

# CHEMISTRY OF NANOSTRUCTURED SYSTEMS

## Plasmon spectra`s analysis for Ag, Au sols with acrylic acids

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Gold and silver plasmon spectra (PS) of metallic particles with diameter 8–10 nm were obtained and analyzed for hydrosols before and after addition of acrylic (AA), methacrylic (MAA) and propionic (PA) acids. The purpose was to compare the influence of  $C_3$  acids adsorption on the state of some metal nanoparticles (NPs) characterized by the volume fraction ratio  $NV$ , damping factor of metal electron plasma vibrations  $\gamma$  and the effective concentration of conduction electrons  $N_e$ . These parameters have been calculated from the dependence of the optical absorption ( $A$ ) on the wavelength in the long-wavelength range in terms of the Mie theory and the concept of plasma-resonances absorption theory. The changes of coefficient of scatter of conduction electrons can be written by equation

$$\Delta\gamma = \Delta\gamma_{ee} + \Delta\gamma_{ef} + \Delta\gamma_{ed} = \Delta(n_d\sigma_s V_F),$$

Where  $\gamma_{ee}$ ,  $\gamma_{ef}$ ,  $\gamma_{ed}$  are connected respectively with the scatter of conduction electrons by electrons, by phonons and by lattice defects in near-surface layer of NPs. At given temperature the coefficients  $\gamma_{ee}$  and  $\gamma_{ef}$  remain constant, and  $\Delta\gamma_{ed} \neq 0$  reflects the changes of defects concentration  $n_d$ , or effective cross section of surface defects  $\sigma_s$  or electron speed at Fermi level [1]. So, a change in  $\gamma$  upon the adsorption depends on the amount of an adsorbate and its orientation.

The influence of AA and MAA adsorption on the absorption spectra was different (Fig. 1). At an increase in acid concentration the amplitude of PS peak decreased for Ag but also shifted for Au. A similar result was obtained for AA, PA.

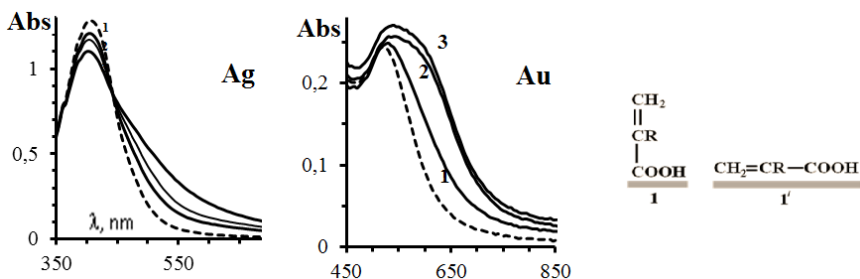


Fig. 1. Absorption spectra of silver and gold sols without (dotted line) and with methacrylic acid ( $C_A = 0.2; 0.3; 0.4$  M (1, 2, 3)) and reorientation of adsorbate

Acid's adsorption changes the volume fraction NV of silver and gold particles as well as the parameter  $\gamma$ . The AA and MA adsorption is accompanied by its molecules reorientation in the surface layer when acids  $C_A$  concentration increases.

The relative change of NPs volume fraction (Fig. 2), when an acid is added, can be  $\Delta NV > 0$  (increase in NV) or  $\Delta NV < 0$  (decrease in NV) that is associated with disaggregation of NPs (i. e. the system becomes more dispersed) and aggregation or flocculation proceed respectively. It should be noted that in case of Au NPs we observed simultaneously the change in the conduction electron density that was not more than 4 % for PA and 12–15 % for AA and MAA. In was derived the linear relationship between the change in the conduction electron density  $\Delta Ne$  and the change in the coefficient  $\Delta\gamma$  which characterizes the donor-acceptor interactions between adsorbed molecules and gold NPs (Fig. 3).

