Introduction

The concept of nanotechnology has stimulated the collective imagination of engineers, scientists and business communities. The highlight of what may be possible through the exploration and development of nanoscale science and engineering, reinvigorated efforts of researchers from the entire spectrum of scientific fields.

Studies of nanostructured materials exhibiting well-defined nanoscale dimensions shapes have led to the possibility of their manipulation and control on atomic scale and to the development of structures, devices and miniaturized systems with new properties and functions.

There are two fundamental aspects characterizing the behavior of nanostructured materials: increasing specific surface, which leads to increased chemical reactivity, and increasing dominance of quantum effects, influencing optical, magnetic or electrical properties of materials.

For wastewater containing non-biodegradable organic pollutants, the most effective treatment methods involve the use of advanced oxidation processes (AOPs). One of these processes is heterogeneous photocatalysis, which involves the generation of hydroxyl radicals at room temperature and pressure, in the presence of photocatalysts activated by radiation with different wavelengths.

Despite the promising aspects for using TiO_2 as photocatalyst, there is a big disadvantage namely that fotoexcitation can only be effective with UV light (λ> 350 nm) which leads to the use of only a small fraction (approximately 3%) of solar light and to a high recombination rate of charge carriers.

The research work carried out during this thesis aimed redesigning TiO_2 photocatalysts in order to expand light absorbtion to visible range, but also to increase photocatalytic activity.

The overall aim of the thesis was conducting studies and experimental research for new designs of next generation semiconductor photocatalysts using innovative and effective methods.

The thesis is divided into three chapters, containing a total of 184 pages, 102 figures, 11 tables and 268 references, of which Chapter 1 is allocated to the study of the current state of knowledge and the other two chapters to the description of the original research.

The thesis concludes with references including papers and publications in various journals or participation to scientific events.

Current state of knowledge

Chapter 1 briefly describes the importance of nanoporous materials, factors which increase their performance, their synthesis strategies and their use as semiconductors nanofotocatalysts for the treatment of wastewater from the textile industry.

Heterogeneous photocatalytic process is a surface process that follows the next sequence (Figure 1.1):

1. semiconductor radiation fotoexcitation with light having energy equal to or higher than the band gap energy;
2. generating the electron-hole pairs;
3. separating the electrons and holes; The reaction speed of this process must be higher than the speed of the recombination of electrons and holes, to prevent deactivation of the catalyst;
4. pollutants adsorption on the catalyst surface;
5. redox reactions on the surface of the catalyst between the electrons, holes and the adsorbed molecules on the surface of the catalyst; processes that occur at this stage are crucial in the formation of the final products;
6. final products desorption from the catalyst surface.

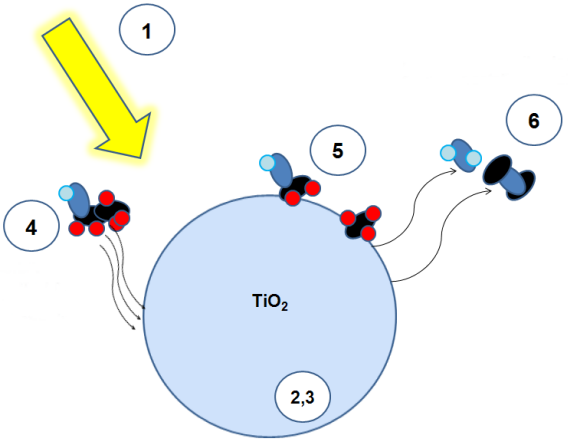

Figure 1.1. Processes taking place at the surface of a catalyst

The literature states as key factors in the design of semiconductor photocatalysts with visible response: crystallinity, purity and controlled growth of crystal size on the one hand and doping and hetero-structuring photocatalysts on the other hand.

An ideal photocatalyst should be stable, inexpensive, non-toxic and, of course, very photosensitive. In order to obtain such nanomaterials, it was aimed to achieve a new design of next generation semiconductor photocatalysts.

