Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2014, Article ID 632068, 7 pages
http://dx.doi.org/10.1155/2014/632068

Research Article

A Novel Oxidation-Reduction Route for Layer-by-Layer Synthesis of TiO_2 Nanolayers and Investigation of Its Photocatalytical Properties

Konstantin Semishchenko, Valeri Tolstoy, and Artem Lobinsky

Department of Solid State Chemistry, Saint Petersburg State University, Universitetsky pr. 26, Saint Peterhof, 198504 Saint Petersburg, Russia

Correspondence should be addressed to Konstantin Semishchenko; k.semishchenko@gmail.com

Received 22 October 2013; Revised 21 January 2014; Accepted 28 January 2014; Published 10 March 2014

Academic Editor: Alireza Khataee

Layer-by-layer (LbL) synthesis of titanium dioxide was performed by an oxidation-reduction route using a $Ti(OH)_3$ colloid and $NaNO_2$ solutions. A model of chemical reactions was proposed based on the results of an investigation of synthesized nanolayers by scanning electron microscopy, electron microprobe analysis and X-ray photoelectron spectroscopy, and studying colloidal solution of $Ti(OH)_3$ with laser Doppler microelectrophoresis. At each cycle, negatively charged colloidal particles of $[Ti(OH)_3]HSO_4^-$ adsorbed onto the surface of substrate. During the next stage of treatment in $NaNO_2$ solution, the particles were oxidized to $Ti(OH)_4$. Photocatalytic activity was studied by following decomposition of methylene blue (MB) under UV irradiation. Sensitivity of the measurements was increased using a diffuse transmittance (DT) method. The investigation revealed strong photocatalytical properties of the synthesized layers, caused by their high area per unit volume and uniform globular structure.

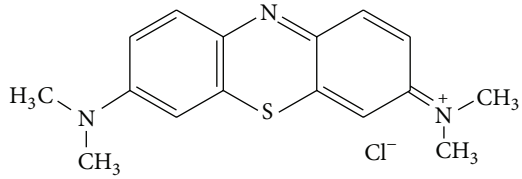
1. Introduction

Titanium dioxide is one of the most perspective photoactive materials. It is intensively used in the development and for manufacturing of photocatalysts, superhydrophilic and self-cleaning surfaces, solar elements, and so forth. Research in the area of thin layered structures opens vast opportunities for creation of new materials with unique properties. A number of techniques are used for this purpose, for example, Langmuir-Blodgett [1], sol-gel method [2–5], dip coating [6], liquid-phase deposition [7], chemical bath deposition [8], CVD [9], spray pyrolysis deposition [10], and magnetron sputtering [11].

Special attention is paid to the layer-by-layer (LbL) synthesis. Its main advantage is the possibility of obtaining layers on the surface of arbitrarily complex shapes with precisely specified composition and thickness. Dozens of articles are devoted to the synthesis of solid thin films of titanium dioxide by LbL method. These compositions are commonly obtained using easily hydrolyzed organic containing compositions of titanium (IV). For example, titanium isopropoxide [12, 13], salts of titanium (IV) $(NH_4)_2TiO(C_2O_4)_2H_2O$ [14], and titanium(IV) bis(ammonium lactato) dihydroxide [15].

Titanium dioxide layers can be synthesized LbL using an oxidation-reduction route, which was proposed in our earlier work on the synthesis of nanolayers of hydrated oxides of Sn^{4+} [16, 17], Mn^{4+} [18], Fe^{3+} [19], and Ce^{4+} [20]. In these papers, the LbL method was named the Successive Ionic Layer Deposition (SILD). The synthesis consists of sequential treatment of substrate in the solution of precursor in the lowest oxidation number, followed by removal of excess reagent with water. At the second stage, the sample is immersed in the solution of oxidizer and the excess is again removed. A similar approach was subsequently applied to the synthesis of layers of titanium dioxide (IV) colloidal solution from $Ti(OH)_3$ [21, 22]. In this case, the method was named

Table 1: General characteristics of methylene blue.

Molecular formula	Molar mass, g/mol	Chemical structure	λ_{max} adsorption, nm	C.I. number
$C_{16}H_{18}N_3SCl$	319.85		650	52015

Successive Ionic Layer Adsorption and Reaction (SILAR) and $Ti(OH)_3$ colloid was obtained by partial hydrolysis of $TiCl_3$. At every cycle, after titanium particles adsorption, the substrate was immersed in NaOH or NH_4OH solution, pH = 11. Under these conditions, oxidation of Ti^{3+} into Ti^{4+} by atmospheric oxygen takes place. Therefore, nanoparticles of $(TiOH)_4$ appear on the surface of the substrate and convert into $TiO_2{\cdot}nH_2O$ after drying.

