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TITANIUM DIOXIDE AND GOLD NANOPARICLES FOR ENVIRONMENTAL AND BIOLOGICAL APPLICATION

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ABSTRACT: In the work presented here we wished to study the role of clay minerals as environmentally friendly supports of the photocatalyst P 25 TiO₂ in detail. The reason for our interest is that layer silicates are outstandingly efficient adsorbents for organic pollutants, since organic molecules are adsorbed on the surface of clay minerals, which, so to say, accumulate environmentally harmful substances [5,6]. We wish to point out that the layer silicate component has a significant influence on the rate of catalytic degradation and, therefore, TiO₂/montmorillonite nanocomposites are eminently suitable for practical applications such as air and water purification technologies.

In the second part of this work reproducibly size-controlled gold nanoparticles reduced and stabilized by citrate were synthesized in aqueous dispersions. Gold nanorods were grown on functionalized gold surface and the kinetics of growth was studied. The surface of Au nanoparticles was modified by thiol-containing compounds, namely cysteine and glutathione, and the effect of pH and increasing cysteine concentrations on the dispersions was investigated by UV-Vis spectrometry.

KEYWORDS: Nanocomposites, nanoparticles, gold, application

❖ INTRODUCTION

The heterogeneous photocatalysis one of the most dynamically developing fields of high-efficiency oxidative procedures. This method based on irradiation of metal oxide semiconductor nanoparticles using visible light. These procedures show high significance because environmentally hazardous materials can be efficiently degraded by conversion of solar energy into chemical energy [1-3]. Degradation of these toxic substances by photocatalysis in aqueous medium could be the basis of a novel waste treatment method [4-6]. Volatile organic components are widely applied not only in industrial procedures but also in households, which leads to water and air pollution. In the presence of water vapor, the intermediate and final products accumulate on the catalyst surface, causing its deactivation.

In the work presented here we wished to study the role of clay minerals as environmentally friendly supports of the photocatalyst P 25 TiO₂ in detail. The reason for our interest is that layer silicates are outstandingly efficient adsorbents for organic pollutants, since organic molecules are adsorbed on the surface of clay minerals, which, so to say, accumulate environmentally harmful substances [5,6]. We wish to point out that the layer silicate component has a significant influence on the rate of catalytic degradation and, therefore, TiO₂/montmorillonite nanocomposites are eminently suitable for practical applications such as air and water purification technologies.

The preparation and biological applicability of gold nanoparticles are available in the special literature. Reduction of transition metal ions to colloids in aqueous or organic media in the presence of stabilizing agents was first published by M. Faraday in 1857 [7]. The first reproducible method was presented by Turkevich, who synthesized Au nanoparticles with a diameter of 20 nm via reduction of HAuCl₄ by trisodium citrate, while boiling and continuously stirring the reaction mixture [8]. In general, particles of different geometries are obtained depending on the quality of the precursor used [9], whereas the size of the particles obtained depends on the precursor/reductant ratio; the plasmon resonance peaks of the gold nanodispersions were between 520 and 530 nm. The color of the Au nanodispersion ranged from reddish orange (520 nm) to reddish purple (530 nm) depending on particle size [10].

The work of Liz-Marzán *et al.* is of fundamental importance in the preparation of nanoparticles of various shapes (spherical and anisometric [rod-like and prism-shaped]) [11, 12]. These authors summarize basic procedures and protocols for the preparation of Au, Ag and Cu nanoparticles and explain their optical properties in the journal *Materials Today* [13]. The resonance wavelength of anisometric particles such as nanorods depends on the orientation of the electric field. Two types of oscillation are possible, namely longitudinal and transverse. The longitudinal and transverse plasmon modes are both found to blue-shift, and the shift is larger for rods with larger aspect ratios. The color changes are visible to the eye for rods with aspect ratios around 2-3 [14].

Zhong *et al.* showed that gold nanoparticles reduced and stabilized by citrate have a negative surface charge and preferentially bind to thiol, amine, cyanide or diphenylphosphine functional groups [15]. They also showed that the reactivity of the amine group of amino acids is pH-dependent. Binding via α -amino groups is preferential at low pH and is suppressed at neutral and high pH, due to electrostatic repulsion between the surface of gold and the charged carboxyl groups.

