LASER-ASSISTED SYNTHESIS OF WATER COLLOIDAL METALLIC NANOCOMPOSITES

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ABSTRACT

Picosecond and Nanosecond Nd:YAG laser systems with a fundamental wavelength of 1064 nm are utilized for green synthesis of bimetallic nanocomposites based on metal combinations of Pt/Ti, Pd/Ti, Pt/Zn and Pd/Zn. The laser assisted method is based on pulsed laser ablation of metal targets, which are immersed consecutively in bidistilled water to obtain water colloids of the corresponding bimetallic nanostructures. Comparative study of the structural and optical properties of the nanocomposites is conducted by means of transmission electron microscopy in its corresponding main modes and by optical spectrometer measurements, respectively. Suspensions of water colloids of the nanocomposites and methylene blue dye prepared in 1 : 2.5 ratio, respectively, are exposed under sunlight irradiation for 3 h. Photocatalytic activity of the nanocomposites against methylene blue (MB) dye is tested by measuring the optical absorbance of the suspensions before and after the sunlight irradiation.

Keywords: laser-assisted synthesis, picosecond and nanosecond pulses, water colloids, bimetallic nanocomposites, noble metals, Pt/Ti, Pd/Ti, Pt/Zn and Pd/Zn, photocatalytic ability, methylene blue, photodegradation.

INTRODUCTION

Great attention is focused to degradation of dyes like methylene blue, methylene orange, toluidine blue, aniline blue, alcian blue, crystal violet, which are one of the main and popular synthetic dyes widely used for pigmentation of different materials, paper, leather, ceramic, plastics and especially in the textile and clothing industries [1 - 4]. This causes extremely large annually industrial production of thousands of tons synthetic dyes. Unfortunately, parts of dyes are regularly discharged with the wastewater during preparing and cause enormous danger to human health and the environment, because they are carcinogenic and toxic, especially azo dyes. Dyes bring tremendous pollutions as most of them are difficult to biodegrade due to their stability to water, light, temperature, soap, and detergents, and thus persisting in environment become of a global problem. Methylene blue is one of this widely used synthetic dye in coloring of silk, cotton, wool, paper, food, pharmaceutics, cosmetics. Photocatalytic degradation of synthetic dyes, by incorporating advanced nanomaterials, has become more efficient and preferred over other methods [5 - 9]. Nowadays, this methodology for removal of the dye pollutants from wastewater is a widely reported method because of its simplicity of operation and numerous advantages such as utilizing of the sunlight as a light source (renewable resource), efficient and complete decomposing of the dye into eco-friendly mineral substances, lower cost and shorter reaction time of the operation process.

The methods utilizing for synthesis of bimetallic nanoparticles can be categorized generally like physical, biological and chemical, which have been reviewed in detail in [5]. Each of them involves numerous methods based on a top-down approaches (the physical methods) and a bottom-up approaches (the chemical and the biological methods).

Various types of bimetallic nanocomposites have been synthesized in different combinations between noble-noble metals or noble and transition metals, known as gold-based, silver-based, copper-based, nickel-based, iron-based, platinum-based, or palladium-based [1 - 12]. Such bimetallic nanocomposites have been already applied for degradation, reducing and removing different toxic contaminants (metal ions, pesticides or nitrate, phosphate, dyes, antibiotics, fluoride, arsenic, hazardous pollutants etc.) from the wastewater [1 - 11]. The enhanced catalytic efficiency of the bimetallic nanocomposites in comparison with the monostructured nanoparticles is due to the synergistic effect resulted from the combined metals, which induce new structural and physical properties of the obtained nanocomposites. Moreover, the mono and bimetallic nanoparticles have already proved their high capabilities and benefits for various applications (biological, agriculture, environmental, engineering, in physics and chemistry).

Bimetallic nanocomposites based on noble metals like Pt, Pd, Au, and Ag or noble metal combined with semiconductor oxides such as titania or ZnO, prepared mostly by chemical methods, have been attracted more attention in recent years [8, 11], since they revealed highly photocatalytic activity, chemical and biological stability, non-toxicity, and high surface area.

