

Rapid Synthesis of Silver Nanoparticles and Their Decoration on TiO₂ by Plasma-Over-Liquid Process: Characterization and Application for Tetracycline Antibiotic Degradation

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ABSTRACT

The results of studies on obtaining and characterization of silver nanoparticles aqueous solution under the action of the contact non-equilibrium low-temperature plasma and stabilizing agent (sodium citrate) are presented in the paper. The influence of the basic parameters on the synthesis of silver nanoparticles was studied. Different physicochemical characteristics were investigated: initial precursor concentration, reagent ratio, duration of plasma discharge treatment. [Ag⁺]:[Cit] ratio as 1:1 at silver ion concentrations of Ag⁺ 0.1-3.0 mmol/L and treatment of the reaction system for 4-5 minutes was found to be appropriate. Under these conditions, the surface plasmon resonance (SPR) was observed at 405-420 nm on UV-Vis spectra. Particles with the average diameter of 35.0 ± 2.0 nm, spherical shape and polydispersity index of 0.032 ± 0.01 are typical amongst synthesized nanoparticles at [1]:[1] molar ratio. It was found that the reaction of nanoparticle dispersion formation was a pseudo-first order reaction with the reaction rate constant of 0.61 min⁻¹. It has been established that sodium citrate is the capping agent and acts only as the stabilizer of Ag NPs. To prepare the nanocomposite material (TiO₂/Ag NPs), silver nanoparticles have been deposited on photocatalyst (TiO₂ rutile phase) by plasma discharge. EDS and SEM analysis showed that composite material has core-shell structure including Ag nanoparticles (NPs) shell with size of 15-25 nm. The results indicated that TiO₂/Ag exhibited good photoactivity under ultraviolet radiation. It was found that 98.7% of tetracycline was decomposed at photocatalyst TiO₂/Ag NPs under the light irradiation. The experimental data of photochemical decomposition of tetracycline under the light irradiation at 430 nm showed that reaction is described by the pseudo first order kinetic model with rate constant (k value) of (3.6)×10⁻³ min⁻¹.

Keywords: Silver nanoparticles, Citrate, Plasma-liquid phase, Titanium dioxide, Photocatalys, Tetracycline, Degradation

1. Introduction

Nowadays, the industry of nanomaterials of different composition and structure is developing very intensively. The development of new and improvement of existing methods of obtaining of nanomaterials is carried out by scientists around the world [1-3]. One of the major areas of nanotechnology is the study of metallic nanoparticles, namely Ag nanoparticles, since they have a set of valuable properties: antimicrobial, catalytic, photocatalytic, sensory, etc [4, 5, 2]. Silver nanoparticles are the most interesting materials for industrial applications.

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Nanotechnology opens new opportunities in the creation of materials and products based on nanoscale Ag compounds [6, 7, 4]. This tendency aims to find the optimal conditions and to develop more sophisticated methods for the synthesis of nanostructures depending on their further use. Currently, there are quite a few synthesis methods that can be used to obtain metal nanoparticles, the most common of which are nanoparticle recovery and stabilization with colloid formation. Modern environmental requirements and ISO standards recommend using «green technologies», non-toxic and more environmentally friendly reagents for synthesis of nanomaterials and stabilizing agents. «Green» technologies are currently used in various aspects in the industry. For instance, the use of waste from the agro-industrial plant raw materials or

minimization of reagent components using highly efficient methods are the main components of green production guidelines. Considerable attention has been paid to so-called plasma based advanced technology methods [8-10]. It is known that plasma-liquid system is complex and involves many different physical and chemical processes. Plasma is a mixture of different active components such as electrons, ions, molecules, radicals, photons, and excited species. In general, it is a partially ionized gas [11, 12]. Therefore, a plasma discharge can induce certain reactions that would not occur under the normal conditions. Nowadays, many practical applications can take advantage of the specific properties of plasma discharge that is generated above or in liquid system. In the literature, different equipment and setups of plasma discharge formation have been reported [10-14]. Thus, parameters were varied to form different types of plasma discharge: gas discharge between an electrode and the electrolyte surface, direct discharge between two electrodes, contact discharge between an electrode and the surface of surrounding electrolyte etc. The use of direct current glow discharge (plasma/contact non-equilibrium low-temperature plasma (CNP)) at atmospheric pressure to reduce Ag ions and synthesize Ag NPs is a green process and novel method. The main advantages of this method are safety and low cost in comparison to other traditional chemical methods of nanoparticles' formation [13, 14]. In contrast to different plasma configurations, CNP can produce a high quantity of active species and reduce metal ions in the solution to form metal silver nanoparticles (NPs) without the presence of any additional reducing agents. Consequently, CNP is considered a "green", environmentally friendly and promising method from the point of view of practical application [15].

Previous studies have found that in the case of the formation of colloidal solutions under the CNP discharge, the products that are generated in the aqueous environment act as a reducing agent [16].

The analysis of the literature data [17, 18] shows that in addition to the choice of the synthesis method, the choice of a stabilizing agent is also an important factor in the formation and subsequent practical use of Ag nanoparticles in various fields. The authors [17, 18] classify stabilizers into the following groups: inorganic, natural organic compounds, natural organic matter, ionic surfactants, non-ionic surfactants, synthetic polymers, natural polymers, and natural peptides. In previous studies, the authors have proved the efficiency of use of CNP for the preparation of silver nanoparticles in the presence of various types of «green» and traditional stabilizers: waste compounds (orange peels

extract [19], peach pomace extract [20], black currant pomace and grape pomace extracts [22, 22]), polysorbate 80 [23], sodium alginate [24, 25] etc. However, the list of widely used stabilizers is very significant and it is advisable to investigate and characterize the properties of silver nanoparticles synthesized with various types of capping agents. It will also be useful for the development of the plasma technology which will be suitable for industrial implementation.