The above method is limited by the necessity to use alkali solution. This not only decreases variety of substrates that can be used for TiO_2 deposition but also negates the possibility of obtaining layers constructed from minimum sized nanoparticles; dissolution-precipitation of the smallest particles into larger ones takes place within at high pH.

The aim of the research reported on here was to develop an LbL method for synthesis of photoactive layers of TiO_2 using readily accessible low-cost reagents, at a pH close to neutral.

2. Experimental Section

2.1. Preparation of the Reagents. A colloidal solution of $Ti(OH)_3$ was obtained by partial hydrolysis of 0.02 M $Ti_2(SO_4)_3$ solution at pH 3.2. Adjustment of the pH of $Ti_2(SO_4)_3$ solution was achieved by addition of 5% NH_4OH solution. A solution of $NaNO_2$ (C = 0.01 M, pH = 7.6) was prepared by dissolving dry salt in double-distilled water. All reagents were obtained from Vekton LLC. The substrates used are polished single crystalline silicon wafers with orientation ⟨100⟩ and resistance of 30–40 Ohm 10×10×0.3 mm and grinded quartz KU type 10 × 20 × 2 mm.

2.2. Synthesis of the Layers. Computation of chemical equilibrium in 25°C solution was performed by Hydra-Medusa [23] software. It was found that, within current pH = 3.2, titanium dioxide existed in the form of colloidal particles of $Ti(OH)_3$, which adsorb onto the surface of the substrate. On the second step, after washout of excess of deposited reagent, these particles transform into $Ti(OH)_4$ during immersing in $NaNO_2$ solution (oxidizer). Double-distilled water was used to flush excess of every reagent from the surface of substrate. Time of treatment in solutions of reagents was 30 seconds and in washout water 5 seconds. One cycle of the synthesis was formed by sequential treatment of the substrate in solutions of Ti(III), washout water, $NaNO_2$ solution and washout water.

2.3. Surface and Structural Analysis. Synthesized layers were characterized with scanning electron microscopy (SEM). The composition was determined by electron probe microanalysis (EPMA) and XPS. These studies were made on a Zeiss EVO 40EP scanning electron microscope (Carl Zeiss Microscopy) with a LaB_6 cathode, equipped with an energy dispersive microanalyzer (Oxford INCA 350) and a Si(Li) detector of 30 mm^2. Accelerating voltage was 20 kV. XPS spectra were recorded on a photoelectron spectrometer (SPECS). Photoelectrons were excited by X-rays of the Mg$K\alpha$ line. Radiograms of synthesized layers were made on an X-ray diffractometer DRON-3.0 (NPO Burevestnik, USSR) for Cu$K\alpha$ emission. Electrophoretic mobility of colloidal particles was measured on a Zetasizer Nano analyzer (Malvern Instruments Ltd.) using M3-PALS technology.

2.4. Photocatalytical Properties Investigation. Photocatalytical properties of titanium dioxide layers synthesized on the surface of grinded quartz were studied applying standard method [24], which is based on analysis of degradation under UV irradiation of methylene blue adsorbed on the substrate. General characteristics of MB are presented in Table 1. Sample of quartz was immersed in 50 mg/L solution during 20 minutes to obtain a layer of adsorbed dye on the surface [25, 26]. Descent of value of optical density at maximum was used for calculating degree of MB decomposition and photocatalytic activity of synthesized layers of titanium dioxide on quartz surface accordingly.

To increase the value of intensity of adsorption bands in visible range spectra, a diffuse transmittance method (DT) [27] was applied. The samples of grinded quartz were placed in front of aluminum (Al) mirror for obtaining spectra of diffuse scattering (DS). In this set-up, the beam twice penetrates the plate, which is covered with titanium dioxide layers on both sides (Figure 1). The beam firstly penetrates the sample without scattering (minorly informative), then is reflected back by the Al mirror to the light receiver aperture (majorly informative). This latter diffusely scattered part of beam is reflected from the inner surface of the integrating sphere to the detector. Thus, the beam goes through the sample twice and increases bands' intensity. Application of this method provides the increasing sensitivity of this Application of this method increases sensitivity of this spectrometry. It provides possibility to carry out investigations not only for the dispersed but also for bulk substances with a minimized thickness of photocatalytical layer All DT spectra

