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ARTICLE

A facile sol-gel synthesis of impurity-free nanocrystalline titania

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This paper reports an original technique that provides a highly pure crystalline sol of titania with controllable particle size by ultrasonic activation of the hydrolysis products of titanium isopropoxide in an aqueous medium at a near-neutral pH, which is potentially promising in impurity-sensitive electronics and biochemical engineering. Optimal conditions (H_2O/TIP ratio, sonication time, *etc*.) for preparation of stable nanocrystalline titania sol were adopted. A new mechanism of regulation of aggregation and polycondensation under ultrasonic irradiation is proposed. Entrapment of human serum albumin (HSA) in the formed porous titania matrix results in high thermal stability of the proteindopants: The denaturation temperature of HSA is shifted by 31 °C.

Introduction

Nano-sized titania has unique properties and finds its application in many branches of science and technology[1-13]. Its high chemical and thermal stability and photoactivity turned it into a real commercial product of nanoindustry. Its production usually involves high-temperature or harsh chemical conditions to convert the amorphous phase of titanium oxohydrate to the active phase of anatase[14-16]. The most recent prospects of nanocrystalline TiO_2 concern electronics and biochemical engineering where the problems of adjusting the growth of the crystalline phase and nucleation as well as those of synthesizing impurity-free materials remain unsolved. 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_2nanocrystals, which results in a number of certain benefits:

1) it allows to perform functional and structural modification with thermally unstable species, such as biomaterials[10], metal-organic frameworks (MOFs)[17], dyes[18], organic LED, in situ by entrapping directly in 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. A description of potential applications of low-temperature methods of crystallization of colloidal phases in aqueous solutions is also reported in a recent review[19].

A low-temperature procedure for the synthesis of TiO_2 using a water-soluble titanium complex and enzymes was developed[20]. Furthermore, the formation of nanocrystalline and monodisperse TiO_2 from a water-soluble and stable precursor, ammonium oxo-lactato-titanate, $(NH_4)_8Ti_4O_4(lactate)_8\cdot 4H_2O$ was described[21]. Previously, we have studied mechanisms of the growth of TiO_2 crystalline phasecaused by chemical peptization in aqueous solutions[22]. The processes of thermal dehydration of hydrolysisproductsof $TiCl_4$ to obtain a crystalline sol of anatase was investigated[23]. Ref. [24] reports an original method of obtaining a suspension of nanocrystalline TiO_2 powder using titanium methoxide as a precursor, which possesses an anomalous 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, which appeared to be inorganic salts in most studies, inevitably resulting 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[25]. Above all, a complex effect of low-temperature conditions on the formation of crystalline titania, growth of crystalline phaseand nucleation remains unclear.

A solution to these problems is the use of physical methods of activating the colloidal phases in nano-sized titania-based aqueous solutions. For example, B. Reeja-Jayan et al. were the first to perform microwave-assisted formation of TiO_2nanocrystalline films on a flexible polymer substrate, which were suitable for use in electronics[26]. In our recent paper[27] we also report potential applications of low-temperature sol-gel methods for the formation of conducting coatings. M. Kanna et al.[28] employed hydrothermal treatment at 80°C to obtain an anatase-rutile photocatalyst. Besides, it was shown that obtaining nanoparticles of anatase in water can be achieved by dialysis and aging without heat treatment. Abedini et al.

[29] synthesized 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 obtaining stable sol-gel systems.

In this work we have used a low-temperature ultrasonic-assisted method to directly prepare nanocrystalline TiO_2 sol-gel materials from hydrolysis products of titanium isopropoxide in an aqueous medium with no addition of modifying agents.

Such an approach eliminating high-temperature effects with the purpose of forming active crystalline phases in an aqueous medium at a neutral pH enables obtaining an impurity-free sol of crystalline TiO_2.