The category of natural organic compounds includes citrate, which is characterized by the steric type of stabilization of the nanoparticles. Nowadays, sodium citrate is one of the most studied types of stabilizer reagents [26, 27]. It is known that citrate ions have weak interaction of citrate molecules with metal surfaces and can be simply replaced with other compounds. Thus, the main advantage of citrate application is the possibility of further NP functionalization. Along with the study on the production and characterization of Ag NPs, it is important to establish directions for the practical application of nanomaterials. Modification of TiO₂ by doping with Ag NPs results in greater activity under UV-irradiation. Many authors used different ways and traditional/modern techniques to synthesize modified composite materials Ag/TiO₂ [28]. Most traditionally used methods do not allow synthesis of nanoparticles of a given size, moreover they are not eco-friendly and expensive. Usually, authors use different types of impregnation or modifications of above-mentioned methods to obtain Ag/TiO₂. The main disadvantage of these methods is that they result in big Ag-particles. The more effective methods are based on photo and plasma reduction of Ag nanoparticles on surface of commercial TiO₂ [29, 30]. This «in-situ» synthesis method is eco-friendly and not expensive.

1% photocatalyst TiO₂ composite demonstrated the highest photocatalytic activity among other catalysts with 2-10% of Ag NPs under photocatalysis with both UV light and visible light irradiation for the degradation of different pollutants (antibiotics, azo dyes etc.).

However, according to the literature, their use in advanced oxidative processes for wastewater treatment as a modifying additive to the photocatalyst titanium oxide to increase its photocatalytic activity is quite promising. The purpose of this work is to investigate the patterns of formation of Ag nanoparticles by plasma chemical synthesis using sodium citrate stabilizer and to demonstrate the efficiency of its deposition on the surface of the titanium oxide photocatalyst to increase its photocatalytic activity.

2. Experimental

2.1. Materials

Silver nitrate (ACS reagent, $\geq 99.0\%$), trisodium citrate ($C_6H_5O_7Na_3$), tetracycline hydrochloride ($C_{22}H_{25}N_2O_8Cl$) (AR, 99 %), titanium dioxide (TiO_2) were of analytical grade and were used as received without any further purification.

2.2 Synthesis of Ag-NPs

The studies were performed with various initial Ag^+ concentrations ranging from 0.3 to 3.0 mmol/L and a constant molar ratio $[Ag^+]:[Cit] = [1]:[0.2-3.0]$. In a typical experiment, 40.0 mL of $AgNO_3$ solution with constant (0.3-3.0 mmol/L) Ag^+ ion concentration was dissolved in the solution of trisodium citrate (5.0 ml) of different concentrations. Example at $[Ag^+]:[Cit] = [1]:[1]$ (0.5g/L $AgNO_3$ ($M=169.7$ g/mol), ($C_{M_{AgNO_3}}=0.5/169.7=3.0$ mmol/L). For 40 ml solution $AgNO_3$ $n=3.0 \times 0,04$ L=0.12 mmol. By proportion if necessary, stabilizer 1 (40 mL):1 (5 mL) $C = 0.12/0.005=24 \times 258,06=6.19$ g/L. The powder of CitNa was dissolved in double-distilled water to prepare trisodium citrate solution. The prepared reagents solution was placed in the plasma reactor with discharge directed through solution. Initial pH of the solution $[Ag^+]:[Cit]$ was $\sim 7.2-7.5$ at different molar ratios of reagents. The parameters of solution processing and labeling of the samples are given in **Table 1**. A diagram and image of CNP are provided and described in detail in the works [31, 32]. After treatment of solution by CNP discharge, a colloidal solution of Ag NPs is obtained.

2.3 Characterization techniques

The spectrophotometric measurements were made using UV-5800PC, Shimadzu, Japan). The ion-selective electrode ELIS-131Ag was used for study of Ag^+ reduction depending on different times of plasma treatment (kinetic dependencies). The value of the hydrogen index of the initial reagent solutions and the

Table 1. Sampling conditions parameters

Sample	Ag^+ , mmol/L	Ratio $[Ag^+]:[Cit]$	Current strength	Parameters
S ₁	0.3	[1]:[0.65]	120 mA	pressure at 80 kPa, $\tau=1-5$ min distance from the electrode (X18H10T) to the surface of the solution was not more 10 mm
S ₂	0.5	[1]:[0.55]		
S ₃	1.0	[1]:[0.4]		
S ₄	3.0	[1]:[0.2]		
S ₅	3.0	[1]:[1]		
S ₆	3.0	[1]:[2]		
S ₇	3.0	[1]:[3]		

synthesized colloidal solution of Ag NPs (dispersion) was measured using a pH meter. The prepared samples of Ag NPs were analyzed using a JEOL JSM-6510LV (JEOL, Tokyo, Japan) scanning electron microscope. Size distribution and ζ potential of prepared silver NPs in colloid solution was carried out using analyzer Zetasizer Nano ZS (Malvern Instruments Ltd., Great Britain).

2.4 Preparation of Ag-TiO₂ nanocomposites and photocatalytic activity

Surface modification of photocatalyst TiO_2 by Ag nanoparticles was done by a plasma reduction method in CNP reactor which is described in detail in the work [30]. After modification, samples of composite materials had 2% wt of Ag on the surface [32] and were of pale-grey color [33]. Oxford INCA X-sight 200 System was used to detect the Ag NPs on the TiO_2 surface. Photocatalytic activity of prepared composite materials was examined by determination of the decomposition rate of TC water solution at model conditions: (21 W (432 nm) ultraviolet (UV) lamps), TC concentration = 2.5 mg/L and photocatalyst powder concentration = (2.5 g/L). The degree of decomposition of the antibiotic was determined using the UV-Vis spectrophotometer based on the values of absorption at the appropriate wavelength. The change in concentration of solution was determined by using the UV-Vis spectrophotometer.

3. Results and Discussion

It is now generally accepted and proven by a significant number of studies that the main parameters influencing the synthesis of Ag NPs are: the initial concentration of the precursor, the type of reducing agent/stabilizer in the reaction system and the duration of the formation of NPs.