In the second part of this work reproducibly size-controlled gold nanoparticles reduced and stabilized by citrate were synthesized in aqueous dispersions. Gold nanorods were grown on functionalized gold surface and the kinetics of growth was studied. The surface of Au nanoparticles was modified by thiol-containing compounds, namely cysteine and glutathione, and the effect of pH and increasing cysteine concentrations on the dispersions was investigated by UV-Vis spectrometry.

❖ EXPERIMENTAL SECTION

Materials and Methods

Degussa P25 TiO₂ photocatalyst was used ($a_{\text{BET}}^{\text{s}}=50 \text{ m}^2/\text{g}$), Ca-montmorillonite (Süd-Chemie AG, Germany, $a_{\text{BET}}^{\text{s}}=72.95 \text{ m}^2/\text{g}$) and their mixtures with TiO₂ contents of 25%, 50%, 65% and 80%. Phenol used for degradation was 99% purity (Aldrich). Anhydrous ethanol used in vapor phase degradations was 99.8% (Molar Chemicals Ltd, Hungary), and toluene was 99.94% (Molar Chemicals Ltd, Hungary).

Preparation of the photocatalyst

In each case, 10% suspensions made of Degussa P25 TiO₂ and Ca-montmorillonite were ground in an agate vibration mill (type GIF 3600, Hungary) with agate balls for 30 min. Suspensions were next dried at 110°C and, in order to ensure identical particle size in each experiment, sieved on a 90 μm sieve.

Preparation of gold nanoparticles

Materials used for the preparation of Au nanoparticles were: HAuCl₄·3H₂O (Sigma-Aldrich), tri-Na-citrate (Reanal) which served the dual role of a reductant and stabilizer and MQ water. The HAuCl₄ was dissolved in deionized water and the result a faintly yellowish solution. It heated until in boils and continued the heating, and while stirring vigorously, was added the sodium citrate solution and kept stirring for the next 30 minutes. The colour of the solution would changed from faint yellowish to clear to grey to purple to deep purple, until setting on wine-red. Added water to the solution was necessary to bring the volume back up to the original volume (to account for evaporation). The identification of prepared gold nanoparticles was performed by their plasmon resonance maximum value. The formation of Au nanoparticles was followed by Ocean Optics Chem 2000-UV-Vis spectrophotometer at wavelength 200-800 nm. During the preparation, the absorbance spectrum was recorded.

Preparation of gold nanorods

Materials used for the preparation of Au nanorods were: 3-mercaptopropyl-trimethoxysilane (MPTMS, Aldrich), HAuCl₄·3H₂O (Sigma-Aldrich), cetyl-trimethyl-ammonium-bromide (CTABr, Reanal), L+ ascorbic acid (Reanal) and MQ water.

For the preparation of nanorods were treated the glass substrates with MPTMS and then with citrate stabilized gold nanoparticle seeds at different concentrations and growth solution which containing cetyl-trimethyl-ammonium- bromide, ascorbic acid and gold ions.

Transmission electron micrographs (TEM) were performed in Philips CM-10 transmission electron microscope with an accelerating voltage of 100 kV. The microscope was equipped with a Megaview II digital camera. TEM grids were prepared by placing one drop of undiluted sols on a Formvar foil covered copper grid. The size distribution of the particles was determined by using UTHSCSA Image Tool 2.00 software. The growth of Au nanorods was also monitored by a Nanoscope III Multimode Atomic Force Microscope (AFM Digital Instruments) using a piezo scanner. Particle size and size distribution was measured by dynamics light scattering (DLS) with a Zetasizer Nano ZS ZEN 4003 (Malvern Instrument, UK).

Degradation of phenol in aqueous TiO₂/ Ca-montmorillonite suspensions

An aqueous solution containing 0.5 mM/L phenol was degraded in a thermostatically controllable reactor ($t = 25 \pm 0.1^\circ\text{C}$) with a submerged lamp (a high-pressure mercury vapor lamp, 150 W, Heraeus TQ 150). The lamp emits predominantly in the range of 250-440 and 540-590 nm.