Materials, syntheses and methods

Chemicals

Titanium(IV) isopropoxide (TIP) 99.999% (Aldrich), Albumin from human serum (HSA) >99%(Aldrich) and deionized water (□5μS/cm) were used without additional purification.

Synthesis of TiO_2nanoproducts

TiO_2 nanoparticles were synthesized by hydrolysis of TIP in deionized water, under vigorous stirring (1000 rpm) and ultrasonic (US) irradiation (24 KHz, 300 W/cm^2). TIP was injected dropwise into the deionized water during 3 min. The mixture was sonicated continuously in air for 1–3 hours. As previously shown[29], the use of short intervals of US treatment does not provide size regulation. The sonication was conducted without cooling so that the temperature was raised from 25 to about 75°C at the end of the reaction. Fig. 1(a) shows the diagram of producing a colloidal sol of TiO_2 depending on the H_2O/TIP ratio and sonication time. The data obtained allow to determine optimum conditions for the formation of a stable nano-sized TiO_2 sol as indicated by the smallest dynamic light scattering (DLS) particle size.

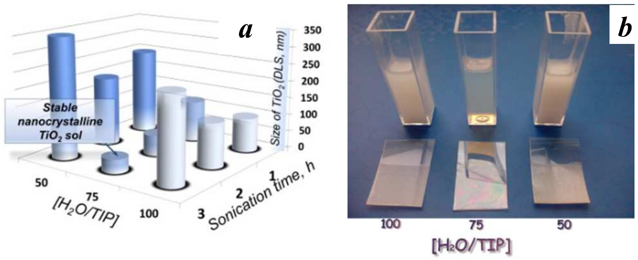

Figure 1. (a) A 3D plot of TiO_2 size (determined by DLS) vs. sonication time and H_2O/TIP ratio.(b) Visualization of the formation of TiO_2 nanoparticles in the suspension and films obtained as a result of ultrasonic irradiation for 3 h.

Upon ultrasonic treatment for 3 h the most stable colloidal system appeared to form at the ratio H_2O/TIP = 75, see Fig.1 (a,b). Images of solutions produced after 3-hour ultrasonic treatment and respective dip-coating TiO_2 films are shown in Fig. 1(b). The films were dip-coated (V = 0.2mm/s) from water solutions on poly(ethylene terephthalate)(PET) substrate.

Entrapment of proteins in TiO_2

Production of hybrids HSA@TiO_2 involved two stages:

Stage 1. A nanocrystalline sol of titania was produced at 75 °C under 3-hour ultrasonic irradiation in a procedure similar to that described above.

Stage 2. The albumin entrapment was carried out at room temperature by dissolving 0.03 g of the protein in 20.0 mL of the titania sol. The suspension was aged for 3 h and dried at 20 °C under vacuum overnight.

Characterization techniques

The equipment employed in this work was a 24 kHz ultrasonic generator (UP400S), with a standard titanium horn and a 7 mm diameter replaceable flat titanium probe. The oscillator power was set at various points in the range from 40 to 80 (on a scale of 100). The acoustic power was 300 W/cm^2.

Wide-range X-ray powder diffraction data have been processed using Bruker D8 Advance equipment with CuKα (λ = 154.18 pm).

The samples for transmission electron microscope (TEM) and scanning transmission electron microscopy (STEM) characterization were prepared by dispersing a small amount of sample in ethanol to form a homogeneous suspension. A drop of the suspension was deposited on a carbon-coated copper grid for HR TEM and STEM observation (FEI TECNAI G2 F20, operated at 200 kV).

The size of the sol particles in an aqueous solution has been characterized by dynamic light scattering data (DLSD) using Malvern ZetaSizer Nano equipment at 20 °C with He-Ne 10 mV laser at a wavelength of 633 nm.

To study the samples using scanning electron microscopy (SEM) and EDS analysis, a silicon wafer was coated with a solution of the sol and, after complete drying in a vacuum desiccator, was investigated without additional sputtering with an ultra-high resolution electron microscope Magellan 400L (Field Emission Inc.).