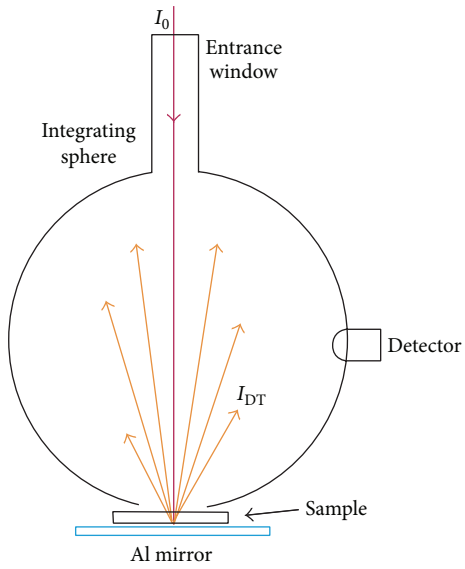


FIGURE 1: Registration of diffuse transmittance spectra. Beam penetrates through the sample twice: initial irradiation (I_0) and after reflecting from the mirror (I_{DT}).

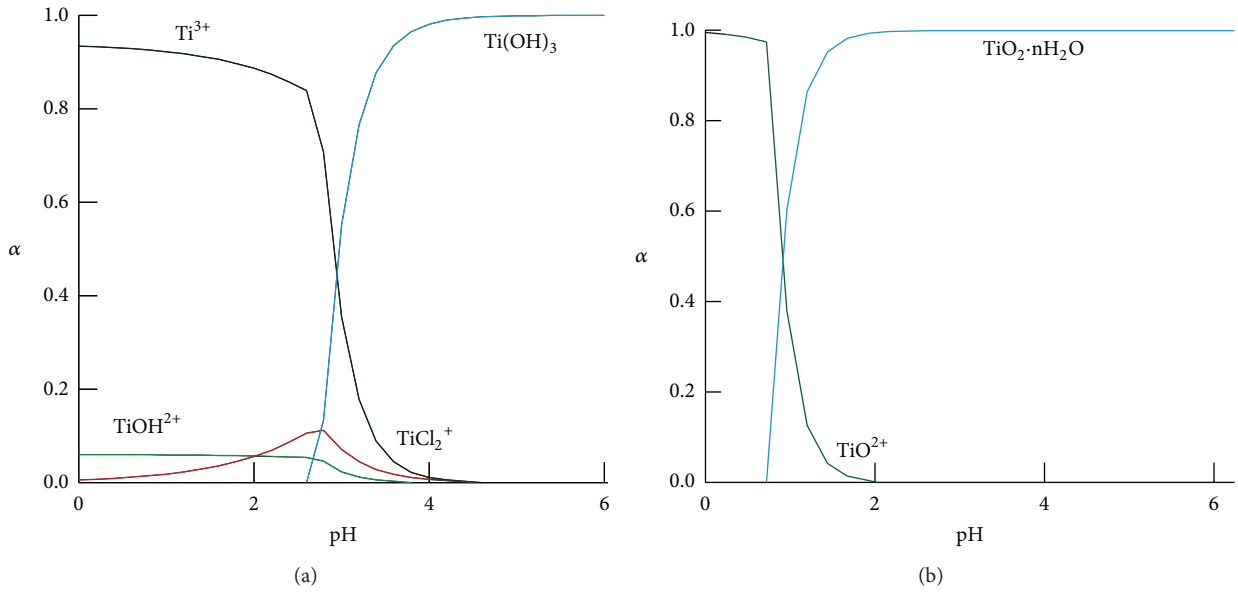


FIGURE 2: Variation of molar fractions α of different titanium compositions in water solution of Ti^{3+} (a) and Ti^{4+} (b) against pH. C (Ti) = 0.01 M.

were registered by Lambda-9 spectrophotometer (Perkin-Elmer).

Before investigation of photocatalytical activity, the sample was preheated in the open air for 1 hour at 500°C to remove molecules of water.

3. Results and Discussions

Analysis of solubility and hydrolysis of titanium salts with an oxidation number 3+ and an oxidation number 4+ showed (Figure 2) that the best reagent for synthesis of layers of $TiO_2 \cdot nH_2O$ was a solution of Ti^{3+} salt. In this solution, the formation of titanium hydroxide proceeds under higher pH. The experimental results showed that stable colloidal solutions can be prepared at a pH of about 3.0. $Ti_2(SO_4)_3$ was chosen for experiments because of its low cost and prevalence.