Chapter 2. Working protocol and experimental infrastructure

The second chapter describes the tools, plant and laboratory equipment used to study the characteristic properties of the synthesized materials and the dyes used as model organic compounds to study fotcatalytic properties of semiconductors.

Chapter 3. Synthesis and characterization of photocatalytic active materials

3.3. Mesoporous TiO_2

3.3.1. Synthesis of mesoporous TiO_2

A mesoporous TiO_2 material with high catalytic activity has been synthesized by assembling the nanocrystalline particles using a modified hydrothermal method, ultrasound assisted. The first step was the synthesis of nanocrystalline particles. This was followed by a treatment at 80 °C, with stirring, under reflux. This step replaces the autoclave synthesis as reported in the literature.

The second step was the synthesis of mesoporous TiO_2, followed by sonication step, which was carried out for 2 hours.

3.3.2. Study of the properties of the synthesized mesoporous TiO_2

N_2 adsorption / desorption

The BET isotherms for N_2 adsorption / desorption and BJH pore size distributions of the synthesized samples are presented in the following graphics.

All of them can be considered type IV isotherms according to the IUPAC classification, presenting an hysteresis loop, characteristic to mesoporous materials. The hysteresis loops are identified as being of type H3, which are usually given by flattened particles or adsorbent containing slit-shaped pores. Differences between isotherms suggests different characteristics of porosity. The sample 2c, autoclave synthesized using Pluronic P123 as template, exhibits relatively uniform pores, with less regular shape, but larger.

The 3c sample, obtained by ultrasound-assisted hydrothermal method in the presence of Pluronic F127 template, exposes regular, small pores, with the hysteresis loop closing at a lower value of relative pressure. The 7c powder obtained by reflux, followed by sonication using Pluronic P123 as template, has partially obstructed pores with two characteristic dimensions. These properties are confirmed by the pore size distribution chart, the characteristic dimensions obtained being of approximately 5 nm for sample 2c, 3.7 nm for sample 3c and 5 – 6 nm for sample 7c. The high density of pores with a diameter of 3-7 nm and BET surface values of 200-290 m^2 / g also confirm that the prepared samples are mesoporous materials.

Table 3.8. Dimensional properties of synthesized materials.

	2c	3c	7c
BET Surface Area (m^2/g)	229,60	290,00	211,00
Pore Diameter (nm)	5,3	3,9	5,1
Pore Volume (cm^3/g)	0,33	0,46	0,42
Particle Diameter (Debye – Scherrer formula) (nm)	14,17	7,44	7

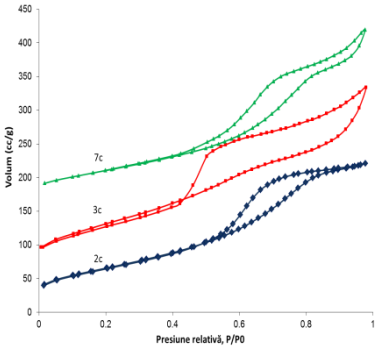

Figure 3.31. N_2 Adsorption-desorption isotherms

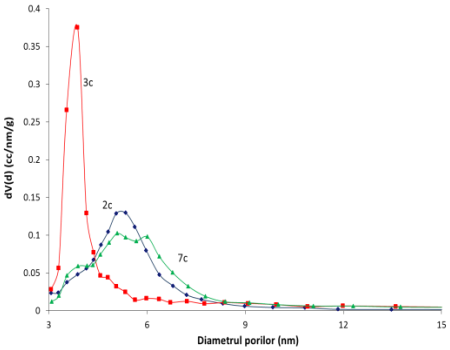

Figure 3.32. Pore size distribution of the synthesized samples.

3.3.3. Photocatalytic activity of the synthesized samples

For all the tested fotocatalysts, strong adsorption of the dye occurs in the first 30 minutes prior to the UV exposure, and the degree of discoloration of the solution by adsorption was 19.4% for 2c sample, 19.9% for 3c sample and 52% for the 7c sample. Photocatalytic reaction follows a slowly decreasing slope. After two hours of irradiation, the values of RB degradation using the samples synthesized in autoclave (53% and 58%) are significantly lower than the situation when sample 7c, subjected to refluxing, was employed (93%).