The advantage of the synthesis of bimetallic nano-composites by pulsed laser ablation in water, which belongs to the physical synthesis methods, is that this method does not require clean room, allows easy control and contactless processing, the duration of the synthesizing process takes a very short time (up to several minutes) in comparison with other methods, and the most important the products obtained are contaminant-free. Looking forward, the development of this method will enhance the manufacturing of bimetallic nanostructures from various combination of metals with controlled properties (morphological, optical, crystal, or electrical), which will allow tuning of their catalytic ability and selectivity for water treatment, air pollution control and many other environments, agriculture, engineering, medical, sensors applications etc.

In this study, a two-fold objective was set, firstly, a comparative study of the properties of bimetallic nanocomposites in different combinations such as Pt/Ti, Pd/Ti, Zn/Ti, Pt/Zn and Pd/Zn synthesized by laser ablation in water using picoseconds and nanosecond pulsed laser systems, respectively. And secondly, investigation of the photocatalytic activity of selected nanocomposites for mitigation of methylene blue as pollutant model dye under sunlight illumination for certain time. Meanwhile, to the best of our knowledge, these bimetallic combinations have not been investigated and compared simultaneously in the case of synthesis by picosecond laser processing of metal targets in water.

EXPERIMENTAL

Water colloids of metallic nanocomposites were synthesized by pulsed laser ablation of metal targets immersed in bidistilled water by means of two Nd:YAG laser systems: one generating nanosecond pulses (LOTIS with pulse duration of 15 ns and repetition rate of 10 Hz); and second generating picosecond pulses (CNI Laser, PS-A1-1064 with pulse duration of 10 ps and repetition rate of 1 kHz). The metal targets used were Ti (Merck, 99.995 %), Zn (Merck, 99.995 %), Pt (Merck, 99.9 %), and Pd (Merck, 99.9 %). In both cases of laser processing the metal targets successively one after other were immersed in water and were ablated with the fundamental wavelength of 1064 nm for completing all combinations, such as Pt/Ti, Pd/Ti, Zn/Ti, Pt/Zn, and Pd/Zn. Laser fluence of the picosecond laser irradiation about 2.70 J cm^{-2} and a repetition rate of the pulses of 1 kHz were applied for synthesizing the metal nanocomposites in water. The process parameters and conditions of fabrication of the water colloids of the metal nanocomposites by nanosecond laser pulses, were described in detail elsewhere [12]. It is worth to note that in this case the bimetallic nanocomposites were obtained by two-step laser process - first laser ablation of the corresponding targets in water, which was followed by post-ablation laser irradiation of the water colloids with unfocused laser beam at UV wavelength 266 nm.

However, the experiments at the picosecond laser system were carried out by one-step laser processing by applying only laser ablation of the metal targets in water. Namely, first the metal target of Ti or Zn was placed on the bottom of the vessel filled with bidistilled water and was ablated up to 60 sec. Then the Ti or Zn target was replaced by a target of a noble metal Pt or Pd, respectively, which was ablated for 60 seconds in already obtained water colloids of Ti/Ti_xO_{2x-1} or of Zn/ZnO nanostructures, respectively. Thus, each target was processed with laser number of pulses up to 60000 (at a repetition rate 1000 Hz). The height of the water column was kept at 10 mm. The laser beam was focused perpendicularly to the surface of the target by a lens with focal length of 300 mm. The vessel was placed on the computer-controlled stepper-motor x-y table. Its moving speed was kept high enough in order to minimize overlapping of the laser spots on the target surface and also to minimize the absorption of the laser beam by the plasma plume formed during the ablation.

Optical, morphological, and structural properties of the nanocomposites synthesized by picosecond laser ablation in water were investigated and compared with the properties of the nanocomposites obtained after nanosecond laser processing in water, which were commented elsewhere [12]. Immediately after the laser-assisted synthesis of the nanostructures in water the following three steps were done:

- a drop of the colloid was dropped onto a standard TEM copper grids consisting 300 meshes, which had been preliminary covered by amorphous carbon membrane. After that the drop was left to dry for several hours;
- the water colloid was poured in a UV-transparent crystal cuvette for measuring the optical transmittance and absorbance;
- measurement of the optical transmittance and absorbance spectra of the water colloids immediately after laser processing.