The thin film visually appeared on the surface of silicone substrate after multiple sequential treatment in $Ti_2(SO_4)_3$ and $NaNO_2$ solutions by the LbL technique. It became light blue after approximately 15 cycles.

From the micrographs obtained by SEM (Figure 3), it was evident that the synthesized layers consisted of globules of

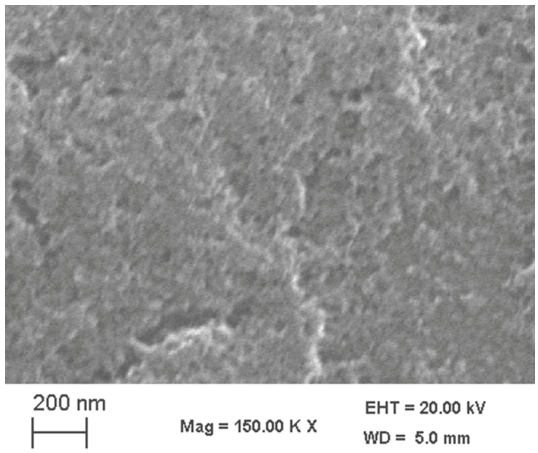


Figure 3: SEM image of $TiO_2 \cdot nH_2O$ layers synthesized on silica surface after 15 LbL cycles.

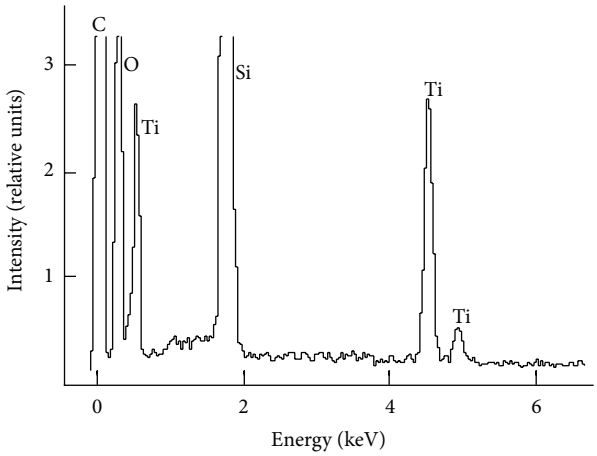


Figure 4: Energy-dispersive X-ray spectrum of $TiO_2 \cdot nH_2O$ layers synthesized on silica surface after 15 LbL cycles.

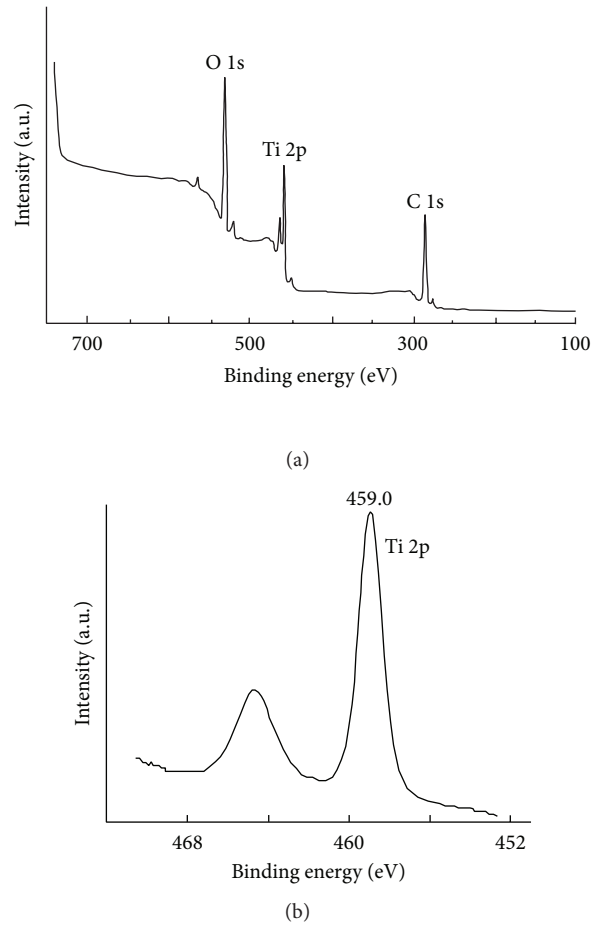


Figure 5: Overview (a) XPS spectrum and ranged one for the area of 453–470 eV (b) of TiO_2 layers synthesized on silica surface after 15 LbL cycles.