Fourier transform infrared spectroscopic (FTIR) data have been processed using Bruker Vertex 80v spectrometer.

Thermogravimetry-differential thermal analysis (TG-DTA) was carried out with an STA 449 F1 Jupiter system (Netzsch).

DSC curves were obtained either with a 204 F1 Phoenix NETZSCH or with a Mettler-Toledo DSC 823e apparatus. Heating rate of 1 °C min^{-1} was used from 25 °C to 170 °C under nitrogen. For the DCS time analysis, the gelation process was stopped by lyophilization after 5 hours and 1,2, and 3 days.

Results and Discussion

In this study there were three challenging questions: 1) Can a stable crystalline TiO_2 sol be obtained only under ultrasonic treatment? 2) How do external conditions affect the formation of the final material? 3) What are the prospects for using such sols in biotechnology and electronics?

The developed technique of obtaining a nanocrystalline TiO_2 sol in an aqueous solution under ultrasonic irradiation implies the use of near-neutral pH values. No mononuclear titanium ions can exist at this pH. Under these conditions, nuclei with an anatase structure are successfully formed at a room temperature[10,19,21], but they are covered with a fairly thick amorphous shell, Fig.2, containing the remaining organic ligands[10]. Generally, the hydrolytic transformation of metal alkoxides occurs via so-called Micelle Templated by Self-Assembly of Ligands (MTSALs) mechanism: the oxide particles nucleate via formation of oxometallate species with crystalline cores possessing the structures analogous to those of the corresponding metal oxides and amorphous shells bearing residual ligands[19].

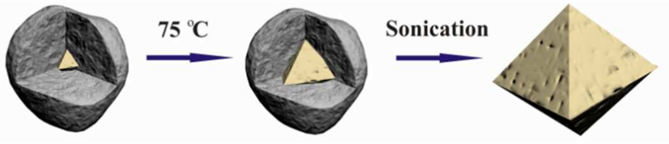

Figure 2. Visualization of crystalline phase growth from an amorphous nanoparticle under the influence of temperature and sonication.

The ligands are desorbed upon heating, the diffusion of cations is accelerated and the size of crystallization centers is increased, Fig.2.

The effect of sonication is just based on selective energy pumping into MTSALs resulting in enlargement of the crystalline domains, fig.2. The successive dehydration via interaction of the water molecule and hydroxyl group gives anatase TiO_2.

Fig. 3 shows the typical TEM and SEM images of the as-prepared TiO_2 nanoproducts. It can be seen that the TiO_2nanoproducts are uniform and have an average size of formations of about 10 nm (see Fig. 3 a, c).

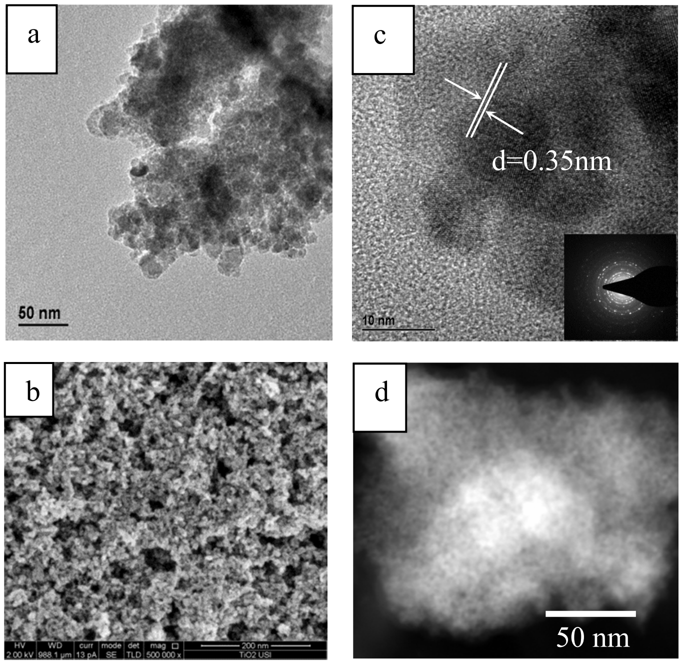

Figure 3. Typical TEM (a), SEM (b), HRTEM (c), and STEM (d) images of the as-prepared nanocrystalline TiO_2.

