

Examination of Silver Nanoparticle Core-Shell Oleic Acid Bonding Characteristics

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ABSTRACT. Inorganic-organic core-shell nanoparticles are considered to be common building blocks for synthesis of multifunctional hybrid nanocomposites, which are promising materials for biomedical and catalytic application. Knowledge of the metal nanoparticle-ligand interaction mechanism is crucial for design strategy of such materials. In the present study silver-oleic acid capped nanoparticles are used as a model for mono- and bi-layer ligand chemisorption. FTIR spectroscopy, TGA and DTA data testify bidentate bonding carboxylic oxygen atoms to Ag nanoparticles and formation of secondary layer chemisorbed at the primary one at excess content of oleic acid (OA). The pattern of activation energy (E_a) versus mass loss (surface coverage) of OA is used as fingerprint to determine the mechanism of chemisorption. Contrary to widely accepted Langmuir adsorption model, which predicts constant value of activation energy, E_a the values calculated from experimental data varies significantly with a fraction of thermally desorbed material testifying increase in adsorption energy with surface coverage. Complex variation of E_a with mass loss in presence of OA excess reflects contribution of several factors: increase in E_a as OA molecules desorbed from sites with higher adsorption energy and simultaneous variation in chemical bond strength in a secondary layer. © 2018 Bull. Georg. Natl. Acad. Sci.

Key words: core-shell nanoparticles, surface inhomogeneity, desorption activation energy, oleic acid, ligand structure

Effective application of nanoparticles as building blocks in bottom-up design of multicomponent nano-composites requires monitoring of fundamental properties, such as size, charge, chemical reactivity and ability of nanoparticles to disperse in various media. Owing to high aspect ratio, metal nanoparticles tend to

agglomeration, aggregation and corrosion processes finally leading to loss of valuable properties inherent to building of blocks. Chemisorption of organic ligand shell provides steric stabilization of nanoparticle core preventing its degradation. The present study is focused on characterization of metal core-ligand shell

interactions as well as on ligands molecules interaction in primary and secondary layers of the shell, phenomena, largely determining bottom-up strategy for synthesis of multifunctional hybrid nanoparticles [1].

Experimental.

Chemicals and instruments. The reagents used in this study are purchased from Sigma-Aldrich unless otherwise specified and used without purification. Chemical interactions of surfactant with NPs studied by FT-IR spectroscopy in a range of 400–4000 cm^{-1} with the resolution of 0.5 cm^{-1} (Thermo Nicolet, Avatar 370) using the KBr technique. Size, shape and chemical composition of isolated NPs are estimated from TEM (Tesla BS 500) and SEM (JSM-6510LV) images. The samples are prepared by placing small drops of a sole onto the carbon-coated copper grid. The size distribution of NPs in a sole is evaluated from laser beam dynamic light scattering data (Zetasizer-Nano, Malvern). Prior to sample placing into a cuvette, the as-prepared sols are diluted with hexane 1:8. The structural and thermal stability properties of nanoparticles are characterized by thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) technique (NETZSCH, STA-2500, Regulus). Activation energies are calculated using Flynn-Wall-Ozawa method derived from the integral iso-conversional method [2, 3].

Preparation of sols of Ag NPs. Sols of silver NPs in a hexane are synthesized by electrochemical method in a reactor consisting of sacrificial silver anode (99.9% purity), and aluminum (99.9%) cathode, which upon rotation crosses immiscible layers of aqueous (0.05 M AgNO_3 , doubled distilled water) and organic (hexane, 0.25% and 0.75% OA) solvents [1,4]. The experimental set-up allows silver ions formed at the anode to discharge at the cathode surface poisoned by surfactant (OA), which adsorbs at sites favorable for silver adatoms and inhibits the growth of silver nanoclusters. The latter is weakly adsorbed at the surface and being

strongly bonded to amphiphile OA molecules which are easily washed out from cathode upon rotation forming stable sols of Ag–OA core-shell NPs in hexane. The method provides ability to tune particle size by variation in residence time τ_r , during which metal cluster formed at cathode-aqueous electrolyte interface. In the present study, electrosynthesis has been carried out at experimental conditions yielding assemblies of spherical silver NPs of $10.8 \pm 1.2 \text{ nm}$ size (Fig.1).