10–20 nm diameters. Based on the energy-dispersive X-ray spectrum (Figure 4) and XPS data (Figures 5(a) and 5(b)), the thin film was composed of atoms of titanium and oxygen. The content of Na, S, and N atoms did not exceed 1–3%, which lies within the range of accuracy for the XPS method. The position of the characteristic band of Ti 2*p* electrons was at 459.0 eV, which indicates the oxidation number of Ti^{4+} in TiO_2 [28]. Based on the analysis by X-ray diffraction, the obtained layers were amorphous (X-ray graphs are not shown in the figures).

Another important result which explains details of the chemical reactions on the surface during the synthesis is the value of ξ-potential of the $Ti(OH)_3$ particles in solution. It was calculated by the Smoluchowski equation based on the electrophoretic mobility data. According to the measurements, the colloidal particles in the solution possessed a net negative charge and ξ-potential of −4.21 mV. This can be explained by adsorption of the SO_4^{2-} anions on the surface. Based on this result and the other experimental data, the following scheme for sequence of chemical reactions on the surface (Figure 6) was proposed.

Thus, at the first cycle of LbL, the substrate is immersed in colloidal solution $[Ti(OH)_3]HSO_4^-$. These particles of titanium hydroxide (III) adsorb on silica surface which is literally zero charged at pH 3.2. At the next step, the excess of adsorbed on the substrate SO_4^{2-} anions is removed by washing in distilled water. During subsequent treatment of the sample in $NaNO_2$ solution, Ti^{3+} ions are oxidized to Ti^{4+} forming $Ti(OH)_4$ nanoparticles layers. After removal of excess of oxidizing agent, the substrate is treated in $Ti(OH)_3$ colloid. Hereby, the next cycle of LbL synthesis starts. It is to be noted that, at a solution pH 3.2, $Ti(OH)_4$ does not dissolve. The charge of $Ti(OH)_4$ nanoparticles layers, obtained after the first LbL cycle, is positive due to adsorption of the protons on the surface of substrate in acidic conditions. This facilitates adsorption of negatively charged $[Ti(OH)_3]HSO_4^-$ and causes formation of $Ti(OH)_4$ layers. After drying in the air, the sample transforms into the layers of hydrated $TiO_2 \cdot nH_2O$. This layer does not dissolve in $Ti(OH)_3$ colloid on the second and following steps of synthesis. Thus, irreversible conditions of synthesis were achieved.

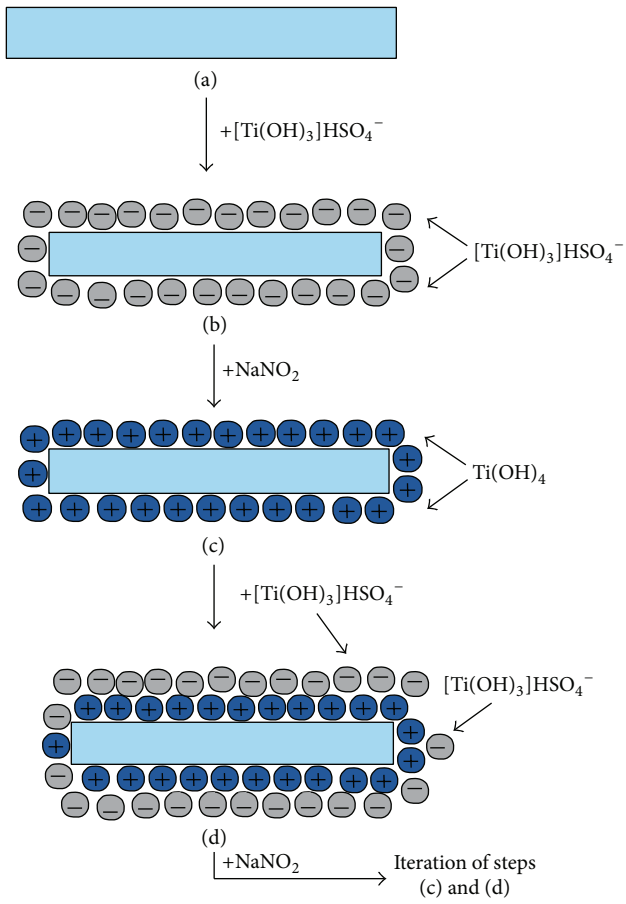


Figure 6: Scheme of sequential chemical reactions of the LbL synthesis of $TiO_2 \cdot nH_2O$ nanolayers on the substrate: (a) substrate, (b) after treatment in colloidal solution of $Ti(OH)_3$ and removal of its excess by washout, (c) after treatment in solution of $NaNO_2$ and removal of its excess by washout, and (d) after retreatment in colloidal solution of $Ti(OH)_3$.