A detailed analysis of morphology of particles of the TiO_2 powder (dried in the air at 80°C) according to STEM, Fig.3d, shows the formation of highly porous aggregates produced from nanoparticles with narrow size distribution. According to HRTEM, Fig.3c, it is found that the material represents a single-phase nanocrystalline system containing TiO_2 (anatase). The structure of the particles is characterized by clear crystalline lattice fringes, with an average size of crystalline formations of about 5–10 nm, Fig. 3c, which correspond to the (101) planes of the body-centered tetragonal structure of anatase (d-spacing 0.35 nm).

The attached SAED pattern (shown as an insert in Fig. 3c) could be indexed as the (101) zone axis diffraction, which further confirmed the single crystalline anatase structure.

An X-ray diffraction (XRD) pattern of the synthesized TiO_2 produced under 3-hour ultrasonic treatment at the ratio H_2O/TIP = 75 is shown in Fig. 4. The diffraction peaks at about 25,4° (101), 37.9° (004), 48.1° (200), 54.1° (105), 54.9° (211), and 62.8° (204) can be also indexed as anatase. In Fig. 5(A) a and b, the bands at 2960–2860 cm^{-1} and 1450–1370 cm^{-1} are assigned to the $–CH_2–$ and $–CH_3$–stretching vibrations in isopropanol, respectively. This means that a certain amount of water and isopropanol (hydrolysis product) was adsorbed at the surface of TiO_2. When sample c is heated at 75 °C for 3 h (Fig. 5(A)c), the bands at 2957–2858 cm^{-1} and 1450–1376cm^{-1} totally disappeared, suggesting the loss of adsorbed isopropanol at the surface of TiO_2.

Sections of the FT-IR spectra are shown in Fig. 5(A). The spectra of samples a, b and c showed the same spectral features.

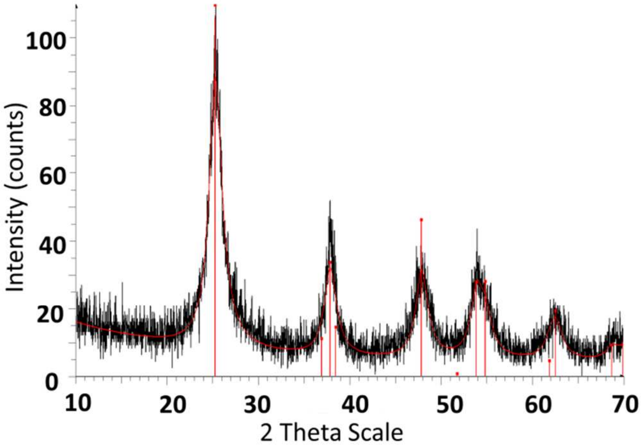

Figure 4. X-ray diffraction pattern of TiO_2, produced by3-hour ultrasonic treatment at the ratio H_2O/TIP = 75.

The OH stretching band at 3350 cm^{-1} is visible. The band at 1625 cm^{-1} corresponds to the bending mode of adsorbed water.

An additional confirmation of a high degree of purity of the synthesized material (≥99%) is also provided by the EDS analysis, Fig. 3B, where the content of pure titania amounts to more than 99%, while the carbon presence of 0.94% is likely to be due to an adsorption of CO_2 from ambient air.