Previously, other authors' and our studies have found that in the case of the formation of colloidal solutions of silver NPs under the treatment of CNP, the products synthesized in the aqueous environment act as reducing agents. Whereas additional reagents, which usually can act simultaneously during chemical reduction both as a reducing and a capping agent, under plasma discharge act only as a stabilizer. The analysis of the literature indicates that usually in the chemical calculations, the ratio of citrate to the precursor is taken in an excess in the range from 1:1 to 1:8 [34, 35]. The effect of precursor concentration, for the ratio $[\text{Ag}^+]:[\text{Cit}]$ and the duration of plasma solution treatment, on the synthesis of Ag NPs was investigated (Figs. 1, 2). Colloidal solutions of Ag NPs were obtained as a result of plasma treatment. The peculiarity of the optical properties of silver NPs in colloidal solution, due to the phenomenon of surface plasmon resonance (SPR), allows conducting a spectrophotometric study of the processes of their formation. The maximum band of SPR of silver NPs is noticed at 400-450 nm [1-11, 34, 36]. The position, intensity, and shape of the SPR absorption band depend on the size, shape, dispersion, degree of aggregation of the nanoparticles, etc. Fig. 1 shows that at all the initial concentrations of precursor and reagent with ratio of $[\text{Ag}^+]:[\text{Cit}]=[1]:[0.2-3.0]$ at 0.3–3.0 mmol/L, silver NPs are formed as a result of CNP treatment. This is described by peak absorbance of SPR at 405 - 425 nm, which according to the well-known statements [37, 38], corresponds to the colloidal solution of Ag NPs of spherical shape. In this study, the authors consider the dependence of the average particle size of silver NPs in the system on the nature of the SPR position. Therefore, the maximum peak of SPR (405-415 nm) is characterized by nanoparticles with a size of 10-50 nm. It is established that at all initial concentrations of Ag^+ , the increase of the ratio $[\text{Ag}^+]:[\text{Cit}]$ from $[1]:[0.65]$ to $[1]:[0.2]$ contributes to the formation of expanded peaks, which indicates an increase in the size of Ag NPs and their polydispersity. The results obtained are expected, since during the synthesis a decrease in the amount of the capping agent leads to an enlargement of the synthesized NPs. For all investigated initial concentrations and ratios after 5 minutes of treatment, the maximum value of the absorbance is in the range of 3.2-3.4. In this case, the decrease in the content of Ag^+ ions in all samples indicates that they are almost completely restored to Ag NPs. It was found that for all samples, 4-5 minutes of CNP discharge is sufficient for the recovery of argentum ions and the formation of silver nanoparticles. It is obvious that the absolute value of the concentration of silver nanoparticles at a certain point in time cannot be determined directly by the value

of the optical density. However, such measurements allow scientists to compare the general kinetic behavior of the reactions by changing the concentrations of the reagents for the synthesis of Ag NPs.

The change in the kinetic dependence of the optical density has two-stages (Fig. 2). There is a "critical" plasma treatment time (τ_{cr}) (1-2 min) at which the absorption intensity increases linearly with a simultaneous intensive decrease in the equilibrium concentration of silver cations in the treated system. In the second stage, after τ_{critical} , the slow growth of intensity and completion of the formation of stabilized particles continue. According to the changes of the argentum ions in the plasma treated solution, the reaction order and the rate constant of the synthesis of colloidal solutions under CNP discharge and the action of a stabilizer were determined.

The kinetic investigation of Ag NPs formation showed that the reaction was a pseudo-first order with reaction rate constant of 0.61 min^{-1} for all samples S1-S4 (d) (Fig. 3). An important observation is that the nature of the SPR in different samples (S1-S4) differs depending on the duration of CNP discharge (10 sec-5 min). In the meanwhile, the dependences of the change in equilibrium concentration are approximately the same under the same conditions and the contact rate calculated is in average the same. Such data once again confirm that the spectra are more sensitive to the size of the nanoparticles, which is shown by the width of the peak. However, it does not characterize the concentration of nanoparticles formed. In the previous works [23-25], it was shown that without usage of capping reagent, plasma synthesis is a pseudo-first order reaction with the reaction rate constant of 0.4 min^{-1} . Thus, it can be concluded that under conditions of plasma discharge, sodium citrate acts as only a stabilizer. Citrate does not react with products of plasma reaction such as $\text{e}^{\text{aq-}}$ and it is also not attacked by $\cdot\text{OH}$ and $\cdot\text{H}$. Thus, the active products of plasma reaction reduce the silver ions and citrate is solely a spectator for the ongoing redox processes, but it plays significant role as a capping agent.

The obtained dependences of the intensity change of absorption and concentration of Ag^+ in time are most closely consistent with the growth model of nanoparticles by Polte 2015. This model is characterized by colloidal systems with a stabilizer, for example, citrates. These stages will be discussed in more details now. Initially at stage 1, there is a reduction of Ag^+ to Ag^0 , the formation of clusters and the subsequent formation of NP embryos. According to the data