Unfortunately, determination of the size of colloidal particles in $Ti(OH)_3$ solution was not possible due to the effect of fluorescence of the solution during study by dynamic light scattering (DLS).

It should be noted that NO_2^- anions can, possibly, adsorb onto the surface of $Ti(OH)_4$ nanoparticles during immersion of sample in $NaNO_2$ solution. They can partially transfer into $Ti(OH)_3$ solution and, therefore, participate in reaction of oxidation of Ti^{3+} to Ti^{4+}. Oxidation of colloidal particles of $Ti(OH)_3$ is also possible by reaction with atmospheric oxygen. However, we believe that, during synthesis, the reaction of oxidation by atmospheric oxygen does not play a role, since control experiments of the synthesis of thin layers without treatment in $NaNO_2$ solution revealed no reproducible growth of the layer thickness.

Results of the study of photocatalytic activity of synthesized layers are shown in Figures 7 and 8. Sample synthesis involved 20 cycles. After irradiation with UV light (Hg lamp), the intensity of the characteristic band of MB at 650 nm decreased in the spectrum of DT.

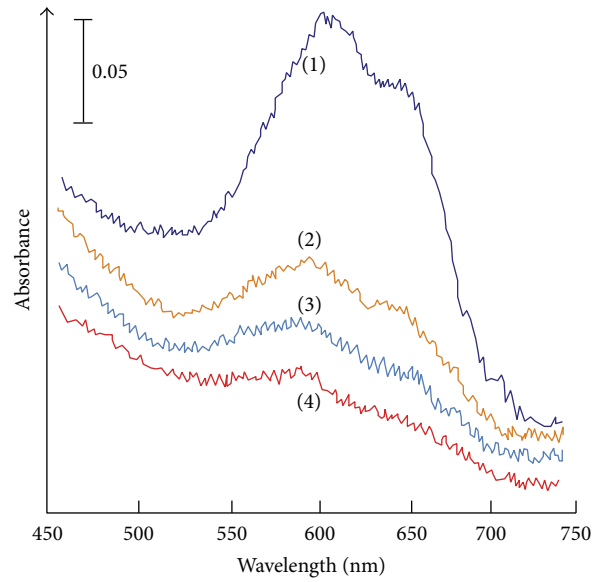


Figure 7: Diffuse transmittance spectra in the Vis region of the quartz wafer synthesized by 20 LbL cycles layers of TiO_2 and kept in MB solution. (1) After removal from MB solution and drying at warm air and (2) after UV irradiation of sample for 10 min, (3) 20 min, and (4) 30 min.

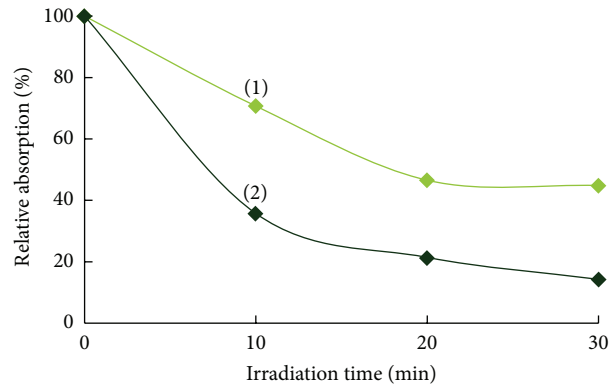


Figure 8: Changes in the relative optical density of maximum at λ = 650 nm absorption band in the spectrum of MB according to the duration of irradiation of UV lamp: (1) MB on the quartz surface and (2) MB on the quartz surface with TiO_2 layers, synthesized after 20 LbL cycles.

It follows from the results presented in Figure 8 that, after 20 minutes of exposure, the intensity of the band decreases by 80%. Similar results [24] have been reported for thin-layer structures of TiO_2 and SiO_2 obtained by the LbL technique. An equal decomposition ratio was achieved for thicker structures and longer irradiation time: 120 layers and 60 min correspondingly. Apparently, the effect achieved in our work is caused by higher specific surface area and uniform globular morphology of the layers, which consist of nanoparticles of 10–20 nm diameters.