TG-DTA results for the nanocrystalline TiO_2 are illustrated in Fig. 5(B). The data obtained reveal that the total mass loss upon annealing amounts to 5.8 %. The first portion of the mass loss up to 480 K can be due to removal of adsorbed water (2.6%). The mass loss at a higher temperatures can be caused by elimination of H_2O from surface $–Ti(OH)_3$ groups (3.2%). There is no exothermic peak in the range of 673–1073 K, which indicates that no crystallization or phase transition occurred in this temperature range.

Effect of Sonication and H_2O/TIP ratio

It is obvious that water plays an important role in the nucleus formation and the crystal growth. The nucleus formation can take place only at a H_2O/TIP ratio >10 [30]. Multiple nucleus formation can frequently occur rather than crystal growth as the H_2O/TIP ratio increases and this leads to small particles[30]. The formation of particles with maximum diameter was also observed at the minimum ratio H_2O/TIP = 50 (Fig. 1). At the same time, increasing this value to 100 results in an increase in average particle size, particularly upon prolonged ultrasonic treatment. Such nonlinear behavior can be explained by different interconnected factors: An increase in sonication time leads to a decrease in vapor pressure at the boundary surface between reagents in a solution[31], which results in an intense coagulation of particles after their activation by ultrasonic irradiation. If the ratio H_2O/TIP is about 75, this is no longer the case, because high concentrations of nuclei in a solution generate many local hot spots within the sol, so the polycondensation of Ti–OH or Ti–OR is promoted[25] and this enhances the loss of the organic residue (isopropanol) and water, facilitating the formation of a stable highly crystalline sol.

Entrapment of biomolecules

The key prospects of applying this technique for the formation of highly pure titania with adjustable particle size and high degree of crystallinity are due to a possibility of entrapping thermally unstable biomaterials in a porous inorganic matrix of TiO_2. Fig. 6A shows a SEM image of the as-synthesized composite HSA@TiO_2. For successful entrapment, it is of utter importance that the use of a biological modifier should not lead to a change in morphology of the matrix medium, nor should it affect the crystal structure providing high thermal stability.

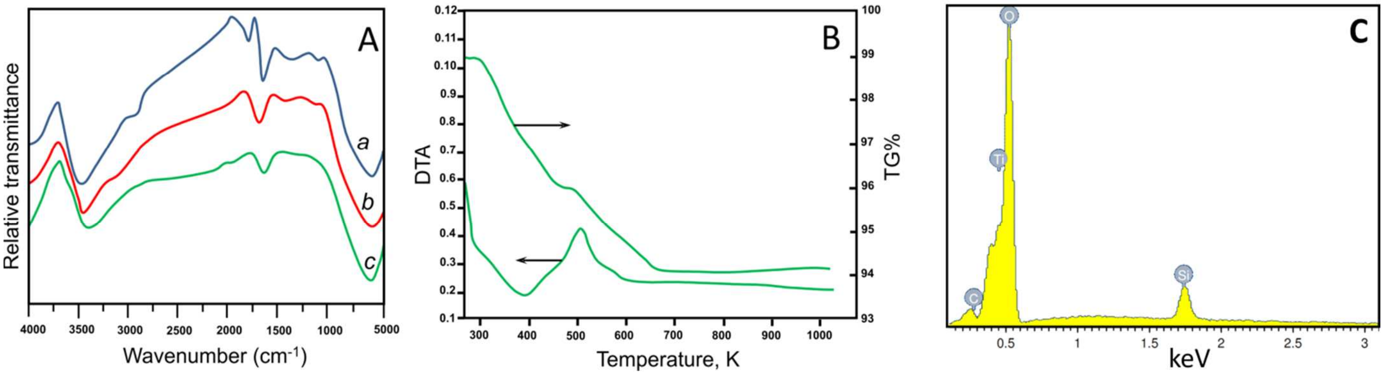

Figure 5. FT-IR spectra (A) of nanocrystalline TiO_2 prepared under 3-hour ultrasonic irradiation at 40 °C (a), 60 °C (b), and 75 °C (c). TG-DTA (B) curves and EDS analysis on silicon wafer (C) for a sample prepared under 3-hour ultrasonic irradiation at 75 °C.