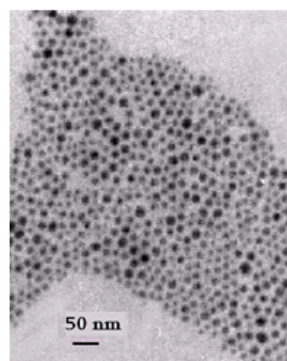


Fig. 1. TEM image of silver NPs capped of oleic acid

FT-IR spectroscopy. The chemical bonding of OA molecules to silver nanoclusters in diluted OA solutions are characterized by appearance of two new bands at 1635 and 1380 cm^{-1} which are typical for the asymmetric and symmetric carboxylate stretch. These effects are interpreted as the evidence of OA bidentate bonding to silver via two symmetrically coordinate oxygen atoms of the

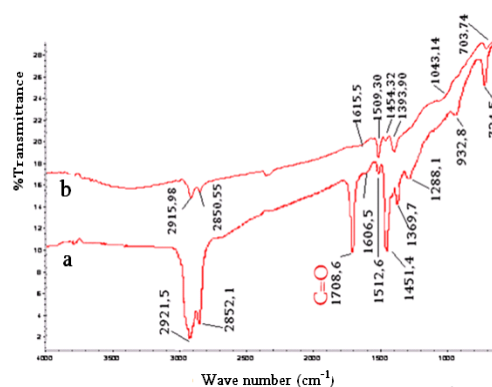
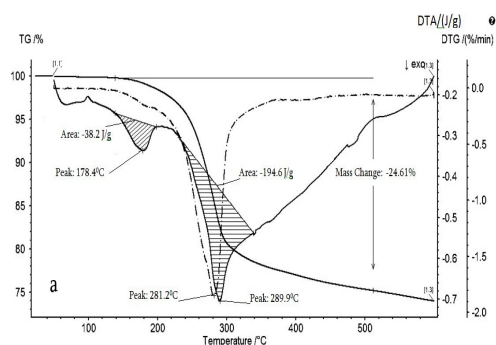


Fig. 2. FT-IR spectra silver nanoparticles capped by bilayer (a) and monolayer (b)

carboxylate head [5]. The effect of increase in oleic acid concentration on FT-IR spectra characteristics is shown in Fig.2 - a, b. The major effect is appearance of a new peak at 1708.6cm^{-1} that is characteristic for C=O bond stretch.

TGA and DTA measurements data. The application of dynamic TG methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes occurred during



Contrary to this NPs capped by bilayers of ligand are well dispersed in aqueous media due to interaction with polar carboxylic head of secondary layer directed to the solution (Fig.4 b).

Calculation of desorption activation energy (E_a). Thermodesorption E_a values have been calculated by Flynn-Wall-Ozawa (FWO) method derived from the integral iso-conversional method using Doyle's approximation (1) [6].

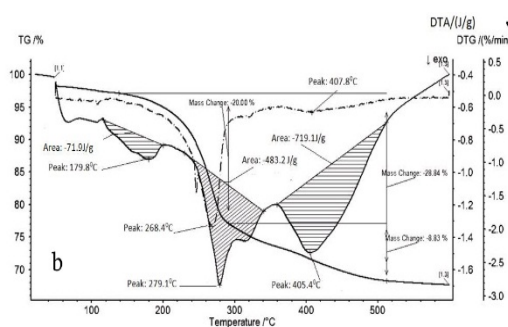


Fig. 3. TGA and DTA curves of Ag-0.25% OA (a) and Ag-0.75% OA (b) samples.