The lamp was surrounded by a quartz shield in order to be able to also utilize high-energy photons (< 310 nm) of the lamp's UV light. A 280 ml stirred 0.1% TiO_2/Ca -clay suspension was filled into the reactor and flushed with air, ensuring a constant concentration of dissolved oxygen. 30 min adsorption time was allowed before the start of photooxidation reactions. For analysis of 2 ml samples were withdrawn from the illuminated suspensions at 20-min intervals and their total organic carbon (TOC) contents were measured in a Euroglas TOC 1200 (The Netherlands) apparatus. The total carbon contents of the suspensions were measured directly, injecting 100 μl aliquots.

If the adsorption equilibrium of solute is obtain, the original solution concentration c_0 is reduced to c_0' . In the course of the subsequent photooxidation, phenol concentration decreases to various extents depending on irradiation time, making possible the determination of the concentration vs. t function (Fig. 1).

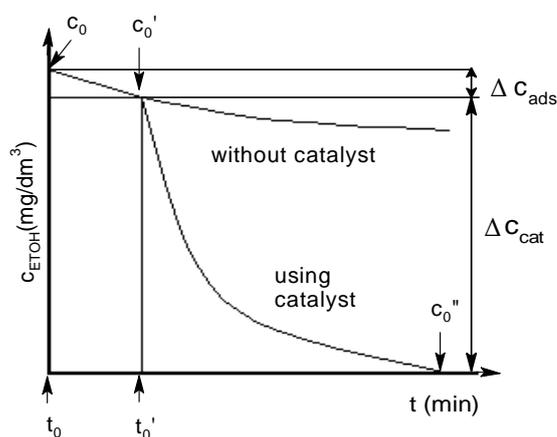


Figure 1. Schematic curve of photooxidation: t_0' is the switching of the light source. The time difference $t_0 - t_0'$ is the adsorption time

❖ RESULTS AND DISCUSSION

Phenol degradation in aqueous TiO_2/Ca -clay suspensions

Studies on the structure of TiO_2/Ca -montmorillonite nanocomposites clearly show that Bragg-reflexions characteristic of TiO_2 and montmorillonite are both present. In other words, no intercalation takes place during the grinding step, since the diameter of the TiO_2 nanoparticles is ca. 50 nm. Particles of such copious size would only be induced by surface charges to interact with the negatively charged lamellae of the clay mineral and to form a heterocoagulation structure.

Photocatalytic degradation of the aromatic phenol molecule was performed in 0.1% aqueous suspensions made of Ca-montmorillonite composites containing 0, 25, 50, 65, 80 or 100% Degussa P25 TiO_2 in a reactor with a submerged lamp, using 2-hour irradiations. The c/c_0 values calculated from the data measured after irradiating the samples, represented as a function of catalyst mixture composition are shown in Fig. 2.

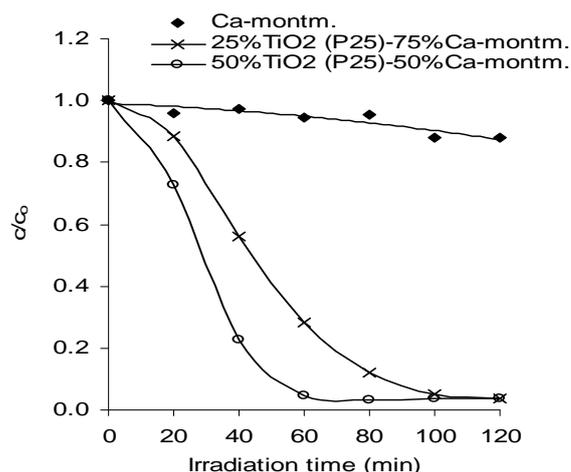


Figure 2. Photooxidation of phenol on Ca-clay and Ca-clay/ TiO_2 composites

Ca-montmorillonite does not have a significant photoactivity, as demonstrated by a decrease of only 12% in the amount of phenol present after 2 hours of UV irradiation. Photoactivity increases parallel with the increase in the amount of TiO_2 : the mixture containing 25% TiO_2 degrades 70% of the phenol present in 60 min, whereas the samples containing 80% TiO_2 and pure P25 TiO_2 break down 95-98% in 40 min. In all cases, the decrease in phenol concentration achieved in 60 min is expressed as ΔTOC . $\Delta\text{TOC} = \text{TOC}(t_0') - \text{TOC}(t_{60\text{min}})$, i.e. ΔTOC means CO_2 production realized in 60 min,