The possibility of recovering the TiO_2 catalyst by washing with isopropanol was studied. Thus, after 180 minutes of photocatalytic reaction time, the solid was recovered by centrifugation, washed 3 times using 15 mL of alcohol, then centrifuged and dried at 60 °C.

It was concluded that photocatalyst could be reused in the same process several times to give the following degree of degradation of the Rose Bengal: 95,16%, 83,43% and 80,69% for the first, second and, respectively, third time of the same catalyst use.

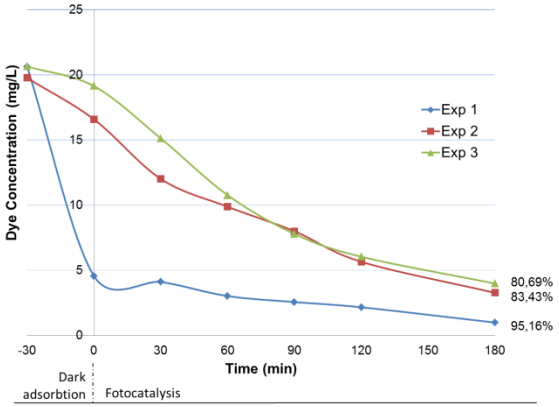

Figure 3.37. Reusing of mesoporous TiO_2 catalyst synthesized by reflux and ultrasound

3.4. Modified TiO_2 - mesoporous carbon coated with TiO_2 composite

Mesoporous carbon coated with TiO_2 photocatalysts were successfully prepared by an ultrasound assisted sol-gel method, followed by various thermal treatments (assisted by microwave or oven calcined) in the air.

After the TiO_2 coating, the influence of conventional or microwave heat treatments on TiO_2-C composites properties was investigated. The structural, textural, chemical and morphological characteristics have shown that the use of microwaves has improved the characteristics of the TiO_2-C composite. The 7MW sample showed the highest specific surface area, the largest total pore volume, the smallest crystallite size, the smallest particle size, the highest carbon content and the lowest value of the band gap, these features being are very useful for the heterogeneous photocatalytic processes.

The photocatalytic tests showed the following:

• TiO_2-C nanocomposites showed higher activity than pure TiO_2 nanoparticles.

• the TiO_2 – C composite calcined under microwaves for the shortest time (7 minutes) presented the highest removal capacity of MO, with a degradation percentage of 92%.

• The TiO_2 dispersion into the nanocomposite was good, emphasizing the synergic effect of adsorption and catalytic degradation.

3.5. Modified TiO_2 powders – TiO_2 / ordered mesoporous C composites

3.5.1. Synthesis of TiO_2 / ordered mesoporous C composites

A photocatalytic active material was obtained by inserting the precursor of the mesoporous TiO_2 between the carbon fibers by an ultrasound assisted impregnation method.

3.5.2.2. Study of textural properties by N_2 sorption technique

The BET method allowed the calculation of the textural characteristics of samples MC and MC-TiO_2, as shown in table 3.10. One can observe a decrease in the BET specific surface area and total pore volume, indicating blockage of carbon mesopores by the TiO_2 particles. The emergence of microporous characteristics could be also attributed to the formation of micropores between TiO_2 nanoparticles and MC walls.

Table 3.10. Textural characteristics of the synthesized samples

Characteristics	MC	MC-TiO_2
Specific Surface Area (m^2/g)	1483	1034
Total Pore Volume @ STP (cm^3/g)	1,91	0,8
Pore Diameter (nm)	3,8	3,8
Micropore Volume @ STP (cm^3/g)	0	0,09
Micropore Specific Surface Area (m^2/g)	0	196

The graphitic nature of carbon plays a key role in improving the efficiency of photocatalysis in the presence of TiO_2.

3.5.2.3. SEM imaging

The thin fiber type morphology of the mesoporous carbon material was observed as shown in SEM images (Figure 3.50). SEM image of the MC-TiO_2 composite clearly shows that on the carbon surface there are some functional groups that are appropriate to fix nanoparticles of titanium dioxide. Due to the graphite-like structure, there are also many hydrophobic sites on the carbon surface that are responsible for fixing molecules of phenol to the surface and thus increase the local concentration of the phenol species.

