-doped TiO_2 nanocrystals as compared to pure titania. It was found that the most pronounced photocatalytic effect is attained upon doping the anatase crystal lattice with more than 7 at.% and less than 13 at.% of iron. It has been shown that excessive dopants can act as recombination centers[32], promoting the recombination of electron-hole pairs and increasing semiconductor properties. These results imply high potential for application in the utilization of solar light, the absence of annealing stage for preserving functional characteristics of materials allowing to coat a photocatalytically active layer of the Fe-TiO_2 nanoparticles on finished surfaces, including those possessing low thermal stability. According to a photovoltaic test, these films demonstrate an excellent superiority photoresponce, even those annealing-free.

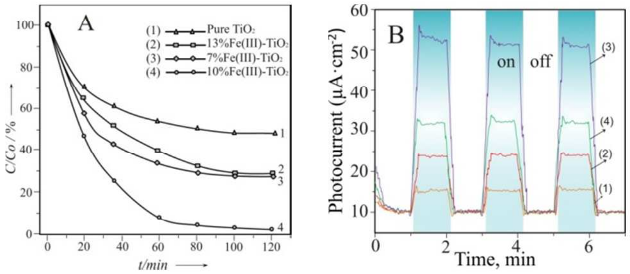


Figure 14. Photocatalytic activities (A) and photocurrent responses (B) of Fe(III)-doped TiO_2 samples containing different amounts of iron: ((2) 13 at.% Fe(III); (3) 7 at.% Fe(III); (4) 10 at.% Fe(III)) and pure TiO_2 (1) under visible light.

Photoactivity of nanosized titania produced using low-temperature sol-gel method in the treatment of textile materials. Production of textile materials is an age-old branch of industry, which provides multibillion profits for the enterprise owners. The basis for modern development of this branch is determined by adoption of new and economically super-accessible methods promoting substantial changes in functional properties of a product with minimum expenses for additional treatment prior to output. Below we give two examples when low-temperature sol-gel method proved to be the most successful way to solve such problems.

A simple modification of the cotton fabric surface with crystalline titania nanosols.

So, the main (if not the most important) subdivision of innovative "smart textile" industry represents products which display unique self-cleaning properties under solar light irradiation[161]. Achieving this effect is performed by cross-linking a textile fiber chemically to nanosized titania crystallites[162]. For this purpose, the majority of classical methods employ suspensions of highly crystallized TiO_2 powders comprising solutions of intermediates, which provide tight covalent bonding and exhibit unique properties of thefinal product. It is hard to imagine, what made the textile giant factories develop and inculcate these approaches, since multistageness, nonuniformity, and commercial inexpediency are obvious drawbacks of these methods. It is clear that the use of low-temperature sol-gel method allowing for the formation of crystalline TiO_2 sols in aqueous solutions with activity analogous to that of annealed samples is the most proper and adequate solution to considered problems. Moreover, the presence of gelation stage will allow carrying out uniform coating of optically transparent nanosized photoactive layer without using modifiers and additional cross-linking agents. In particular, we have carried out experiments on modifying cotton, see Fig. 15, and polyester, see Fig. 16, fibers with crystalline titania nanoparticles produced using low-temperature sol-gel method[24,34].

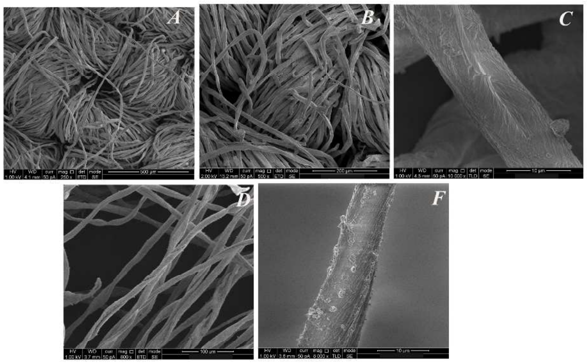


Figure 15. Morphology of cotton fibers for non-treated (A–B) and treated TiO_2 (Acac as a peptizer)[24], C–D, and TiO_2 (physical activation)[34].

As seen in this case, the formation of uniform external coating of fiber is observed, with characteristic composition provided by the EDX analysis data. Photocatalytic measurements have revealed that almost complete destruction of the model dye is achieved in 45 minutes of UV irradiation at specific content of the active component with respect to cotton fiber of no more than 0.1%, see Fig. 16.