Transmission electron microscopy (TEM) in its main modes Bright Field TEM (BF TEM), High Resolution TEM (HRTEM) and Selected Area Electron Diffraction (SAED) were performed to study the microstructural and shape characteristics. The images were acquired with a JEOL JEM 2100 at an accelerating voltage of 200 kV by scanning the as-prepared samples by dropping a drop, described above. Optical transmittance and absorbance of the water colloids of the nanocomposites in the UV-Vis-NIR range (between 190 and 900 nm) of the spectrum were measured by Carry 1E UV-Visible spectrophotometer.

Photocatalytic activity of the synthesized nanocomposites was tested under natural sunlight exposure of suspension of water colloids of nanocomposites and methylene blue. The initial concentration of methylene blue was 20 ppm in water solution, pH 6. The suspensions of MB and the respective water colloid of the nancomposites (Pt/Ti, Pd/Ti, Pt/Zn, Pd/Zn, or Ti/Zn) were prepared in 2.5:1 ratio (2.5 parts MB and 1 part water colloid of the nanocomposite in volume of 3 ml) and shaken by hand for mixing. The suspensions thus prepared (called as initial) were allowed to be illuminated by sunlight from two up to three hours in order to trace the mitigation of the methylene blue by the nanocomposites. The exposure was carried out between 11.00 h and 15.00 h when the sunlight is most intense, and each test was performed on clear day when the average sunlight intensity at noon was about 1 kW m^{-2}. The optical absorbance (and transmittance) of the suspensions were measured before sun exposure, an hour after starting exposure and at end of the exposure. The degree of photodegradation of the methylene blue was assessed by the changes of the optical absorbance spectrum observed for each type of sunlight exposed suspension in comparison with that one of the corresponding initial suspension.

RESULTS AND DISCUSSIONS

The work aims to elucidate the influence of the pulse duration and the repetition rate on the photocatalytic properties of metallic nanostructured composites - Pt/Ti, Pd/Ti, Zn/Ti, Pt/Zn, and Pd/Zn, synthesized by laser ablation in water using picosecond and nanosecond laser pulses, respectively. It must be highlighted that the structural and morphological properties of the Ti/Pt, Ti/Pd, Zn/Pt, Zn/Pd and Ti/Zn nanocomposites fabricated by nanosecond laser processing in water have been previously reported elsewhere [12].

Optical transmittance spectra of the water colloids of Zn and Ti nanostructures obtained by picosecond and nanosecond laser pulses showed similar behavior to the spectra of thin films of ZnO and Ti_xO_{2x-1}, respectively, obtained previously [13, 14]. This means that nanostructures of metal oxides were most likely formed during the laser ablation of these metal targets.

Optical transmission of the water colloids of Zn and Ti up to 70 % in the visible range of the spectrum was measured after ablation up to 60 sec. The corresponding TEM analysis showed formation predominantly of crystalline nanoparticles of oxides such as: cubic or hexagonal ZnO, and triclinic or orthorhombic oxygen deficient oxides of titanium - Ti_xO_{2x-1} (like Ti_7O_{13}, Ti_4O_{11}).

Optical transmittance spectra of the water colloids of Pt and Pd nanostructures obtained by picosecond ablation demonstrated one wide, but well defined, surface plasmon resonance band at 262 nm and 238 nm. Whereas the water colloids of Pt and Pd nanoparticles, respectively, obtained by nanosecond laser ablation did not revealed well defined plasmon resonance band. One possible reason could be the less productivity of the nanosecond ablation with low repetition rate of 10 Hz in comparison with the picosecond ablation with much higher repetition rate of 1000 Hz. The presence of a plasmon resonance in the optical spectrum could due to formation of: (1) pure metal phases (Pt and Pd) and (2) spherical shaped nanoparticles. This was confirmed by TEM images (not presented here), showing very well spherical shaped Pt or Pd nanoparticles. Mainly crystalline nanoparticles of Pt or Pd with cubic structure were detected by HRTEM and SAED measurements after picosecond laser ablation in water. In case of water colloid of Pd traces of tetragonal PdO were also found.