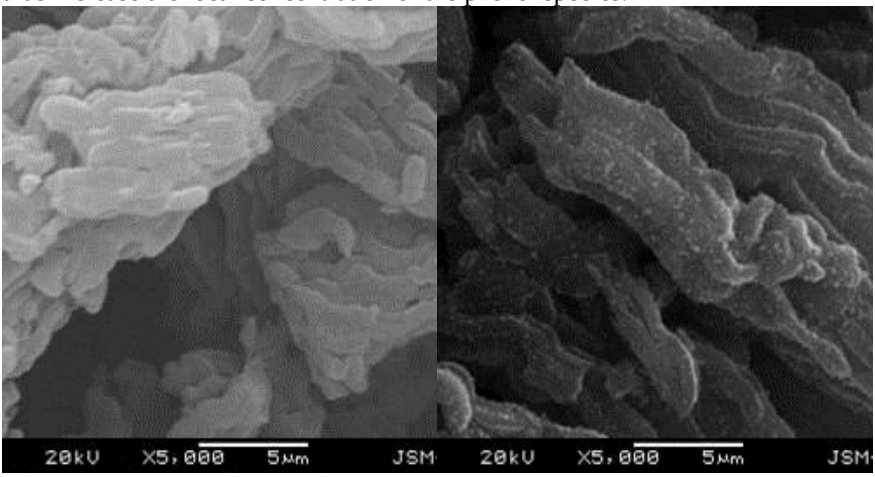

Figure 3.50. SEM images of simple MC and MC-TiO2 composite

3.5.3. Study of photocatalytic activity of MC-TiO_2 composites

When we studied phenol decomposition, we found that MC-TiO_2 sample (synthesized composite) has high photocatalytic efficiency under visible light.

CM – anatase coated showed a high rate of photodegradation and its outstanding performance due to the following causes:

(1) electron capture occurs at the interface between anatase TiO_2 nanoparticles and graphite parts of the MC support and therefore, electron-hole recombination is long overdue;
(2) between TiO_2anatase nanoparticles and the MC support interactions have been observed;
(3) the interface area was wide;
(4) photon absorption was enhanced in the presence of mesoporous carbon.

The results indicate that the TiO_2 coated mesoporous carbon material can be photocatalytic activated under visible light, the procedure being efficient for industrial use and later reuse (Ignat et al., 2012).

3.6. Nitrogen doped TiO_2

3.6.1. Synthesis and study of properties of nitrogen doped TiO_2

Mesoporous TiO_2 obtained as described in section 3.3. has undergone a doping phase using urea as a nitrogen precursor. The solid powders were subjected to impregnation with various amounts of urea, in order to achieve different molar ratios Ti: urea in the final solution: 1: 0.4; 1: 1 and 1: 2. The obtained mixtures were magnetically stirred for 5 hours, then they were allowed to stand still at room temperature, for 48 hours. The obtained solutions were then filtered, and the filtrate was washed with diluted H_2SO_4 and distilled water and dried at 60 °C. The dried residue was transferred to an oven and calcined at 450 °C for 2 hours to obtain the final samples, which were referred to as TiO_2-N 1: 0.4; TiO_2-N 1: 1 and TiO_2-N 1:2.

3.6.2. Study of photocatalytic activity of nitrogen doped TiO_2

For the TiO_2 - N 1: 0.4 sample the possibility of Rose Bengal dye degradation under natural sunlight was explored. The experiments were performed in May 2014, starting at 9.00 o'clock, outdoors. The dye solution - photocatalyst mixture was magnetically stirred in the dark for 30 minutes, after which the reactor was subjected to the action of daylight. After 3 hours of photocatalytic reaction, the N doped TiO_2 sample conducted to a dye conversion of 92.7%, while the un-doped TiO_2 did not show any photocatalytic activity. By doping mesoporous titanium oxide with nitrogen, an innovative photocatalyst with high activity under sunlight irradiation was obtained.