4. Conclusions

LbL synthesis by an oxidation-reduction method, using a $Ti(OH)_3$ colloid and $NaNO_2$ solution on the surface of quartz substrate, resulted in formation of layers of nanostructured titanium dioxide(IV). It had amorphous structure with nanoparticles of approximately 10–20 nm diameters. Formation of these layers at each LbL cycle is originated by successive reactions of adsorption of colloidal particles of $Ti(OH)_3HSO_4^-$ and their subsequent oxidation in $NaNO_2$ solution.

The method of diffuse transmittance in the Vis region of the spectrum can be effectively used to estimate photocatalytical activity of nanolayered catalysts deposed on the surface of bulk substrates; results are obtained by following photodegradation of MB dye.

Application of this method in current research has revealed relatively high photocatalytical activity of the layers of TiO_2 synthesized by LbL technique. This can be explained by a high surface area of the layers and their uniform globular structure.

Abbreviations

LBL: Layer-by-layer method
MB: Methylene blue
DT: Diffuse transmittance
DS: Diffuse scattering
DLS: Diffuse light scattering.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

This work was supported by SPbSU Grant (no. 12.38.259 .2014).

References

[1] Y. Umemura, E. Shinohara, A. Koura, T. Nishioka, and T. Sasaki, "Photocatalytic decomposition of an alkylammonium cation in a langmuir-blodgett film of a titania nanosheet," *Langmuir*, vol. 22, no. 8, pp. 3870–3877, 2006.

[2] J. Zheng, H. Yu, X. Li, and S. Zhang, "Enhanced photocatalytic activity of TiO_2 nano-structured thin film with a silver hierarchical configuration," *Applied Surface Science*, vol. 254, no. 6, pp. 1630–1635, 2008.

[3] T. Thirugnanam, "Effect of polymers (PEG and PVP) on sol-gel synthesis of microsized zinc oxide," *Journal of Nanomaterials*, vol. 2013, Article ID 362175, 7 pages, 2013.

[4] A. A. Haidry, J. Puskelova, T. Plecenik et al., "Characterization and hydrogen gas sensing properties of TiO_2 thin films prepared by sol-gel method," *Applied Surface Science*, vol. 259, pp. 270–275, 2012.

[5] M. Kashif, U. Hashim, M. E. Ali, K. L. Foo, and S. M. U. Ali, "Morphological, structural, and electrical characterization of sol-gel-synthesized ZnO nanorods," *Journal of Nanomaterials*, vol. 2013, Article ID 478942, 7 pages, 2013.

[6] P. Sun, H. Liu, and H. Yang, "Synthesis and characterization of TiO_2 thin films coated on metal substrate," *Applied Surface Science*, vol. 256, no. 10, pp. 3170–3173, 2010.

[7] W. Guo, C. Xu, G. Zhu, C. Pan, C. Lin, and Z. L. Wang, "Optical-fiber/TiO_2-nanowire-arrays hybrid structures with tubular counterelectrode for dye-sensitized solar cell," *Nano Energy*, vol. 1, no. 1, pp. 176–182, 2012.

[8] R. Palomino-Merino, O. Portillo-Moreno, L. A. Chaltel-Lima, R. Gutiérrez Pérez, M. de Icaza-Herrera, and V. M. Castaño, "Chemical bath deposition of PbS:Hg^{2+} nanocrystalline thin films," *Journal of Nanomaterials*, vol. 2013, Article ID 507647, 6 pages, 2013.

[9] Z. S. Khalifa, H. Lin, and S. Ismat Shah, "Structural and electrochromic properties of TiO_2 thin films prepared by metallorganic chemical vapor deposition," *Thin Solid Films*, vol. 518, no. 19, pp. 5457–5462, 2010.

[10] C. Jiang, M. Y. Leung, W. L. Koh, and Y. Li, "Influences of deposition and post-annealing temperatures on properties of TiO_2 blocking layer prepared by spray pyrolysis for solid-state dye-sensitized solar cells," *Thin Solid Films*, vol. 519, no. 22, pp. 7850–7854, 2011.

[11] B. Barrocas, O. C. Monteiro, and M. E. Melo Jorge, "Photocatalytic activity and reusability study of nanocrystalline TiO_2 films prepared by sputtering technique," *Applied Surface Science*, vol. 264, pp. 111–116, 2013.