The analytical transmission electron microscopy and its main modes were applied for characterizing the composite nanostructures prepared by picosecond pulsed laser ablation in water. It helped to determine their morphological and structural features and to compare them with those of the nanocomposites synthesized by nanosecond laser pulses in water. The BFTEM, HRTEM and SAED measurements of all types of water colloidal nanocomposites showed a tendency towards formation of bimetallic nanostructures, as it can be seen in Fig. 1. Namely, in all cases of combinations: Pt/Ti; Pd/Ti; Pt/Zn; Pd/Zn; Ti/Zn, corresponding polycrystalline phases of bimetallic composites were recognized. Also, metal oxides (mainly oxygen deficient phases of titania and PdO) and pure metals phases were found. Formation of these nanostructures was evident by BFTEM and HRTEM images taken at different magnification. The dark-grey imaging contrast, resulting from the difference in the electron densities in the measured planes, helped to distinguish nanoparticles from the heavier metals (Pt and Pd) (which appeared as dark objects) versus the Ti and Zn metals. Usually, the nanoparticles from the metal oxides appeared with white-grey to grey contrast, which could be also recognized in the presented TEM images. The HRTEM as a phase-contrast imaging mode allowed to directly image the atomic structure of the nanoobjects in subnanometers scale. The electrons emitted from the cathode were diffracted from the atoms and sets of atoms. In case of a crystalline sample the diffraction contrast superimposed in the contrast of the transmitted electron beam. Thus, the crystallographic orientations of even very small nanoobjects were revealed. The corresponding lattice constants were calculated by measuring the interplanar distances, which allowed to establish the polycrystalline phases of the bimetallic nanocomposites (commented below) synthesized during the ps-laser ablation in water.

The selected area electron diffraction (SAED) patterns appeared as images of concentric rings due to formation of differently oriented nanocrystallites with high crystallinity. Since the signal was acquired by a certain area contributing to diffraction via adjusting the selected area aperture, which was larger enough than the size of an average-sized nanostructure. The resulting SAED images revealed superposition of the signals diffracted from individual crystalline structures in the area by superimposing the signals from all crystallographic planes in all their possible orientations. The SAED patterns confirmed the HRTEM measurements, disclosing formation of the same polycrystalline phases of heterogeneous nanostructures (bimetallic), metal oxides and pure metal phases from the corresponding targets. Small differences in phase identification were possible, but this could due to the measurement specificity of these modes of TEM analysis.

So, the corresponding results on the structure of Ti and Pt bimetallic nanostructures obtained in the water colloids by ps-laser ablation were identified as orthorhombic Pt_5Ti_3; cubic Pt_3Ti; tetragonal Pt_8Ti. In case of consecutive ablation of Ti and Pd targets, the resulted water colloid was found to consist an orthorhombic Pd_3Ti_2 phase. For colloid of Zn combined with Pt and for colloid of Zn combined with Pd bimetallic nanostructures such as cubic Pt_3Zn_{10} and Pt_3Zn; orthorhombic $PdZn_2$; and tetragonal PdZn were recognized. In case of colloid of Ti and Zn binary systems as hexagonal $TiZn_2$;