thermal decomposition of solids. In this investigation, Flynn-Wall-Ozawa (FWO) methods have been used to analyze the non-isothermal desorption kinetics of silver nanoparticles capped with oleic acid ligand. TGA and DTA curves of Ag-0.25%OA and Ag-0.75%OA samples are measured at heating rate (β) 5 K/min shown in Fig.3 a, b. TGA patterns in diluted OA solutions are characterized by one step mass loss (24.61%) curve. DTA curve measured under the same conditions displays exothermic peaks at 178.4 and 289.9°C . Corresponding enthalpies are 38.2 J/g and 194 J/g. Contrary to these data, TGA curves measured in OA rich solutions display two step mass loss 20.0% ($50 - 300^\circ\text{C}$) and 8.83% ($300-600^\circ\text{C}$). Corresponding DTA curve displays three exothermic peaks at 179.8; 279.1 and 405.4°C . Calculated enthalpies are 71.9 J/g; 483.2 J/g and 719.1 J/g.

Dispersibility. Silver nanoparticles capped by a monolayer of oleic acid (Fig.4a) are perfectly dispersed in organic media but do not disperse in aqueous solutions owing to hydrophobicity of hydrocarbon groups exposed to solvent molecules.

$$f(\alpha) \approx 7.03 \times 10^{13} \times \frac{AE\alpha}{BR} \times e^{-1.052E_a/RT} \quad (1)$$

According to this method:

$$\ln \beta = \ln \frac{AEa}{Rg(x)} - 5.331 - 1.052 \times \frac{E_a}{RT} \quad (2)$$

where A is frequency factor and g(x) is function characterized with conversion rate. Activation energies calculated from (2) are shown in (Fig 5). Sharp increase in E_a observed at low mass losses in concentrated solution indicates the change of desorption mechanism in bilayer system.

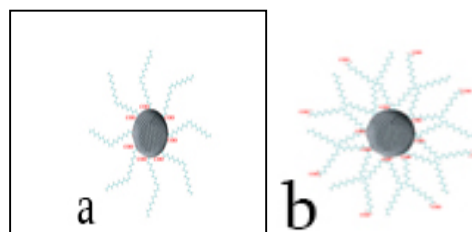


Fig. 4. Silver nanoparticles capped by monolayer (a) and bilayer (b) chemisorbed OA.

Discussion. An increasing volume of studies aimed at examination of the mechanism of unsaturated fatty acid ligands interaction with metals and metal

oxide cores have been conducted by means of TEM, FT-IR, TGA, DTA, XPS and NMR methods [7-9]. The bidentate covalent bonding of oxygen atoms of polar carboxylic groups with core NPs assumed to be the driving force formation of chemisorbed ligand monolayer. Appearance of a new FT-IR peak at 1708.6cm^{-1} characteristic for C=O bond stretch (Fig 2a), as well as two step mass loss TGA curves and appearance of several exothermic peaks at DTA curves (Fig.3b) shown in present study clearly demonstrates that at high OA concentration Ag NPs are capped by adsorbed ligand bilayers. Contrary to widely accepted concept on physical nature of ligands, bonding in the secondary shell [9] significant enthalpies calculated from DTA curves indicates the chemical nature of bonding. Finally this leads to formation of branching ligand network (Fig.4b). The other important conclusion on the mechanism of ligand chemisorption is followed from variation of thermodesorption activation energies with conversion degree (Fig.5). It is widely accepted that formation of ligand primary adsorbed layer follows Langmuir low, which assumes adsorption at homogenous substrate and predicts independence of adsorption energy from surface coverage. Our experimental data are in sharp disagreement with these assumptions. In contradiction to Langmuir adsorption model the data shown in Fig.5 testify a significant change in thermodesorption activation energy with variation in a number of adsorbed OA molecules in a primary shell. To interpret activation energy patterns we have to account for the fact that nanoparticles surface formed under highly nonequilibrium conditions due to artificial termination of crystal grow and freezing irregular structure by capping agent. These lead to more realistic model accounting for effect of surface

inhomogeneity resulting in increase of adsorption energy with surface coverage. Complex variation of E_a with mass loss in presence of OA excess apparently reflects contribution of several factors: increase in E_a as OA molecules desorbed from sites with higher adsorption energy and simultaneous variation in chemical bond strength in a secondary layer.