As shown in Fig. 6A, a change in phase composition after entrapping HSA in a titania matrix is not observed. XRD analyses of all of the titanias indicated typical anatase structure Fig. 6B, and Scherrer-equation analysis provides an elementary crystallite size of a few nm (5–6 nm). The IR spectroscopy (FTIR) commonly used for analyzing organic–bio-organic hybrid materials, which should clearly show a superposition of the typical absorption bands of the matrix and the dopant. This was indeed confirmed, and a representative example – HSA@titania is given in Fig. 6C, demonstrating that the IR spectrum of the composite is indeed a superposition of the spectra of HSA and titania.

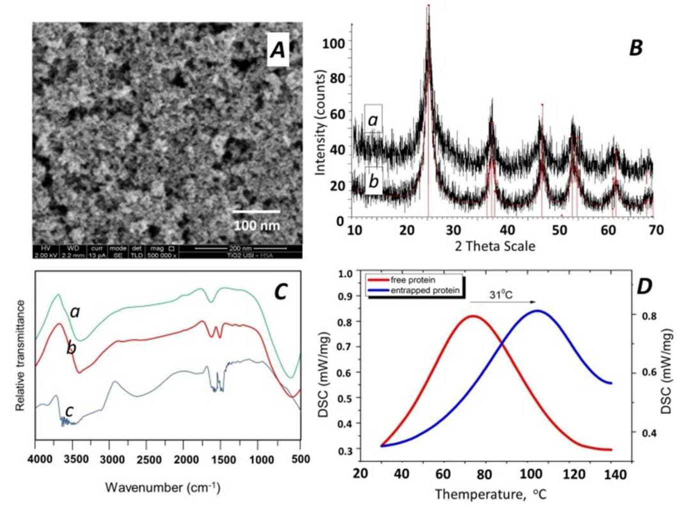

Figure 6. (A) SEM image, (B) X-Ray powder diffraction of (a)composite HAS@TiO_2 and pure TiO_2(b), (C) FTIR spectroscopy of (a) pure titania, (b) composite HSA@TiO_2 and (c) pure HSA. (D) Effect of thermal stabilization of free (red line) and entrapped HSA (blue line) by DCS analysis.

The typical amide bands I and II – the 1700–1600 cm^{-1} stretching vibrations of the C=O bond and in-plane bending vibrations of the N–H bond, and stretching vibrations of the C–N bond at 1570–1510 cm^{-1} [32], are clearly seen both in the IR spectrum of the HSA and in that of the composite.

The thermal behavior is a strong indicator that the proteins were entrapped at all. We have used a sol of the synthesized TiO_2 for thermal stabilization of the proteins with the lowest thermal stability among the known species of biomaterials and have studied the mechanism of entrapping the proteins in a sol-gel matrix and thermal stabilization effects previously[33]. As shown here (Fig. 6), the denaturation temperature of HSA is shifted by 31 °C to 100 °C, an extremely high temperature for denaturation, when entrapped in TiO_2 after three days of aging.

Conclusion

In conclusion, we have developed a new method for the production of a highly pure titania sol with adjustable particle size and a high degree of crystallinity. The ability to produce crystalline thin films and powders of oxide materials like anatase at low temperatures in the absence of isopropanol and amorphous phase has tremendous commercial advantage for thin film electronics, biochemical engineering and, very important, for application in devices utilizing its semiconductor properties, such as solar energy conversion and lithium batteries[34-37]. For the first time, the conditions of formation of stable nanocrystalline titania sol (H_2O/TIP = 75, sonication time 3h) in aqueous media at a neutral pH was proposed. A new mechanism of regulation of aggregation and polycondensation under ultrasonic irradiation is proposed. We have shown that this approach allows an unharmful entrapment of proteins in TiO_2 and that DSC can serve as a sensitive tool for the analysis of the thermal stability of the entrapped proteins. A remarkable stabilization of the entrapped proteins in TiO_2 was found using this method.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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1 R. Comparelli, E. Fanizza, M.L. Curri, P.D. Cozzoli, G. Mascolo, R. Passino, A. Agostiano.*ApplCatal.,* 2005, **55**, 81.