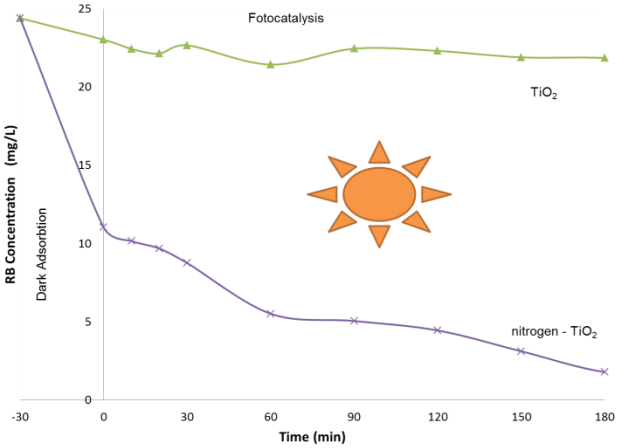

Figure 3.54. Photocatalytic degradation of RB under the action of sunlight in the presence of N doped and un-doped TiO_2 synthesized semiconductors

General Conclusions

Considering scientific and economic activity's urgent request of efficiency improvement methods for the photocatalytic degradation of unwanted organic pollutants present in wastewater, the thesis nemed „Optimization design of semiconductor nanophotocatalysts - efficeient materials used in advanced treatment processes of textile industry wastewater" describes the development of effective next generation semiconductor photocatalysts, which allowed separation of photoinduced charges and their recombination delay, with decreased energy band gap. Therefore new semiconductor materials that lead to the achievement of simple, cheap and clean photocatalytic processes were obtained, processes which can be considered „green technology".

During investigations, new photocatalytic nanostructured systems were obtained: mesoporous titanium oxide powders doped with nitrogen, WO_3, WO_3 + Pt; TiO_2- mesoporous carbon composite; TiO_2 - ordered mesoporous carbon composite; TiO_2-zeolite and TiO_2-ZnO-zeolite composite, $Bi_2Fe_4O_9$ powders, which are characterized by efficiency and originality.

Photocatalytic activity of the new nanostructured photocatalytic systems was studied by comparison with commercial P25 titanium oxide, regarded as a standard photocatalyst. The nanostructured photocatalytic systems were tested for the degradation processes of 4 dyes: Rhodamine 6G, Rose Bengal, Methyl Orange and Methylene Blue, and also for phenol degradation.

The original research went through several stages:

Early studies were focused on the possibility of improving the design of photocatalysts based on nano-zinc oxide, obtained by precipitation method using different basic media during synthesis (NaOH or urea). The photocatalytic activity of ZnO in the process of Rhodamine 6G dye degradation (R6G) used as model organic, was compared to the one exhibited by TiO_2, as a standard photocatalyst. Structural, adsorptive and morphological changes were reflected on the degradation of R6G in both cases, when working under similar conditions, the dye conversion is similar to that of specific commercial TiO_2.

The optimal operational parameters were studied (pH, concentration of catalyst, dye concentration) in the case of Rose Bengal dye degradation in aqueous solutions, using commercial TiO_2 based systems.

It has been found that the degradation was more rapid if the pH value was 5.6, this being explained by the fact that the positively charged TiO_2 surface facilitates adsorption of the anionic colorant, and at the same time, the entire photocatalytic process.

Maintaining constant experimental parameters values (pH = 5,6, C_{CAT} = 0,25 g/L, C_{0dye} = 20 mg/L) the mineralization of Rose Bengal dye was investigated using TOC analysis. The following hierarchy in terms catalysts performance was obtained:

TiO_2 UV 100 (83%)> Degusa P25 (76%) > ZnO (70 %).

A study on the photocatalytic activity of Bi2Fe4O9 particles presenting different micro/nanostructures was conducted. It was revealed that not only the size of the micro / nanocrystals influences their photocatalytic properties, but also their structure, as different facets of the crystals have different energy levels of the conduction and valence bands.