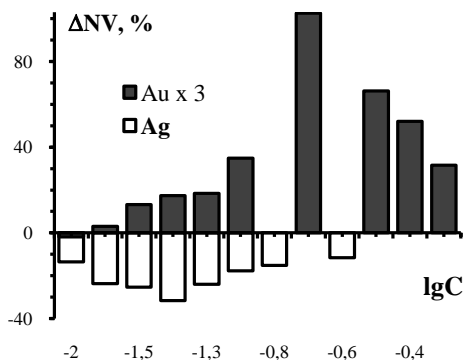


Fig. 2. The changes of NV vs. acrylic acid concentration

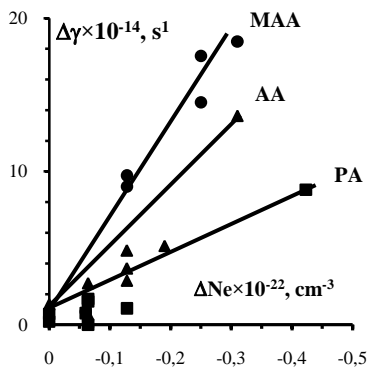


Fig. 3. Correlations between the changes of parameters  $\gamma$  and  $Ne$  for Au sol due to  $C_3$  acid adsorption

So, the electrons of NPs metallic subsurface “feels” adsorption as defect centers with which participation the electrons transfer from Au NPs to adsorbed molecule occurs. The number of Au centers (electrons donors) or the value of effective cross section of electron scattering on such centers depends on the acid nature and augments in the row  $PA < AA < MAA$ .

To compare the influence of AA concentration on NPs dispersion we can note the opposite effect with great relative changes of  $\Delta NV > 0$  ( $100 \times 3 = 300$  %) in case of Au and smaller changes of  $\Delta NV < 0$  for Ag. Concentration dependences of optical density of adsorption peak and NV for Ag hydrosol show discontinuity at  $C = \sim 0.05$  M and  $\Delta NV_{MAA} > 0$  that is explained by reorientation of adsorbed molecule and different shape of aggregated metallic

particles. Electrons transfer occurs only with Au. The same effect was obtained after low temperature treatment [2].

## References

1. E. A. Kononova [et al.]. Prot. Met. (2008) 44:170
2. E. A. Kononova [et al.]. Rus. J. Phys.Chem. (2010) 84 : 1053.

## TiO<sub>2</sub>/epoxy composites as effective anticorrosion coatings for steel

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Epoxy resins are thermosetting polymers which have been widely used in different fields including anticorrosive protection [1]. Incorporation of nanoparticles in epoxy matrix can enhance corrosion resistance as well as improve optical, thermal and mechanical properties of the epoxy coatings [2]. Among different nanoparticles used as additives for epoxy resins, TiO<sub>2</sub> is the most perspective owing to unique properties, relative low cost and wide-spread application. The aim of the present work was to prepare TiO<sub>2</sub>/epoxy coatings on steel and to study the influence of TiO<sub>2</sub> additive on anticorrosive properties of the coatings.

In the experiments, commercially available water-based epoxy resin CHS-Epoxy 200v55 and Telalite 180 amine hardener were used for preparation of the epoxy coatings. The TiO<sub>2</sub> particles were fabricated according to the method described in [3]. TiO<sub>2</sub>/epoxy composite coatings with 0.5, 1 and 2 wt. % of TiO<sub>2</sub> were prepared by adding an appropriate amount of TiO<sub>2</sub> particles into the epoxy resin followed by mechanical dispersing and then addition of the curing agent. The obtained mixture was deposited onto steel plates using casting blade method.

The resultant cured coatings with a thickness of  $60 \pm 3 \mu\text{m}$  were partly transparent, non-porous and demonstrated excellent adhesion to steel surface. The distribution of TiO<sub>2</sub> particles in the cured epoxy matrix was studied by SEM and EDX mapping. In addition, RAMAN spectroscopy was applied for characterization of 3D distribution of titania particles in the coatings. TiO<sub>2</sub> particles were found to be rather uniformly distributed in epoxy network. The corrosion resistance of the epoxy coatings modified with TiO<sub>2</sub> nanoparticles was investigated by standard salt spray test. Unmodified epoxy coatings were failed