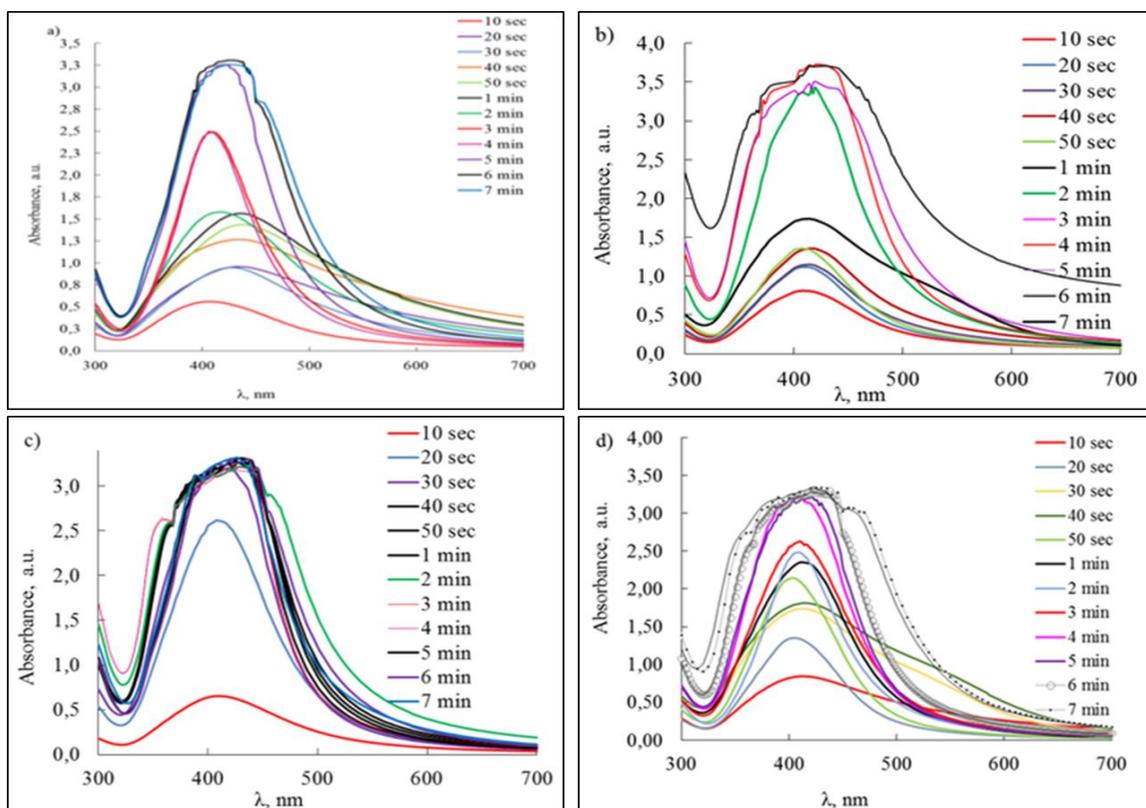


Fig. 1: UV-Vis absorption spectra of colloidal silver NPs synthesized at different duration of CNP treatment at various Ag^+ concentrations and molar ratio of $[\text{Ag}^+]:[\text{Cit}]$. S1=[1]:[0.65] (a), S2=[1]:[0.55] (b), S3=[1]:[0.4] (c), S4=[1]:[0.2] (d)

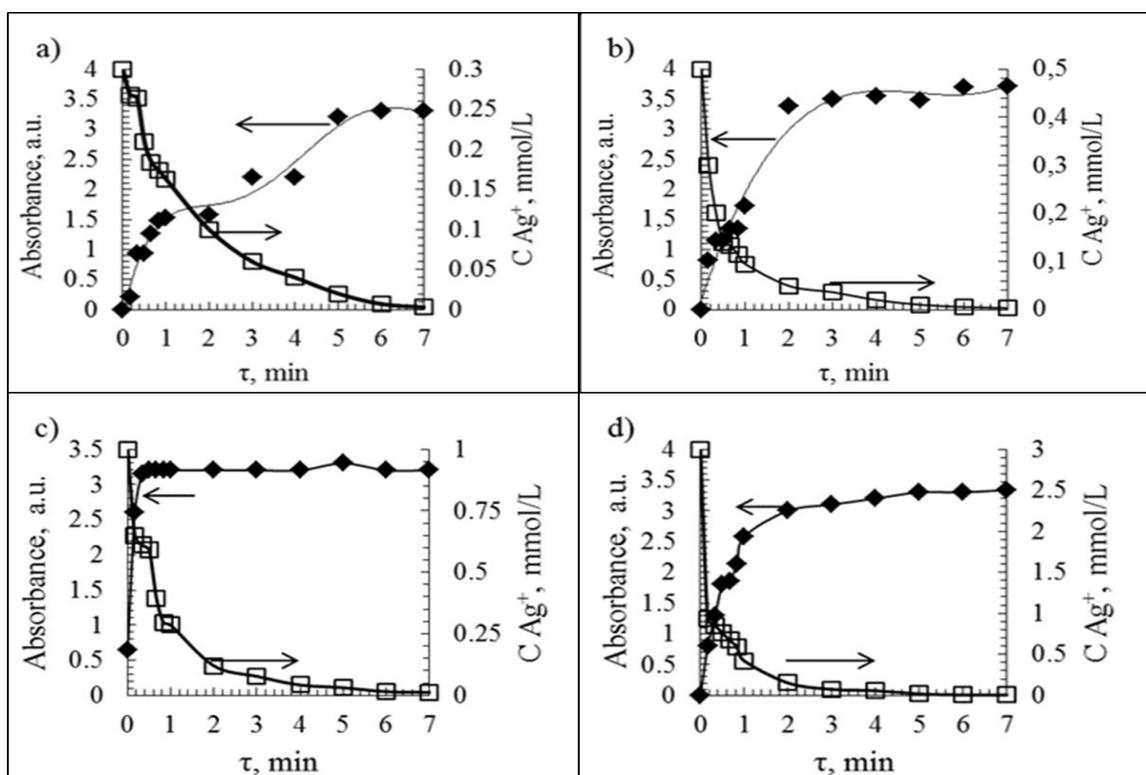


Fig. 2: The relationship between the intensity of the absorption (A), initial Ag^+ concentration and CNP treatment duration at different concentrations of Ag^+ for molar ratio $[\text{Ag}^+]:[\text{Cit}]$: S1=[1]:[0.65] (a), S2=[1]:[0.55] (b), S3=[1]:[0.4] (c), S4=[1]:[0.2] (d)

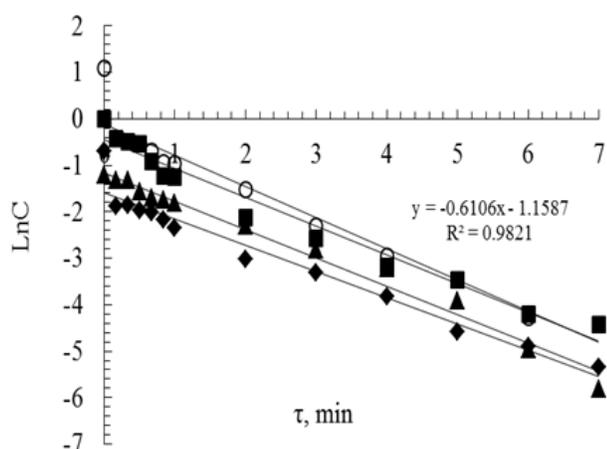
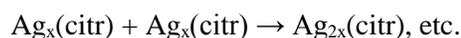
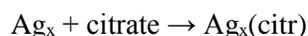


Fig. 3: The relationship between logarithm of equilibrium Ag^+ concentration as a function of the CNP treatment duration for samples with different molar ratios S_1 (a), S_2 (b), S_3 (c), S_4 (d)

presented in [39], the total duration of this stage for different systems is less than 5 sec. Studies of the early stage of NP formation by the method of radiolysis in the presence of citrate show that in the first stages of recovery, the formation of Ag^0 is not affected by the presence of citrate ions. However, the aggregation of the formed Ag^{2+} is affected by the citrate anion. Given the fact established in a number of works [39], the formation of silver clusters at the early stage of plasma discharge (most likely Ag_4^{2+} clusters (or other structure such as Ag_2^+ , Ag_4^{2+} , Ag_8^+) (will be mentioned as Ag_x further) is followed by complexation with citrate ions and further stabilization [39-41].