An original study was performed, aiming to improve the design of mesoporous TiO_2 and P25 TiO2 photocatalysts by doping with 2% WO_3, 5% WO_3 and WO_3 + 2% 1% Pt. The study of Rhodamine 6G dye photocatalytic degradation under the influence of the new photocatalysts, was focused on investigating the influence of operational parameters (catalyst concentration, pH), which led to highlighting some important theoretical and practical correlations: doped mesoporous materials are more effective in the initial step of adsorption of the dye; intense ionization of the dye molecules explained photocatalytic efficiency of the process, which was higher at extreme pH values, due to their adsorption emprovement; at pH> PZC, the catalyst surface is negatively charged and the molecules attract the cationic R6G dye from water.

The design of TiO_2 photocatalysts was optimized by achieving a nanocomposite consisting of a matrix of clinoptilolite (hydrogen form), used as support (photocatalytic inactive) for TiO_2 and ZnO photoactive nanoparticles. The improved photocatalytic activity was asigned to the

formation of hetero-junctions between coupled metal oxides and metal oxides - clinoptilolite. The obtained results emphasize the possibility of transforming the Chilioara clinoptilolite in eco-friendly photocatalytic materials with enhanced applications.

An original aspect of the research has focused on the synthesis of new photocatalysts with high photocatalytic activity, based on a mesoporous TiO_2 innovative synthesis: nanocrystalline particles assembly using Pluronic P123 (autoclave synthesis, synthesis under reflux and ultrasound) and F127 (autoclave synthesis and ultrasound) as templates.

Nitrogen doping of mesoporous TiO_2 photocatalysts with different molar ratios was studied: TiO_2 - N 1: 0.4; TiO_2 - N 1: 1 TiO_2 - N 1: 2. The photocatalytic test was carried out for the photodegradation of methylene blue dye in aqueous solution. Both doped and undoped titanium oxide are highly active photocatalysts under UV light action.

On the other hand, when the photocatalytic activity of the doped and undoped titanium dioxide under the action of sunlight was tested, remarkable results were achieved for the doped photocatalysts (92.7% Rose Bengal), whereas the undoped TiO_2 showed no photocatalytic activity.

In order to increase the efficiency of photocatalytic degradation, a composite photocatalytic system was synthesised. It was a TiO_2 coated mesoporous carbon obtained through a microwave assisted innovative synthesis, by using the synergistic effect of the special adsorptive properties of mesoporous carbon (which facilitated the diffusion and concentration of the dye molecules around the TiO_2 particles) and the great photocatalytic activity exhibited by the TiO_2. Mesoporous carbon samples were prepared by nanocasting method using SBA-15 as a template and glycerol as carbon source, and the composite material was obtained by dry impregnation method, followed by conventional calcination in the furnace at 450° C, or microwave treatment.

Another original aspect of the research refers to the development of a new system, which is photocatalytically active under visible radiation. This system was obtained by dispersion of TiO_2 on the internal and external surface of the ordered mesoporous carbon (CM) using un innovative ultrasound assisted impregnation method. Anatase TiO_2 coating facilitated the capture of electrons at the extended interface between the TiO_2 anatase nanoparticles and the graphite parts of the MC support, substantially delaying the electron – hole recombination, this increasing the speed of phenol photodegradation under the action of visible light.

The experimental results have led to the achievement of the major objective of the thesis: creating a new design of next generation semiconductor photocatalysts showing photocatalytic activity under visible light action and natural sunlight.

References

Allen J. Bard, Design of Semiconductor Photoelectrochemical Systems for Solar Energy Conversion, Journal of Physical and Chemical86, 1982, pp.172-177

Asahi R., Morikawa T., Ohwaki T., Aoki K., Taga Y., "Visible-Light Photocatalysis in Nitrogen- Doped Titanium Oxides", Science, Vol. 293. no. 5528, 2001, pp. 269 – 271.

Beydoun D., Amal R., Low G. and McEvoy S., "Role of Nanoparticles in Photocatalysis", Journal of Nanoparticle Research, Vol. 1, 1999, p. 439-458.