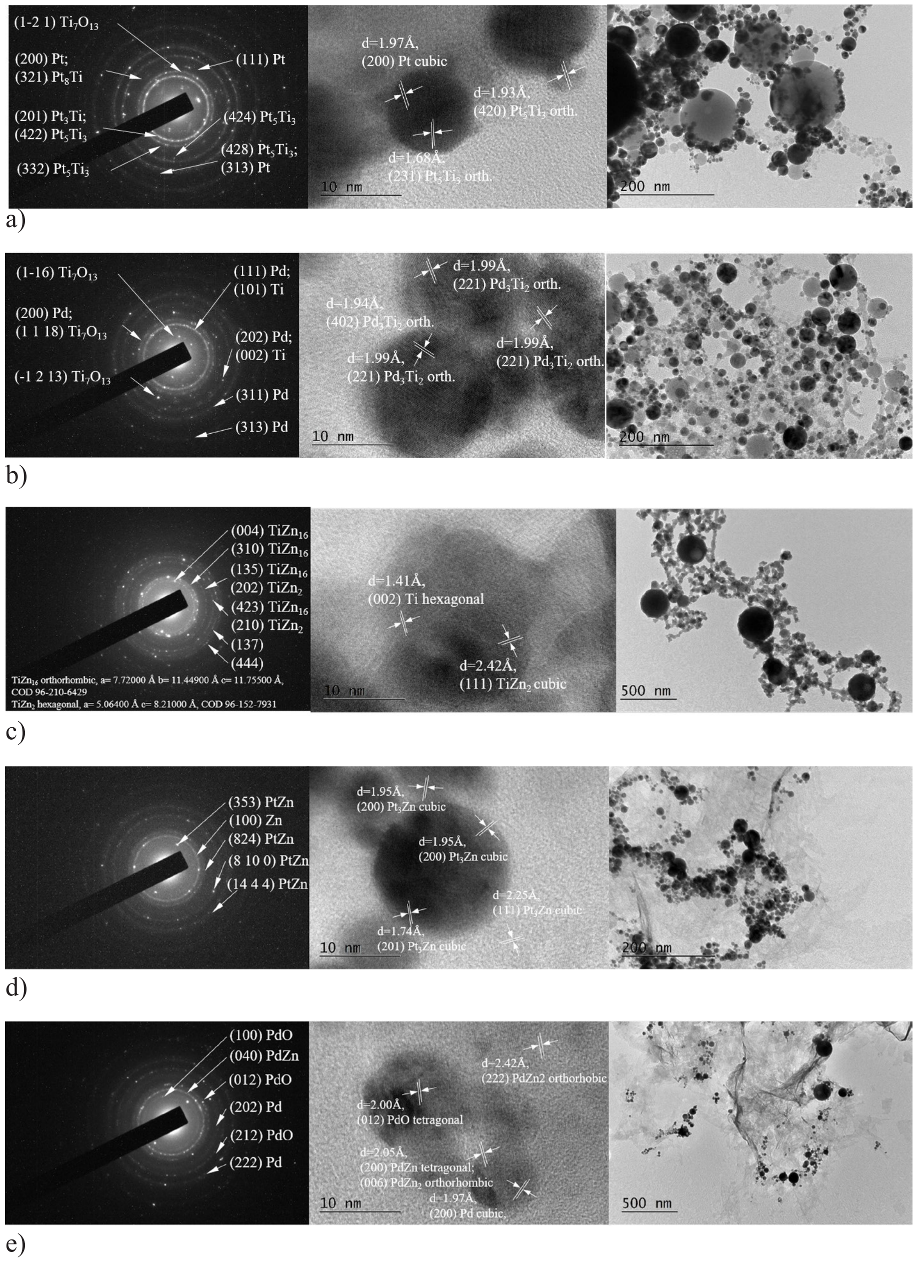

Fig. 1. SAED, HRTEM, and BF TEM images of bimetallic (a) Ti/Pt, (b) Ti/Pd, (c) Ti/Zn, (d) Zn/Pt and (e) Zn/Pd nanocomposites synthesized by picosecond laser ablation (one-step laser processing) in water with wavelength 1064 nm.

cubic $TiZn_2$; and orthorhombic $TiZn_{16}$ were identified. Nanocrystalline pure metals such as Pt cubic; Pd cubic, Ti hexagonal; and Zn hexagonal were also detected, which means that the water colloids consisted not only of the bimetallic phases. Traces of crystalline PdO metal oxide and oxygen-difficient titanium oxides (Ti_7O_{13} or Ti_4O_{11} triclinic) were found in cases of the water colloid: of Zn with Pd; of Ti with Pt and of Ti with Pd, respectively. Formation of PdO could be attributed to specific thermodynamic conditions, which were induced during the laser ablation in water due to fast increase of the local temperature of the target surface and in the near vicinity. This could rice the kinetic energy and thus to activate reaction between the metal nanoparticles and water. Pt is much more resistant to oxidation than Pd and this was probably the reason no oxidized Pt metallic particles were captured. The results obtained from both HRTEM and SAED measurements correlated very well with each other. A specific morphology and size distribution was observed for each type of nanocomposites due to their composite origin.

While in case of laser ablation of the same combinations of the metallic targets in water by nanosecond laser pulses, HRTEM and SAED measurements showed presence only of traces of hetero-nanostructures such as: a) cubic Pt_3Ti, orthorhombic Pt_5Ti_3 in case of Pt/Ti combination; b) tetragonal Pd_5Ti_3 in case of Pd/Ti combination; c) orthorhombic $TiZn_{16}$ in case of Ti/Zn combination. And after post-ablation irradiation with unfocused laser beam (with nanosecond pulsed duration and repetition rate of 10 Hz) the aforementioned bimetallic nanocomposites started predominantly to synthesize. It is noteworthy, dramatic morphological changes of the nanocomposites occured after the nanosecond post-ablation laser irradiation. Tendency towards formation of complex core-shell-like nanocomposites was observed [12].