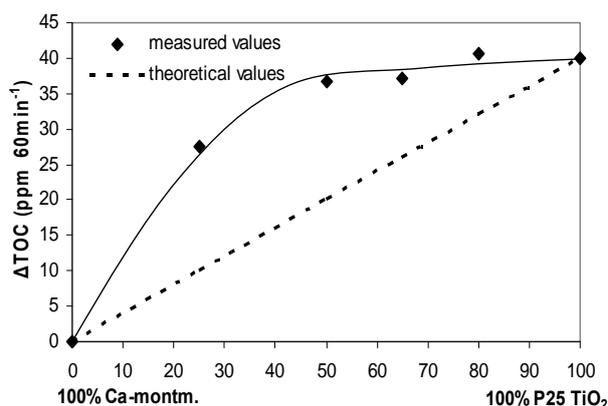


Figure 3. The synergistic effect of photooxidation on Ca-montmorillonite/ TiO_2 composites

starting at the onset of irradiation. When a theoretical phenol consumption is calculated for the TiO_2 -content of composites, taking into account phenol consumption measured in the case of pure TiO_2 (Fig. 3), the degrading capacity of each mixture surpasses the theoretical value. Significant excesses were observed in the case of the mixtures containing 50% and 75% Ca-montmorillonite. When ΔTOC values are normalized to unit weight of TiO_2 and represented as a function of the TiO_2/clay mineral ratio, the synergistic effect is even more conspicuous.

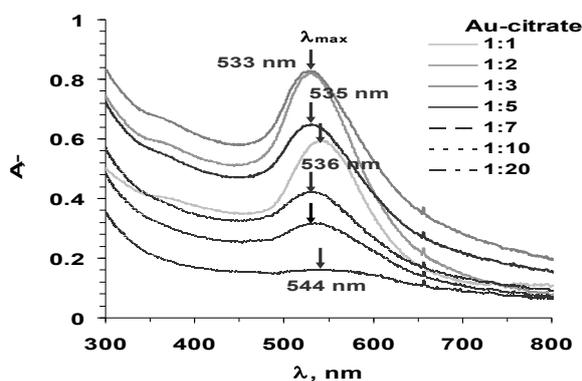


Figure 4. Absorption spectra of gold nanoparticles at ratio of gold/citrate 1:1-1:20 ($c_{\text{citrate}}=0.2\text{-}4\text{mM}$ and $c_{\text{Au}^{3+}}=0.2\text{mM}$) after 30 min reduction time and 24 hours

Interaction of nanostructured gold particles with cysteine

A method was developed for the controlled synthesis of gold nanoparticles in aqueous medium by reduction using trisodium citrate dihydrate at 25°C , and the size and size distribution of the particles formed and the colloid stability of the gold dispersions obtained were studied. The size and size distribution of the particles formed were determined by the analysis of TEM images. The most commonly used preparative method is reduction by trisodium citrate. We studied the effect of variations (i) in the gold: citrate ratio in the composition range of 1:1 - 1:20 (where $c_{\text{Au}^{3+}}=0.2\text{mM}$ and $c_{\text{citrate}}=0.2\text{-}4\text{mM}$) (Fig. 4) and (ii) in the initial gold concentration (in the range of 0-1 mM, $c_{\text{citrate}}=2\text{mM}$) on the size of the nascent particles (Fig. 5). It is clearly shown in Fig. 4 that the plasmon resonance maximum of gold nanoparticles varies within the wavelength range of 533-544 nm, depending on citrate concentration. No systematic shift is observed. Maximum absorbance values are seen to increase when the amount of citrate added is increased from a ratio of 1:1 to 1:3 and to decrease in the ratio range of 1:3 - 1:20, which may be due to the formation of particles of different sizes depending on citrate concentration. The more citrate is present, the smaller are the nascent particles owing to the stabilizing effect of citrate. Relatively large gold nanoparticles are distinguished by narrow, well-defined peaks, whereas smaller particles are characterized by broader, less sharp maxima (Fig. 4). To determine the size of the Au nanoparticles formed in the various gold dispersions on the basis of TEM images, samples were prepared on copper grids. Particle diameters determined in TEM images decrease exponentially with increasing amounts of citrate and absorbance maxima change in a nearly parallel fashion, i.e. an initial maximum is followed by nearly exponential decrease (Fig. 5).