Cai D., Du D., Yu S., Cheng J., Oriented growth of $Bi_2Fe_4O_9$ crystal and its photocatalytic activity, Proc. Eng., 27, 2012, pp. 577–582.

Coromelci-Pastravanu C., Ignat M., Popovici E., Harabagiu V., TiO_2-coated mesoporous carbon: Conventional vs. microwave-annealing process, Journal of Hazardous Materials, 278, 2014, pp. 382–390.

Gheorghiu F., Tanasa R., Buscaglia M.T., Buscaglia V., **Pastravanu C.G**., Popovici E., Mitoseriu L., Preparation of $Bi_2Fe_4O_9$ particles by hydrothermal synthesis and functional properties, Phase Transitions: A Multinational Journal, Volume 86, Issue 7, 2013, pp. 726-736.

Hartmann M., Vinu A., Mechanical stability and porosity analysis of large-pore SBA-15 mesoporous molecular sieves by mercury porosimetry and organics adsorption, Langmuir, 18, 2002, 8010–8016.

Ignat M., **Coromelci C**., Popovici E., TiO_2-coated Ordered Mesoporous Carbon for Phenol Photodegradation, Rev. Chim. (Bucharest), 63, no. 4, 2012.

Jung W.Y., Baek S.H., Yang J.S., Lim K.-T., Lee M.S., Lee G.-D., Park S.S., Hong S.-S., Catalysis Today, 131, 2008, 437–443.

Kim B.-S., Sekino T., Yamamoto Y., Nakayama T., Kusunose T., Wada M., Niihara K., *Mater. Lett.*, 2004, p. 58, 17.

Linsebigler A. L., Lu G., Yates J.T. Jr., *Chemical Reviews*, vol. 95, nr. 3, 1995, pp. 735-758.

Lutic D., **Coromelci – Pastravanu C.,** Crețescu I., Poulios I., Stan C.D., Photocatalytic Treatment of Rhodamine 6G in Wastewater Using

Photoactive ZnO, International Journal of Photoenergy, Volume 2012, Article ID 475131, 2012, 8 pages.

Meynen V., Cool P., Vansant E.F., Verified syntheses of mesoporous materials, Microporous and Mesoporous Materials, 125, 2009, pp. 170–223.

Okamoto K., N. Iyi and T. Sasaki, „The urea method for the direct synthesis of ZnAl layered double hydroxides with nitrate as the interlayer anion", *Applied Clay Science*, vol. 37, pp. 23–31, 2007.

Pastravanu C., Poulios I., Popovici E., Cretescu I., A case study of textile wastewaters treatment by heterogeneous photocatalytic degradation, Annals of the Dunărea de Jos University of Galați, Mathematics, physics, theoretical mechanics, Fascicle II, 2009

Stan C.D., Crețescu I., **Pastravanu C.**, Poulios I., Drăgan M., Treatment of Pesticides in Wastewater by Heterogeneous and Homogeneous Photocatalysis, International Journal of Photoenergy Volume 2012, Article ID 194823, 6 pages, doi:10.1155/2012/194823

Ulmann M., Friedlander S., Schmidt-Ott A., Nanoparticle formation by laser ablation, Journal of Nanoparticle Research, 4, 2002, pp. 499–509.

Umebayashi T., Yamaki T., Ito H., Asahi K., Band gap narrowing of titanium dioxide by sulfur doping, Appl. Phys. Lett. 81, 2002, pp. 454–456.

Ung T., Liz-Marza L. and Mulvaney P., Gold nanoparticle thin films, Colloids and Surfaces A: Physicochemical and Engineering Aspects, no. 202, 2002, pp. 119–126.

Zaleska A., Gorska P., Sobczak J.W., Hupka J., Appl. Catal. B, 76, 2007, p. 1

Zhang M., Yang H., Xian T., Wei Z.Q., Jiang J.L., Feng Y.C., Liu X.Q., Polyacrylamide gel synthesis and photocatalytic performance of $Bi_2Fe_4O_9$ nanoparticles, J. Alloy Compd., no. 509, 2011, pp. 809–812.