Whereas, in case of laser ablation of the aforementioned metal targets in water by picosecond laser pulses, numerous small (dark in contrast) particles (predominantly identified as noble ones) were observed mainly to stick on the periphery of bigger oxides nanoparticles. It is important to underline that no presence of bimetallic nanostructures of Zn and Pt and of Zn and Pd in the water colloids was detected after nanosecond laser processing (ablation and post-ablation irradiation).

In general, the laser processing with picosecond laser pulses should be preferable instead of nanosecond laser pulses for synthesis of bimetallic nanocomposites, since the procedure was simpler, needs shorter time processing, and wanted products - bimetallic nanocomposites - were obtained. This is a good reason for using a picosecond laser system to fabricate bimetallic nanocomposites for industrial applications, over the still expensive femtosecond laser systems.

Different mechanisms of the laser-matter interaction become dominant during irradiation with laser pulses with different duration - nanosecond and picosecond, with different repetition rate - 10 Hz and 1000 Hz, respectively. Much higher repetition rate of the picosecond laser radiation (1 kHz) in comparison with the lower one of 10 Hz of the nanosecond laser radiation additionally could yield higher plasma shielding effects. This could induce the formation of bimetallic nanocomposites directly during the picosecond laser ablation due to absorption of some portion of the laser beam energy by the ablated particles contained in the plasma plume near the focused spot. While in the case of nanosecond laser processing, the bimetallic nanocomposites were formed mainly after post-ablation laser irradiation with unfocused beam. Additional investigations of the thermodynamic and hydrodynamic processes are required to make critical comparison between the mechanisms of formation of the nanocomposites during the picosecond and nanosecond pulsed laser processing of the targets in water.

The photocatalytic activities of the nanocomposites were investigated by measuring the optical absorbance spectra of suspensions of MB day with the water colloids of the corresponding nanocomposites after sunlight exposure for 3 hours, shown in Fig. 2. The suspensions, prepared in ratio 2.5 parts MB and 1 part water colloid of nanocomposites with a total volume of 3 mL, were shaken periodically by hand every 30 minutes during the sun irradiation. The absorbance spectra were measured before, an hour after starting and at end of the sun exposure. For comparison, a solution of MB in water in 2.5:1 ratio with same total volume was also exposed to the sun light for 3 h. From Fig. 2a and Fig. 2b could be seen that the absorbance spectra of all initial suspensions, including also this one of the water solutions of MB, before sun light exposure are very similar and depicted typical for MB blue peaks at 664 nm with a shoulder at 614 nm and an additional peak in UV region at 291 nm. However, after three hours of sunlight irradiation dramatic changes in the absorbance spectra of all suspensions were observed. The significant decrease of the peak's intensity revealed the photocatalytic response of the nanocomposites against the MB dye. The intensity of the main peak (at 664 nm) in the visible region and at 291 nm dropped sharply. The shoulder shape at 614 nm almost decayed except for that one corresponding to the water solution of MB. The most prominent changes were occurred in the optical absorbance spectra of the suspensions containing nanocomposites of noble metals/Ti and noble metals/Zn (namely, the nanocomposites of Zn/Pd, Zn/Pt, Ti/Pd, and Ti/Pt). The peaks of the MB dye not only decreased, but almost disappeared, which confirmed photodegradation of the MB dye. A visible manifestation of the decrease in absorption of the investigated suspensions was expressed in their discoloration after exposure to the sunlight. While initially, before starting sunlight