According to Fig. 6 increasing the initial concentration of HAuCl_4 (in the range of 0.1-1 mM) results in a continuous increase in particle size at a constant citrate ion concentration of 2 mM. As precursor concentration is increased, increasingly larger particles (5-18 nm) are obtained by the evidence of the particle size distribution curves based on TEM images. Particle sizes determined by dynamic light scattering (DLS) (10-22 nm) (Fig. 6), however, do not match those determined on the basis of TEM images (5-18 nm), although the two sets of results are within the same order of magnitude. The TEM image of gold nanoparticles formed in the solution containing 0.8 mM HAuCl_4 and their size distribution are shown in Fig. 7. The average diameter of the particles is $\sim 18\text{nm}$, whereas in the samples containing 0.2 mM HAuCl_4 particles measuring $\sim 5\text{nm}$ were formed (Fig.8). Size distribution is more homogeneous in dispersions containing smaller particles than in those containing larger particles. The higher extent of homogeneity is due to the presence of larger amounts of citrate ions. The application of lower citrate/Au ratio (1-5) leads to a decrease in the stability of Au dispersions, resulting in the aggregation of gold nanoparticles.

Gold nanosols reduced and stabilized by citrate were also used for growing gold nanorods, and the kinetics of growth and the detectability of functionalized surfaces by recording UV-Vis spectra were investigated. Nanorods were grown in the following way. Previously synthesized gold nanoparticles were spread on the surface of microscope slides that had been thoroughly cleaned in chromosulfuric acid and functionalized by mercaptopropyl-trimethoxysilane (MPTMS) (Fig. 9). The silanized glass plates were let to stand in the gold sol for 25 min. The surface-modified glass plates

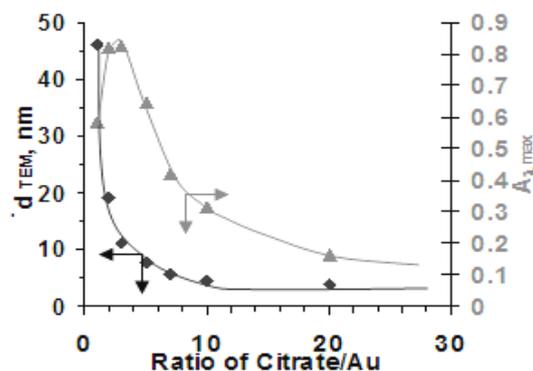


Figure 5. Relation between the maximum absorption values and the diameter at increasing citrate/gold ratio ($c_{\text{Au}^{3+}}=0.2\text{mM}$) after 30 min reduction time and 24 hours

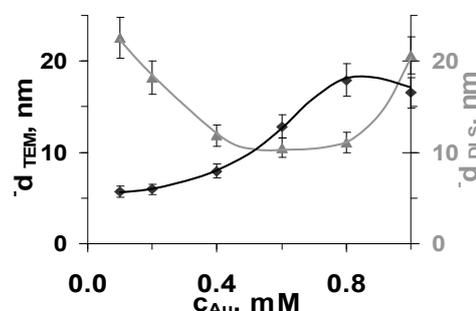


Figure 6. Relation between the particle size measured by TEM and DLS and the original gold concentration ($c_{\text{Au}^{3+}}=0.1\text{-}1\text{mM}$ and $c_{\text{citrate}}=2\text{mM}$).

carrying the gold nanoparticles were next submerged into the “nanorod growth solution” consisting 0.1 M cetyltrimethylammonium bromide (CTAB), and 0.05 M HAuCl₄ and 0.1 M ascorbic acid. Gold nanoparticles were generated in the growth solution via reduction by ascorbic acid, forming gold nanorods on the surface.