It is also possible that the oxidized citrate radical, which is formed by CNP treatment of the system and is a strong oxidant, promotes the common nucleation and growth of reduced silver Ag NPs.

Thus, surface coating with an organic citrate molecule at an early stage of Ag NPs synthesis (cluster growth stage) forms different clusters of smaller size. Thus, the presence of a stabilizer determines the size of the clusters and the subsequent growth of the nanoparticles (**Fig. 4**). At the second stage, the duration of which is from 5 to 10 seconds, there is a growth of small nanoparticles by means of aggregation. According to the literature, their size is 2-15 nm. The spectral curves for 10 seconds already show a clear characteristic of intense

SPR peak. The results of the distribution of NP by size (2-5 sec) serve as a confirmation of the mechanism of NP growth at this stage. According to these results, the average size of NP is about 7 nm (**Fig. 4**). The third and fourth stages of NP growth include two-stage reduction of ionic silver (first slowly, then rapidly). The first stage is slow growth. For all initial concentrations, this is the period from 10 sec to 1 min. During the reduction of Ag^+ ions, there is a consequent increase in absorbance intensity of the SPR. Then, the maximum value of absorbance intensity is observed, and it indicates the highest concentration of synthesized NPs. This period is called metastable in the literature and is characterized by an increase in monodispersity. The next, fourth and final stage of rapid growth from 1 to 5 minutes is characterized by an intense decrease in the concentration of the precursor (autocatalytic reduction), a corresponding increase in the SPR peak and an increase in the mono-dispersion of the colloidal system. After this stage, the particles are stable and have no changes in performance. The flow of electrons is associated with the value of reduced Ag^+ plus produced OH. This indicated that not all hydrated electrons react with the silver cation under the action of CNP plasma. Faraday selectivity for the reaction of Ag^+ reduction is below 100%. This dependence is also observed by [13] who also uses small concentrations of precursor.

The effect of changing the precursor/stabilizer ratio to [1]:[1] and [1]:[2-3] on the formation of silver nanoparticles was investigated (**Fig. 5**). Experimental data show that at a ratio of 1: 1 after 5 min of treatment there is a narrow peak at 410 nm, which indicates a narrow size distribution of nanoparticles [26]. It was established that plasma discharge treatment with double increase of the stabilizer contributes to the shift of SPR peak and its bifurcation (at 420 and 490 nm). These changes indicate growth of Ag NPs and formation of aggregation of NPs with average size more than 50 nm. This phenomenon is well known and is explained by the destabilization of the formed nanoparticles due to the high ionic strength of the formed colloidal solution. Similar patterns were obtained in the work on the production of silver nano-systems using citrate by method of radiolysis reduction.

This can be proved by determining the size of the nanoparticles, the polydispersion index and the stability of the obtained nanoparticle solutions at different precursor/stabilizer reagent ratios (**Fig. 6**).

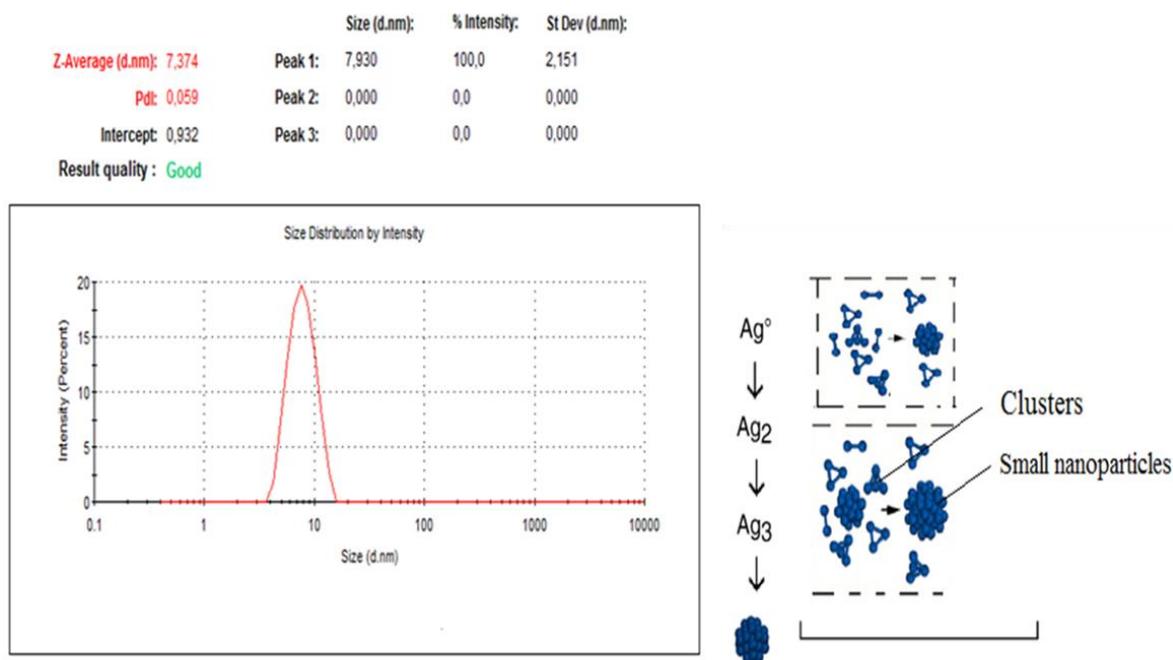


Fig. 4: Particle distribution of silver nanoparticles obtained at initial concentrations of silver ions in solution at 2 growth stages up to 5 sec.