2 L. Gianluca, A. Bono, J.G. Krishnaiah, D. Collin. *J Hazard Mater.,*2008, **157,** 209.

3 D. P. Macwan, Pragnesh N., D. S. Chaturvedi, *J Mater Sci*., 2011, **46**, 3669.

4 M. Addamo, M. Bellardita, D. Carriazo, A. Di Paola, S. Milioto, L. Palmisano and V. Rives, *Appl. Catal., B,* 2008, **84**, 742.

5 H. Q.Huang., X. Y. Liu. andJ.G.Huang, *Mater. Res. Bull.*, 2011, **46**,1814.

6 M. A. Behnajady, H. Eskandarloo, N. Modirshahla and M. Shokri, *Desalination*, 2011, **278**, 10.

7 A. A. Ismail, *MicroporousMesoporous Mater.*, 2012, **149**, 69.

8 7 L. N. Quan, Y. H. Jang, K. A. Stoerzinger, K. May, Y. J. Jang, S. T. Kochuveedu, Y. Shao-Horn and D. H. Kim, *Phys. Chem. Chem. Phys.*, 2014, **DOI:** 10.1039/C4CP00803K

9 I. S. Cho, Z. B. Chen, A. J. Forman, D. R. Kim, P. M. Rao, T. E. Jaramillo and X. L. Zheng, *Nano Lett.*, 2011, **11**, 4978.

10 P. Si, S. J.Ding, J. Yuan, X.W. Lou and D.H.Kim, *ACS Nano*, 2011, **5**, 7617.

11 V. G. Kessler, G. A. Seisenbaeva, S. Hakansson and M. Unell, *Angew. Chem. Int. Ed*., 2008, **47**, 8506.

12 G. A. Seisenbaeva, M. P. Moloney, R. Tekoriute, A. Hardy-Dessources, J. M. Nedelec, Y. K. Gun'ko and V. G. Kessler,*Langmuir*, 2010, **26**, 9809.

13 F. Sauvage, D. H. Chen, P. Comte, F. Z. Huang, Y. L. P. Heiniger, B. Cheng, R. A. Caruso and M. Graetzel, *ACS Nano*, 2010, **4**, 4420.

14 13 A Primo, ACorma and H. García. *Phys. Chem. Chem. Phys.*, 2011,**13**, 886.

15 S. H. Hakim and B. H. Shanks, *Chem. Mater.*, 2009, **21**, 2027.

16 R. J. P. Corriu, D. Leclerq, R. Lefevre, P. H. Mutin and A. J. Vioux, *J. Mater. Chem.*, 1992, **2**, 673.

17 M. Niederberger, G. Garnweitner, F. Krumeich, R. Nesper, H. Colfen and M.Antonietti, *Chem. Mater.*, 2004, **16**, 1202.

18 D. Buso , K. M. Nairn , M. Gimona , A. J. Hill , and P. Falcaro*Chem. Mater.*, 2011, **23**, 929.

19 C.S. Costa, R. M. Gester, J. R. Guimarães, J.n G. Amazonas, J. D. Nero, S. B.C. Silvad, A. Galembeckd. *Optical Material*, 2008, **9**, 1432.