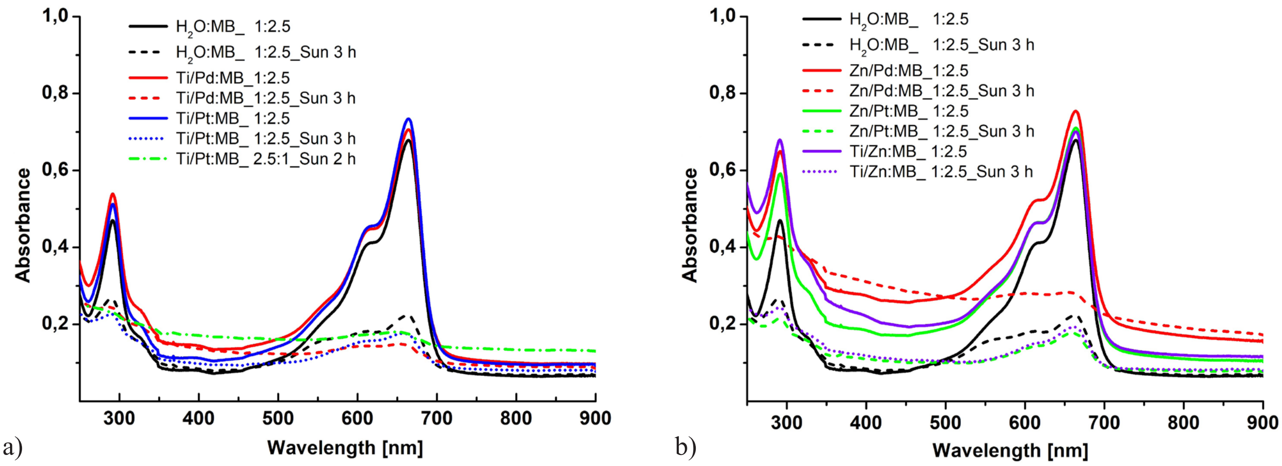

Fig. 2. Absorbance spectra of suspensions of water colloids of (a) bimetallic (Ti/Pt, Ti/Pd) and (b) bimetallic (Ti/Zn, Zn/Pt and Zn/Pd) nanocomposites and methylene blue (MB) dye in ratio 1:2.5, respectively, as well the absorbance spectra of the water solution of MB in 1:2.5 ratio, all measured before and after sun light irradiation for 3 h. The volume of the suspensions and the solution was kept 3 mL.

irradiation, all suspensions had a saturated light blue color. The bimetallic nanocomposites revealed highly efficient photocatalytic activity since the methylene blue was almost entirely decomposed after the sun light irradiation.

High surface area, active sites, adsorption capacity, lattice defects are key characteristics, which determine the photocatalytic properties of the nanocomposites. Therefore, the next step of this study is the optimization of the related process parameters to obtain the desirable size, morphological and crystalline characteristics of the bimetallic nanocomposites synthesized by laser ablation in water.

CONCLUSIONS

In summary, several main conclusions can be drowned about the bimetallic nanocomposites Zn/Pd, Zn/Pt, Ti/Zn, Ti/Pt, or Ti/Pd, synthesized in water colloids by nanosecond and picosecond laser-assisted processing:

- direct synthesis through an one-step process by (i) laser ablation with picosecond laser pulses at wavelength 1064 nm and high repetition rate (1kHz);
- synthesis through two-steps process, when nanosecond laser pulses with repetition rate of 10 Hz were applied: (i) laser ablation at wavelength 1064 followed by (ii) post-ablation laser irradiation with unfocused laser beam at wavelength 266 nm;
- picosecond laser pulses significantly simplified the procedure and reduced the production time of the bimetallic nanocomposites in contrast to the nanosecond laser pulses;
- repetition rate of the pulsed laser irradiation could crucially influence on the process of synthesis of bimetallic nanocomposites;
- synergistic effect of short laser pulses and high repetition rate probably was responsible for direct synthesis of the bimetallic nanocomposites during the picosecond laser ablation in water;
- eco-friendlier nature laser-assisted synthesis in water has revealed many advantages over other methods used to produce bimetallic nanocomposites, expressed in: efficient and contactless laser procedure of fabrication; easy control of the process parameters; contaminant-free products; no waste products; no clean room required; use of relatively low-cost laser systems - nanoseconds and picoseconds, which would facilitate designing of simple and inexpensive technologies for industrial-scale production of bimetallic nanocomposites;
- bimetallic (Zn/Pd, Zn/Pt, Ti/Zn, Ti/Pt, Ti/Pd) nanocomposites produced by picosecond laser ablation in water induced effective photodegradation of the methylene blue dye under sunlight exposure up to 3 h of

suspensions of the water colloids of the nanocomposites and the MB dye in ratio 1:2.5, respectively.

The photocatalytic activity, reaction time and related parameters will be further investigated to find the most effective characteristics of the bimetallic (Zn/Pd, Zn/Pt, Ti/Zn, Ti/Pt, Ti/Pd) nanocomposites for photodegradation of MB dye.

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