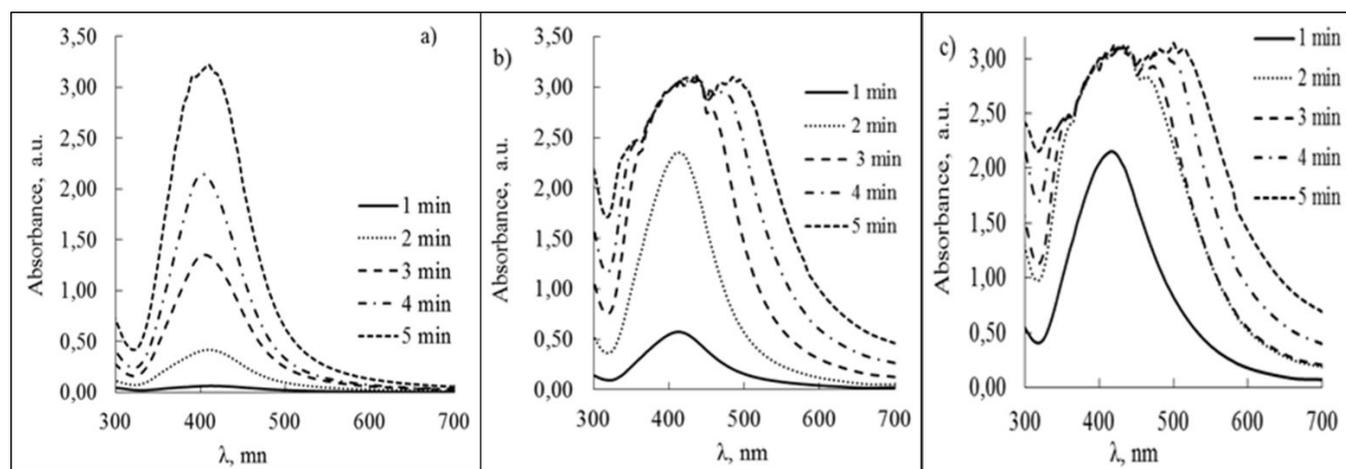


Fig. 5: Absorption spectrums of silver nanodispersions obtained at different molar ratio $[Ag^+]:[Cit]$ S₅ (a), S₆ (b), S₇ (c)

The measurement of zeta potential can characterize the stability of obtained NPs in colloidal solution. This parameter indicates the electrical properties of the interfacial layer. When the particles in colloidal solution have a large zeta potential (negative or positive: -30 mV to $+30$ mV) then the aggregation process will not be observed. It was found that the ζ - potential in all samples was -32 mV, which is known to be sufficient to ensure the aggregative stability of the systems. This negative value is related to the presence of electronegative functional group from the citrate. Thus, the investigation of aggregative stability of synthesized Ag NPs by determining the electrokinetic potential (ζ -

potential) shows that the systems are stable. Therefore, the analysis of the obtained results shows that with the excess of the stabilizer, the average size of the nanoparticles increases, and the index of the dispersion field increases. At a ratio of 1:1, the average particle size slightly depends on the initial concentration of the precursor and is 33.5-35.5 nm. According to size distribution histograms (DLS data), increasing the ratio to 1:1-1:2 increases the average nanoparticle size to (70-80 nm). This increases the index of polydispersity of the samples.

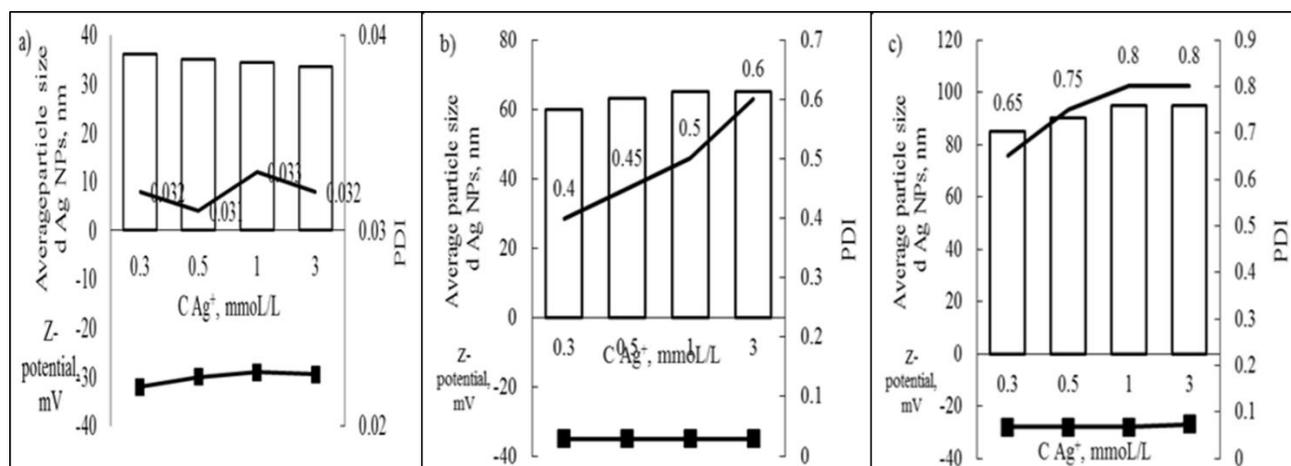


Fig. 6: The size of silver nanoparticles, PDI and Z-potential obtained at different molar ratio $[\text{Ag}^+]:[\text{Cit}]$: S₅ (a), S₆ (b), S₇ (c)

At high citrate concentrations in reagent system, aggregations with big size NPs are present, which are described by the high ionic strength of the colloidal solution and results in destabilization of NPs. For further study of the morphology of nanoparticles, it has been decided to choose sample S₅. In Fig. 7, the results of scanning microscopy are shown. The obtained data show that the average diameter of the synthesized Ag NP does not exceed 30-32 nm. Most of the formed particles have a spherical and pseudospherical shape. There are some non-spherical particles, but their number is generally small. The size distribution obtained from the images shows that the average particle size is 16-22 nm. The size values obtained from microscopic studies are slightly smaller than those obtained on the nanoparticle analyzer but are generally consistent. The discrepancy of 10 nm may be due to the peculiarities of the particle size analyzer, which forms its data based on reflection and may, as it is known, overestimate the performance compared to scanning microscopy. Also,