20 G. A. Seisenbaeva, V. G. Kessler, *Nanoscale*, 2014, DOI: 10.1039/C3NR06336D

21 K. Katagiri, H. Inami, T. Ishikawa, K. Koumoto, *J Am Ceramic Soc*, 2009, **92**, 181

22 G. A. Seisenbaeva, D. Geoffrey, J.-M. Nedelec, V.G. Kessler, *Nanoscale*, 2013, **5**, 3330.

23 A.V.Vinogradov, V.V.Vinogradov, *J Am Ceramic Soc,* 2014, **97**, 290.

24 P. Alphonse, A. Varghese, C. Tendero, *J. Sol-Gel Sci. Technol.,* 2010, **56**, 250.

25 G. A. Seisenbaeva, G. Daniel, J.-M. Nedelec, Y. K. Gun'ko and V. G. Kessler., *J. Mater. Chem.*, 2012, **22**, 20374.

26 T. X. Liu, F. B. Li, X. Z. Li. *J. Hazard. Mater.,* 2008, **155**, 90.

27 B. Reeja-Jayan, Katharine L. Harrison, K. Yang, Chih-Liang Wang, A. E. Yilmaz, ArumugamManthiram, *Scientific Reports 2*, DOI: 1003 doi:10.1038/srep01003.

28 V.V. Vinogradov, A.V. Agafonov, D. Avnir., *Mater. Chem. C*, 2014, DOI: 10.1039/c3tc32462a

29 M. Kanna, S. Wongnawa, *Mater.Chem. Phys.*, 2008, **110**, 166.

30 L. Kavan, M. Gratzel, J. Rathousky, A. Zukal ,*J. Electrochem. Soc*,1996,**143**, 394.

31 D.A. Ward, E.I. Ko, *Ind. Eng. Chem. Res.*,1995, **34**, 421.

31 Guo, Z. Lin, X. Wang, G. Song, *Microelectronic Engineering*, 2003, **66**, 95.

32 K. Flora and J. D. Brennan, *Anal. Chem*., 1998, 70, 4505.

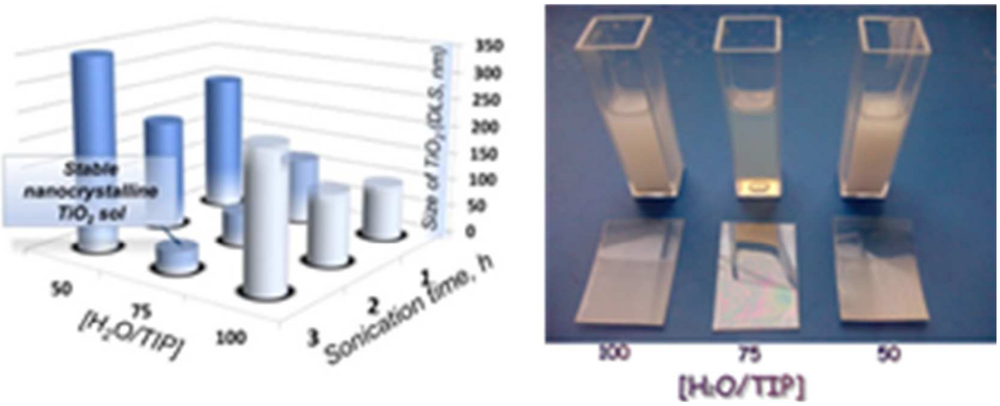
33 A. Rutenberg, V. V. Vinogradov, D. Avnir. *Chem. Commun.*, 2013, **49**, 5636.

34 H. S. Liu, Z. G. Bi, X. G. Su, R. R. Unocic, M. P. Paranthaman, S. Dai and G. M. Brown, *Adv. Mater*., 2011, **23**, 3450.

35 Yoon and A. J. Manthiram, *J. Phys. Chem. C*, 2011, **115**, 9410.

36 T. Brezesinski, J. Wang, S. H. Tolbert and B. J. Dunn, *J. Sol-Gel Sci.Technol*., 2011, **57**, 330.

37 F. Zhang, Y. Zhang, S. Y. Song and H. J. Zhang, *J. Power Sources*, 2011, **196**, 8618.



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