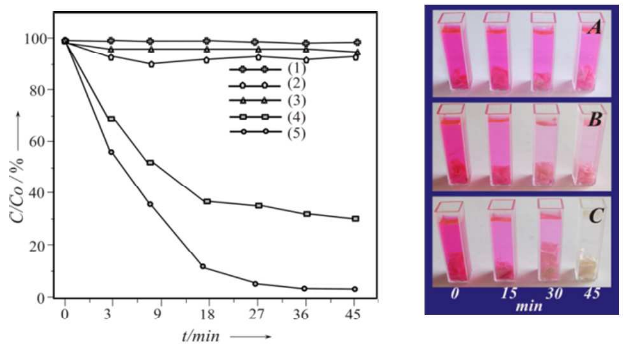


Figure 16. Left side: Decomposition of Rhodamine B dye: (1) Rhodamine B dye solution with no fabric; (2) Rhodamine B dye solution containing control white fabric; (3) Rhodamine B dye solution containing cotton fabric treated with titania nanosols and kept in the dark; (4) Rhodamine B dye solution containing cotton fabric treated with titania nanosols prepared as in Ref.[24], (5) Rhodamine B dye solution containing cotton fabric treated with titania nanosols, prepared as in Ref.[34] and exposed to UV irradiation for different periods of time. Right side: images of Rhodamine B dye decomposition in aqueous solution containing (A) control white fabric cotton; (B) cotton fabric treated with titania nanosols prepared as in Ref.[24], (C) cotton fabric treated with titania nanosols prepared as in Ref.[34].

Coating TiO_2 hydrosol on the surface of a polyester fiber is the second example successfully demonstrating the prospects of low-temperature sol-gel process[136]. A problem with coating a crystalline hydrosol is poor wettability of polyester. In our work[136] , we have developed an original method allowing to simultaneously solve the problems of wettability and tight fixation of titania nanoparticles on the surface of a polyester fiber, which can be easily adopted to the analogous systems. The method consists in using a co-solvent. Hydrosol containing TiO_2 nanocrystals was first mixed with isopropanol and then with chloroform. As a result, a homogeneous sol was formed. Chloroform dissolves the external surface of the polyester fiber providing conditions for penetration of nanoparticles into near-surface layer of the fiber. After drying we obtained a composite with uniform distribution of titania nanoparticles over the entire fiber surface.

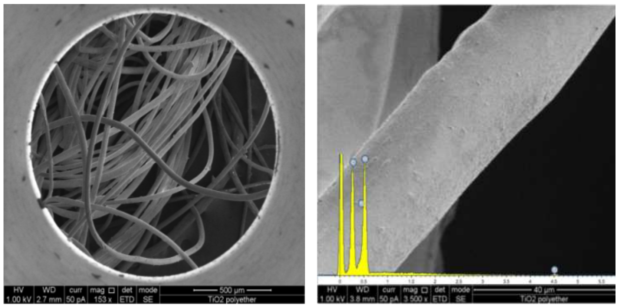


Figure 17. SEM images of polyester fibers treated by TiO_2 hydrosol[136].

As a result of such modification, we have attained unique self-cleaning property of the polyester fiber, which was exhibited even after 20 washing cycles, see Fig. 18.

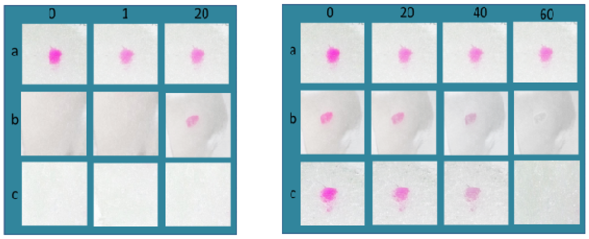


Figure 18. Self-cleaning test using Rhodamine B versus number of washing cycles (left side) and UV irradiation time (right side). The images shown are the exposed sides of only polyester substrates (a), titania[24]-coated original polyester substrates (b), and titania[34]-coated polyester substrates (c). The numbers stand for washing cycles before the test (A) and UV irradiation time (B).

Conclusions

Materials science paradox lies in its infinity. Producing new materials, we do not approach the end point when all possible materials are obtained and studied, but rather, to some extent, move on to infinity. Diversity of produced materials yields even greater diversity of all possible composite derivatives. Revolution in materials science arises from discovery of new methods of synthesis that are usually simpler and less resource-consuming. The history of developing materials science itself is a perfect example. Many great discoveries have been made by improvised methods.

In this review, we draw the reader's attention to the obvious facts. Despite that already a large number of papers is devoted to the low-temperature preparation of crystalline sols of various oxides, the vast majority of works still deals with the preparation of amorphous products. Shifting the trend of development towards the synthesis of crystalline hydrosols using low-temperature methods significantly broadens an outlook for practical applications and leads to the development of low-cost and energetically effective approaches easy to handle even by untrained personnel.

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