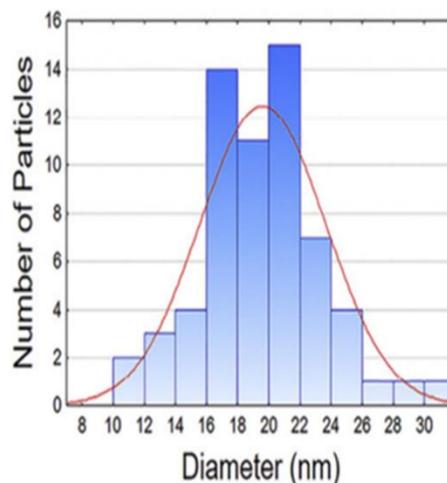
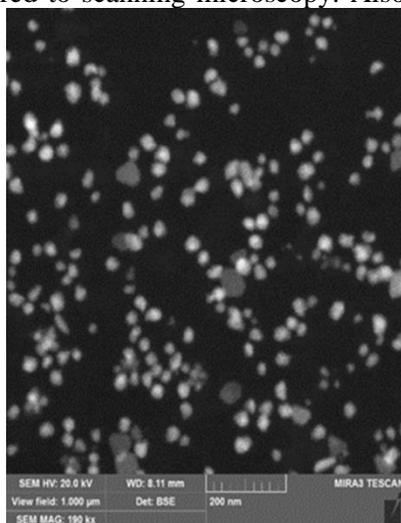


Fig. 7: SEM image and corresponding size distribution Ag NPs synthesized by CNP (sample S₅).

in Fig. 6, some particles in the form of a triangle are visible. In the works of [42, 43], other authors also reported such a phenomenon and such formations of triangular particles along with more spherical are explained by the precedence of the formation of spherical NPs.

Composite materials were obtained using method of plasma deposition on photocatalyst TiO_2 . It is a one-step method involving usage of CNP discharge. Fig. 8 shows the results of morphology and microstructure investigation of the synthesized composite photocatalyst. In scanning electron microscopy images, Ag NPs with size of 15-25 nm were observed on surface of TiO_2 . Thus, synthesized composite nanostructured materials had TiO_2 sphere cores and Ag NPs that are uniformly distributed on the surface. EDX analysis of CNP synthesized composite photocatalyst $\text{TiO}_2/\text{AgNPs}$ confirms that sample consists of ~2% mas. Ag NPs.

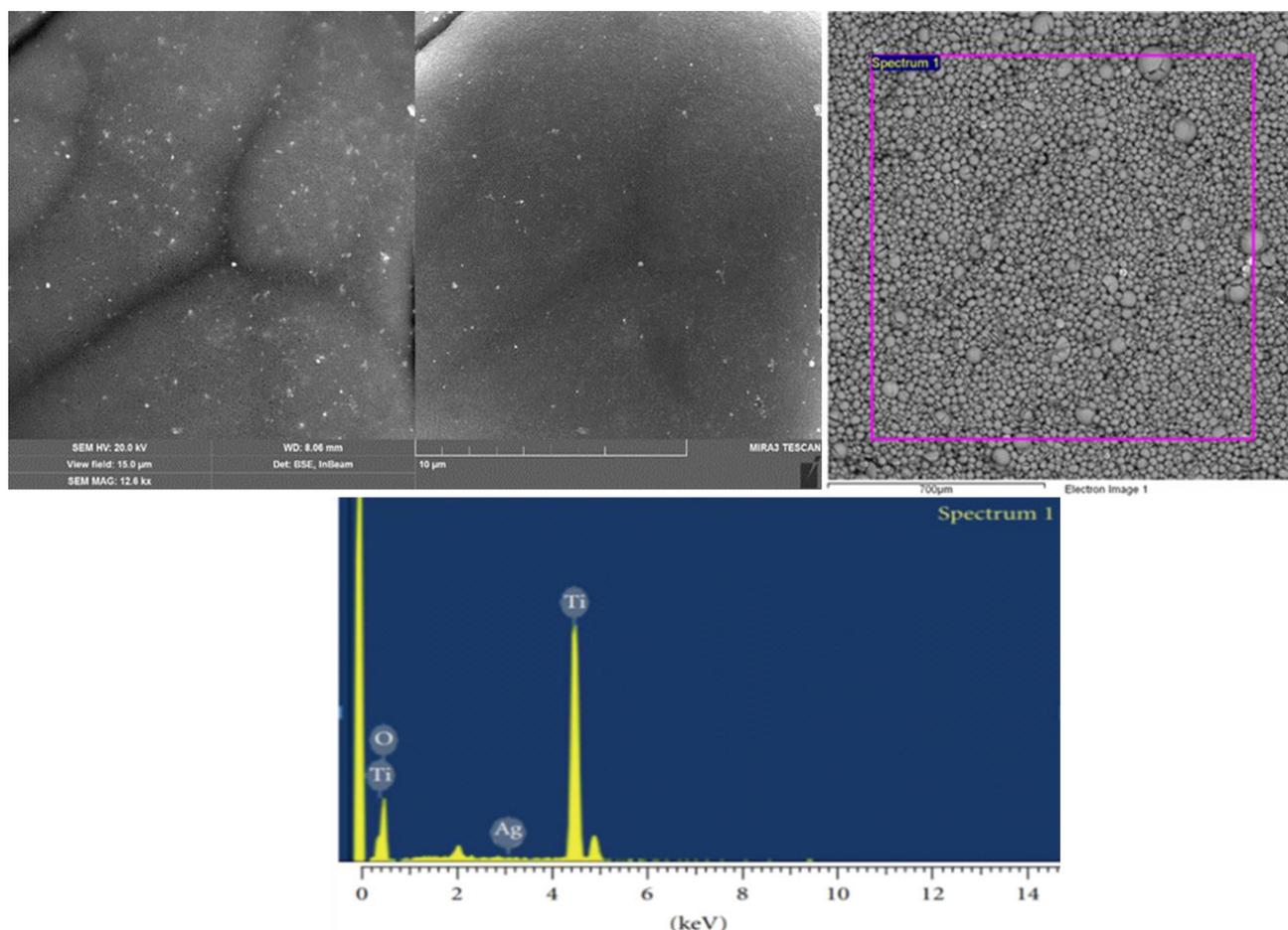


Fig. 8: SEM-EDX analysis of CNP synthesized composite photocatalyst $\text{TiO}_2/\text{AgNPs}$