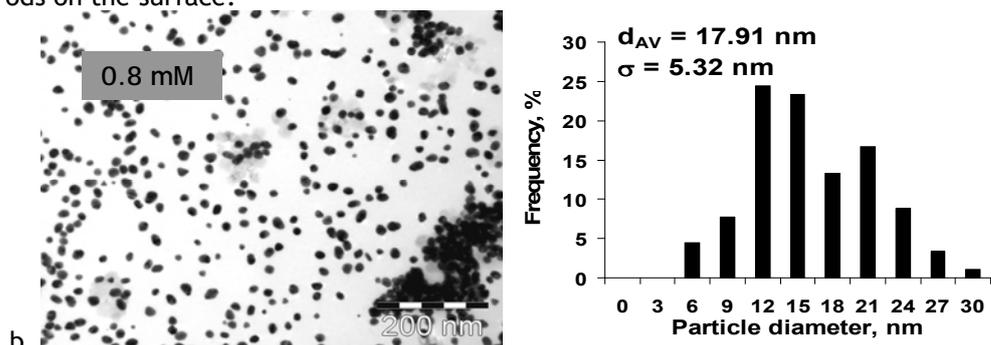


Figure 7. TEM pictures of $c_{Au} = 0.8$ mM (~18 nm) gold.

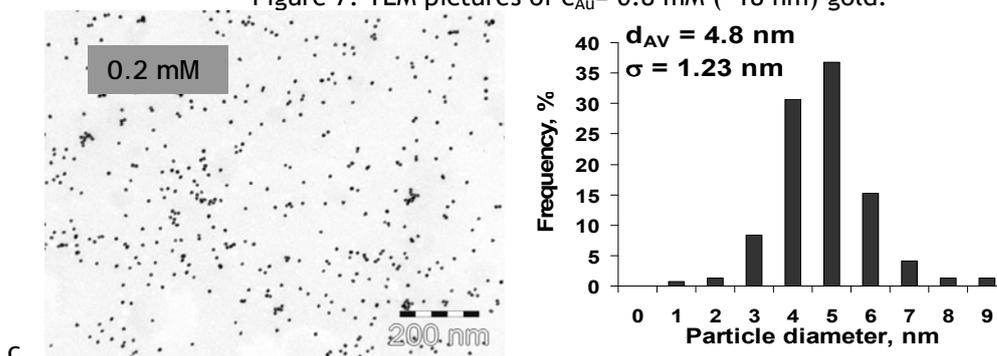


Figure 8. TEM pictures of $c_{Au} = 0.2$ mM (~5 nm) gold

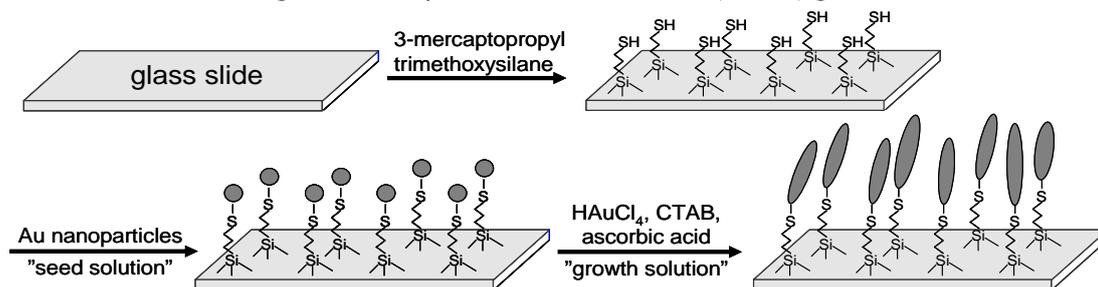


Figure 9. The scheme of the formation of gold nanorods on modified glass surface „Seed” Au nanoparticles on glass slide