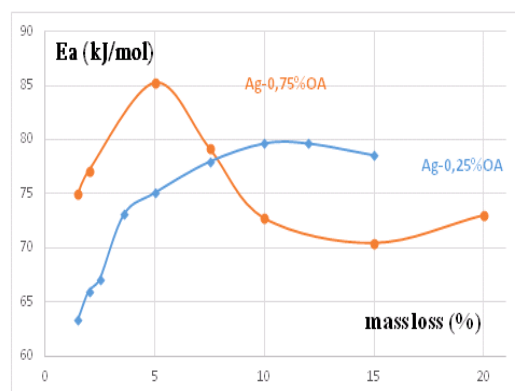


Fig.5. Thermodesorption activation energies calculated by OFW method as a function of the conversion degree.

Conclusion. In the present study we claimed that the secondary ligand layer of the shell forms branching structure of chemically bonded ligand molecules. Desorption activation energy patterns displayed significant variation in activation energies with ligand surface coverage testifying inconsistency with widely accepted Langmuir adsorption model. More realistic model of ligand chemisorption accounting for energetic inhomogeneity of metal nanoparticle surface is proposed.

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ორგანული და არაორგანული ქიმია

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არაორგანულ-ორგანული „ბირთვი-გარსის“ ტიპის ნანონაწილაკები წარმოადგენს ელემენტურ საამშენებლო ბლოკებს ბიოსამედიცინო და კატალიზის დარგის პერსპექტიული მასალების - მულტიფუნქციური ჰიბრიდული ნანოკომპოზიტების სინთეზისათვის. ამგვარი მასალების კონსტრუირების სტრატეგიის შემუშავებისთვის მნიშვნელოვანია ლითონის ნანონაწილაკისა და ლიგანდის შორის ურთიერთქმედების მექანიზმის დადგენა. წარმოდგენილ ნაშრომში ოლეინმჟავათი სტაბილიზებული ვერცხლის ნანონაწილაკების სისტემა გამოყენებულია მონო და ბი-ლიგანდის შრეების ქემოსორბციის მოდელირებისათვის. ფურიე ტრანსმისიური ინფრაწითელი სპექტროსკოპიის, თერმოგრაფიმეტრიის და დიფერენციალური თერმული ანალიზების მონაცემები ადასტურებენ კარბოქსილის ჯგუფის ჟანგბადის ატომების ბიდენტურ ბმას ვერცხლის ნანონაწილაკების ზედაპირსა და მონოფენის გარე ზედაპირზე, ლიგანდის მეორეული ფენის ქემოსორბციას ოლეინმჟავათი მდიდარ ზოლებში. დესორბციის აქტივაციის ენერგიის (E_a) მასის დანაკარგზე (ლიგანდის ზედაპირული კონცენტრაციის) დამოკიდებულების კანონზომიერების ანალიზის საფუძველზე გაკეთებულია დასკვნები ოლეინმჟავას ქემოსორბციის მექანიზმის თაობაზე. ფართოდ აღიარებული ლანგმიურის ადსორბციის მოდელის საწინააღმდეგოდ, რომელიც ითვალისწინებს აქტივაციის ენერგიის სიდიდის მუდმივობას, ექსპერიმენტული მონაცემებიდან გათვლილი E_a -ს სიდიდეები მნიშვნელოვნად იცვლება თერმულად დესორბირებული მასალის წვლილთან ერთად, რაც მიგვითითებს ზედაპირის დანაფარის შესაბამისი ადსორბციის ენერგიის ცვლილებაზე. ოლეინმჟავას სიჭარბის შემთხვევაში აქტივაციის ენერგიის ზრდა მასის დანაკარგთან ერთად, სავარაუდოდ, გამოწვეულია ოლეინმჟავას მოლეკულების დესორბციით მაღალი ადსორბციის ენერგიის ცენტრებიდან.

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