Tetracycline (TC) is a commonly used antibiotic and has been frequently detected in different environmental matrices. As there is a risk due to antibiotic-resistant pathogens, the need for treatment of tetracycline-containing wastewater does not raise any questions. Given the demonstrated efficiency of plasma-chemically modified titanium oxide over a commercial sample, subsequent studies have been carried out without their comparison, using only a modified sample [30, 32]. The photocatalytic performances of the prepared photocatalytic composite were investigated by decomposition of TC in photocatalytic system in reactor Ecosoft (wavelengths 432 nm, 21 W). It is known that the amount of pollutant (contaminant) of the antibiotic tetracycline at the same dose of photocatalyst affects the efficiency of decomposition and its kinetics. A wide range of TC concentrations in model laboratory conditions is studied in the literature: 10 mg/L-100 mg/L [44]. The kinetics of decomposition of tetracycline at different concentrations and UV irradiation were studied (**Fig. 9**). The photocatalytic activity of synthesized composite was investigated in model reaction degradation of TC at fixed irradiation wavelengths and different initial concentrations of TC

in solution (10 and 20 mg/L). It was found that reaction is described by a pseudo first order kinetic equation. Thus under light irradiation with wavelengths of 432 nm, rate constants are $(3.6) \times 10^{-3} \text{ min}^{-1}$ and $(1.5) \times 10^{-2}$ respectively. It was seen that for 60 min of irradiation almost complete decomposition of tetracycline at concentration 10 mg/L is attained, and an increase in the initial concentration to 20 mg/L requires an increase in irradiation time.

The obtained rate constants indicate that at higher concentrations of TC the rate of decomposition is faster at higher concentrations of antibiotic. The obtained dependences can be described as results of the different effects. First, the increase in the concentration of antibiotic molecules can lead to collision of molecules and as a result can increase the degradation efficiency of antibiotic. Secondly, as the concentration of antibiotic in the solution increases, the TiO_2 adsorbs more TC molecules and as a result the rate of hydroxyl radicals generation decreases. Thirdly, a decrease of excitation of the photocatalyst can be observed as at higher concentrations of antibiotic, the light absorption by

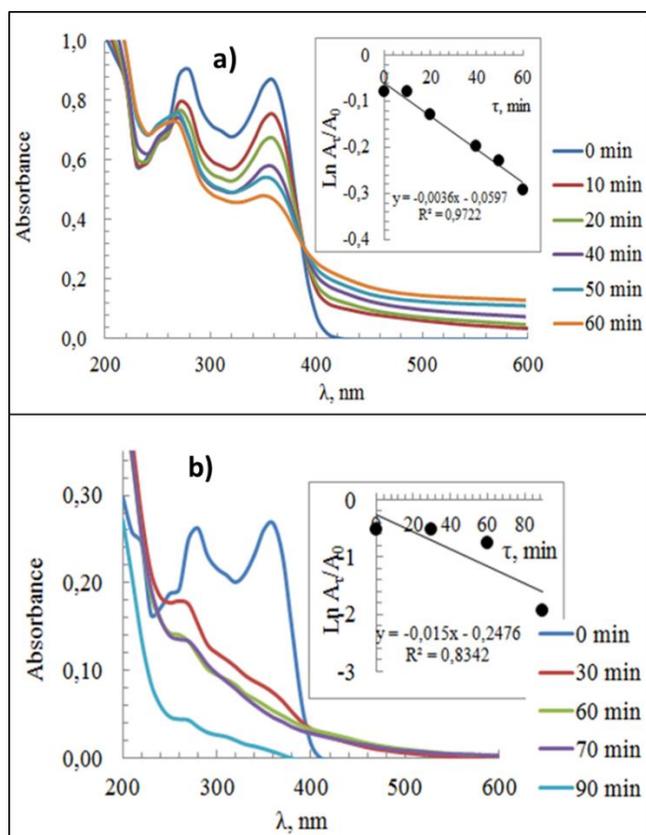


Fig. 9: The relationship between absorption spectra of TC and different durations of photocatalysis and TC concentration in reactor Ecosoft (wavelengths $\lambda=432$ nm, 21 W): TC 10 mg/L (a), 20 mg/L (b)

molecules of TC increases. These effects are in good accordance with the literature [44, 45].

Metallic nanomaterials such as Ag have a property known as SPR. Upon irradiation, if the incident energy is enough to prevent the positive nuclei-restoring force, the valence band of the metallic particle will be generated. When metallic nanoparticles are combined with semiconductor material, the light absorption will be enhanced, as electrons will migrate to the conjugated semiconducting material; thus, overall photocatalytic efficiency will be improved. When irradiated with different visible/U-vis light, TiO_2 is excited to create photogenerated electrons and holes in VB and CB, respectively. As a result of oxidation reaction in the VB, photocatalyst holes react with $\text{H}_2\text{O}/\text{OH}^-$ to produce OH [45]. The deposited Ag NPs on surface of TiO_2 create conditions for the formation of Schottky junction and internal electric field near the interface of Ag metal NPs and TiO_2 [45]. As result, through the formatted Schottky barrier, the photogenerated electrons of TiO_2 photocatalyst shift into the Ag NPs. During this process, Ag NPs trap the photogenerated electrons that enhance

photocatalytic activity via efficient separation of electrons and holes on the surface of TiO_2 .

4. Conclusions

The synthesis of silver NPs in aqueous solution under the action of plasma discharge and citrate stabilizer was studied in the work. It has been established that sodium citrate is the capping agent and acts only as the stabilizer of Ag NPs in the plasma chemical method of formation of nanoparticles. The influence of the main factors on the process of NPs synthesis was shown. A reagent ratio of [1]:[1] is recommended. Under such conditions, stable Ag NPs with diameter of $\sim 25\text{-}30$ nm and SPR 400-420 nm are formed. Modification surface of photocatalyst TiO_2 by Ag nanoparticles employed a plasma reduction method in reactor by CNP. On scanning electron microscopy images, it was observed that on TiO_2 surface Ag NPs with size of 15-25 nm are situated. It was demonstrated that their deposition on the surface of the titanium oxide increases its photocatalytic activity. It was seen that after 60 min of irradiation, almost complete decomposition of tetracycline at concentration of 10 mg/L is achieved. An increase in the initial concentration to 20 mg/L requires an increase in irradiation time. Thus, under light irradiation at 432 nm, rate constants are $(3.6)\times 10^{-3} \text{ min}^{-1}$ and $(1.5)\times 10^{-2} \text{ min}^{-1}$ respectively. The obtained results emphasized the potential of plasma treatment as a "green", ecofriendly and controlled method of synthesis of nano- and composite materials.

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