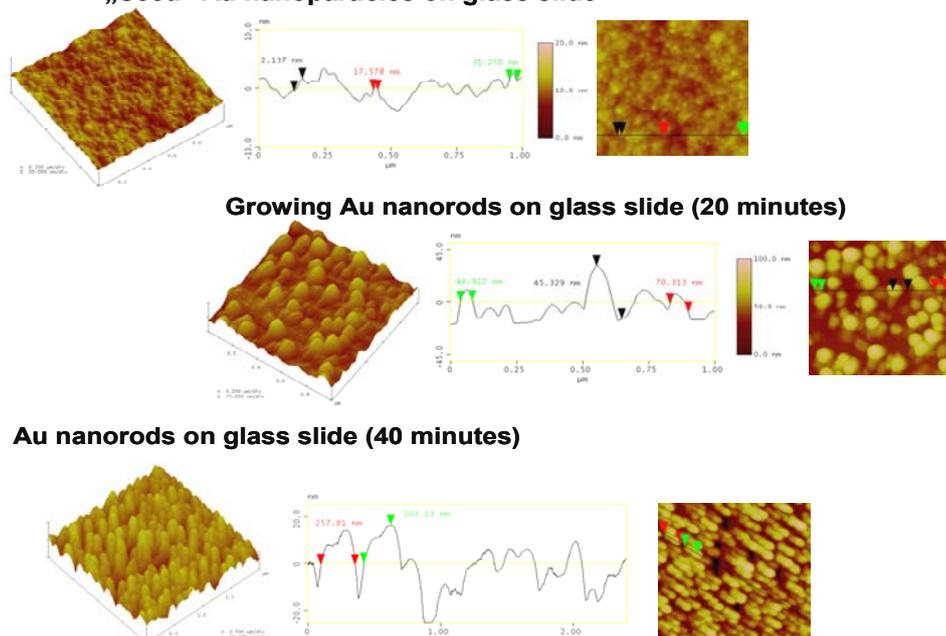


Figure 10. Growing of the gold nanorods on modified glass surface

The nanorod growth process was studied by AFM (Fig. 10). In the course of growth, the difference between rods grown for 0, 20 and 40 min is well discernible in the diameter analysis plot based on the AFM images. The diameter and height of rods grown for 20 min were ~45 nm, whereas the height of rods grown for 40 min was ~200 nm and their diameter was ~120 nm. After growth for 40-45 min the height of rods did not change any more.

❖ CONCLUSION

Photocatalytic efficiency of TiO₂/Ca-montmorillonite composite suspensions was studied in liquid phase. We developed a double-walled photoreactor, in which TiO₂-composite thin films are spread on glass surface, for measurements on the solid/liquid interface. It was established that aqueous phenol solution and VOCs are degraded at a significantly higher efficiency on TiO₂/Ca-montmorillonite composites than on pure (Degussa P25) TiO₂.

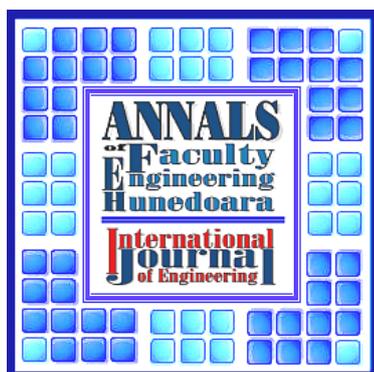
Size quantized gold nanoparticles reduced and stabilized by citrate were synthesized. The particles were identified on the basis of their plasmon resonance maxima by UV-Vis spectrometry and their sizes were determined by particle size distribution functions calculated from images obtained by transmission electron microscopy. It was demonstrated by UV-Vis spectrometry that the rate of particle formation depends on the gold/citrate ratio: the higher the concentration of reductants and stabilizers in the dispersion, the lower are the apparent rate constants, i.e. the rate of particle formation decreases. The rate of aggregate formation in the liquid phase of dispersions containing gold and cysteine at various ratios was also studied by DLS. These experiments revealed that large aggregates are not formed in samples containing high amounts of cysteine and, due to the stabilizing effect of cysteine, the rate of aggregation is slower. Nanorods were synthesized on silanized glass surfaces and particle growth was followed by AFM. Our experience shows that growth solutions containing relatively high concentrations of HAuCl₄ deposit thicker gold layers on the surface; the thickness of the gold layers was determined as ~200 nm by AFM measurements.

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