[12] A. M. More, J. L. Gunjakar, C. D. Lokhande, and O. S. Joo, "Fabrication of hydrophobic surface of titanium dioxide films by successive ionic layer adsorption and reaction (SILAR) method," *Applied Surface Science*, vol. 255, no. 12, pp. 6067–6072, 2009.

[13] S. S. Kale, R. S. Mane, H. Chung, M.-Y. Yoon, C. D. Lokhande, and S.-H. Han, "Use of successive ionic layer adsorption and reaction (SILAR) method for amorphous titanium dioxide thin films growth," *Applied Surface Science*, vol. 253, no. 2, pp. 421–424, 2006.

[14] S. A. Darko, E. Maxwell, and S. Park, "Photocatalytic activity of TiO_2 nanofilms deposited onto polyvinyl chloride and glass substrates," *Thin Solid Films*, vol. 519, no. 1, pp. 174–177, 2010.

[15] K. Katagiri, T. Suzuki, H. Muto, M. Sakai, and A. Matsuda, "Low temperature crystallization of TiO_2 in layer-by-layer assembled thin films formed from water-soluble Ti-complex and polycations," *Colloids and Surfaces A*, vol. 321, no. 1–3, pp. 233–237, 2008.

[16] V. P. Tolstoi, "The synthesis by SILD of $SnO_2 \cdot nH_2O$ nanolayers," *Russian Journal of Inorganic Chemistry*, vol. 38, pp. 1146–1148, 1993.

[17] G. Korotcenkov, V. Macsanov, V. Tolstoy, V. Brinzari, J. Schwank, and G. Fagila, "Structural and gas response characterization of nano-size SnO_2 films deposited by SILD method," *Sensors and Actuators B*, vol. 96, no. 3, pp. 602–609, 2003.

[18] V. P. Tolstoy, I. V. Murin, and A. Reller, "The synthesis of Mn(IV) oxide nanolayers by the successive ionic layer deposition," *Applied Surface Science*, vol. 112, pp. 255–257, 1997.

[19] V. P. Tolstoy, "LBL synthesis of FeOOH on the silica surface," *Russian Journal of Applied Chemistry*, vol. 72, pp. 1259–1262, 1999.

[20] V. P. Tolstoy and A. G. Ehrlich, "C—The synthesis of $CeO_{2+n} \cdot n\ H_2O$ nanolayers on silicon and fused-quartz surfaces by the successive ionic layer deposition technique," *Thin Solid Films*, vol. 307, no. 1-2, pp. 60–64, 1997.

[21] H. M. Pathan, S. K. Min, J. D. Desai, K. D. Jung, and O. S. Joo, "Preparation and characterization of titanium dioxide thin films by SILAR method," *Materials Chemistry and Physics*, vol. 97, no. 1, pp. 5–9, 2006.

[22] U. M. Patil, K. V. Gurav, O. S. Joo, and C. D. Lokhande, "Synthesis of photosensitive nanograined TiO_2 thin films by SILAR method," *Journal of Alloys and Compounds*, vol. 478, no. 1-2, pp. 711–715, 2009.

[23] S. E. Cabaniss, "Uncertainty propagation in geochemical calculations: non linearity in solubility equilibria," *Applied Geochemistry*, vol. 14, no. 2, pp. 255–262, 1999.

[24] S.-H. Lin, Y.-N. Wu, Y.-C. Lin, and Y.-M. Yang, "Design and fabrication of antireflective nanoparticulate thin films with superhydrophilic self-cleaning properties on glass substrate," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 42, no. 5, pp. 852–859, 2011.

[25] L. Rojas-Blanco, M. D. Urzua, R. Ramirez-Bona, and F. J. Espinoza Beltran, "Photocatalytic thin films containing TiO_2:N nanopowders obtained by the layer-by-layer self-assembling method," *Applied Surface Science*, vol. 258, no. 6, pp. 2103–2106, 2012.

[26] C. Wang, H. Liu, and Y. Qu, "TiO_2-based photocatalytic process for purification of polluted water: bridging fundamentals to applications," *Journal of Nanomaterials*, vol. 2013, Article ID 319637, 14 pages, 2013.

[27] V. P. Tolstoy, I. V. Chernyshova, and V. A. Skryshevsky, *Handbook of IR Spectroscopy of Ultra Thin Films*, John Wiley & Sons, New York, NY, USA, 2003.

[28] B. V. Crist, *Handbooks of Monochromatic XPS Spectra*, vol. 1, XPS International, Mountain View, CA, USA, 2004.