New Photonic Materials based on Ag Nanoparticles Modified with Stilbene Dyes and Its Peculiar Behavior Studied with SERS

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Abstract: In the recent years, there has been a growing interest in development of smart photoactive materials with variable properties. This work presents the SERS study of behaviour of organometallic composites obtained by modification of Ag nanoparticles in hydrosols with several amino derivatives of stilbene. The feasibility of bifunctional stilbenes to be the molecular linkers of Ag nanoparticles is discussed. The hot spots activity of such modified Ag nanoparticles is considered. Two exciting but not fully understood finding were made: i) tertiary amines can be used as the effective molecular linkers; ii) the structure of central fragment between two benzyl rings has a strong influence on the modifier ability to incorporate the Ag nanoparticles into agglomerates with hot spots. The limitations consisting in the pH value and the presence of chloride ions are described for a potential application of the developed hot spots substrates.

1 INTRODUCTION

Development of new photonic materials is a subject of great interest in modern physics, chemistry and materials science. Integration of photoactive molecules with plasmonic nanostructures represents one of the most promising approach for engineering such materials. Among the plasmonic nanostructures, the substrates with hot spots are particularly attractive. Hot spots are the regions between closely located nanoroughnesses where a superposition of local electromagnetic fields occurs (Schlücker, 2014; Roelli 2016). Inside the hot spots greater enhancement of optical signal, e.g. Raman scattering, is provided. Hot spots can be obtained by self-assembling nanoparticles using molecular linkers. The term "molecular linkers" denotes the molecules which have a capability of simultaneous attachment to two different surfaces. Due to higher optical response from hot spots, among the photoactive molecules able to electrostatically or chemically interact with a substrate the choice is preferable for bifunctional ones.

In this study, we present the investigation of organometallic composites based on Ag nanoparticles (Ag NP) modified with aminostilbenes. This class of organic pigments has the pronounced photoactivity (Su, 2017; Liu, 2000). A combination of aminostilbenes photophysical properties with the plasmonic properties of Ag NP is promising strategy for obtaining the systems whose optical properties can be controlled by external forces. In our previous work, we focused on 4,4'-diaminostilbene and its ability to link the metal nanoparticles was demonstrated (Solovyeva, 2018). In the present study, the particular attention was paid to exploring an influence of dye's structure on the molecule-surface interaction. Three dyes differing in the functional groups and saturation of central bond (see Fig. 1) were investigated in silver hydrosols by surface enhanced Raman spectroscopy (SERS) and transmission electron microscopy (TEM). It was also importantly to evaluate a behavior of obtained systems under changing conditions. Such parameters as pH or presence of chloride anions may be crucial for electric double layer structure and Ag NP – molecule interaction consequently.
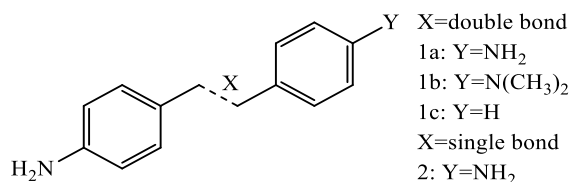

Figure 1: Common chemical structure of investigated compounds. 1a – DAS; 1b – ADMAS; 1c – AS, 2 – DABB (meaning of abbreviations see in Experimental).

2 EXPERIMENTAL

4-aminostilbene (AS) (98%), 4,4'-diaminostilbene dihydrochloride (DAS) (95%), 4-amino-4'-(N,N-dimethylamino)stilbene (ADMAS) (98%) and 4,4'-diaminobibenzyl (DABB) (95%), were purchased from Sigma-Aldrich. DAS was recrystallized in MeOH before using. Other compounds were used without further purification. Methanol solutions of AS and ADMAS with concentration in the range from 1×10^{-7} to 1×10^{-5} M were prepared from stock solution (1×10^{-4} M) by volume dilution method for SERS measurements. Silver hydrosol was prepared by reduction of silver nitrate by sodium borohydride in accordance with the standard procedure. To decrease pH of solution, nitric acid with appropriate concentration was used. To provide the halide anions effect, potassium chloride was added in silver hydrosol.

The SERS spectra were recorded using LabRam HR800 (Horiba Jobin Yvon) spectrometer with CCD detector. The incident laser excitation was 488 nm line from Ar^+ laser source. Laser power at a sample was 20 mW. All SERS spectra were registered in the range of 400-1800 cm^{-1}, in four acquisitions, 20 s accumulations. The images of Ag nanoparticles were obtained with a Zeiss Libra 200FE transmission electron microscope (TEM) at an accelerating voltage of 200 kV. TEM images in scanning mode (STEM) were taken from at least three random domains of the sample. In order to prepare samples for TEM measurements, 10 µl of silver hydrosol were drop casted on top of carbon films and air dried. During solvent evaporation the films were kept in a dark place.

3 RESULTS ANS DISCUSSION

A concentration of organic additives in some cases has a crucial influence on the properties of metal hydrosols. Therefore, a wide range of concentrations has to be considered for firstly applied modifiers. Two types of concentration dependence of SERS spectra were found for the studied stilbene derivatives. As one can see from Fig. 2, the monotonous growth of SERS signal along with the concentration is observed for AS. While the non-monotonic change of SERS intensity together with the significant transformation of spectral profile can be seen for ADMAS. The growth of intensity follows to the increase of ADMAS concentration up to 1×10^{-6} M. The drop of SERS signal is further observed proceeding up to 1×10^{-5} M. The same

type of SERS spectra dependence on concentration was obtained for DAS in our previous study (Solovyeva, 2017).
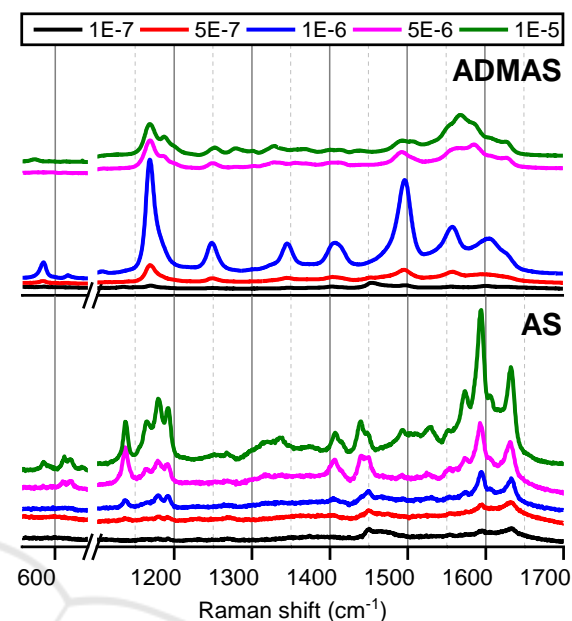

Figure 2: Dependence of SERS spectra on the concentration (M) of ADMAS and AS in silver hydrosol.

The monotonous increase of SERS intensity in case of AS corresponds to conventional gradual filling of surface-solution interface without a substantial alteration of molecular layers configuration and surface morphology. The behavior of ADMAS spectra similar with DAS suggests that the same adsorption phenomena produce the observed spectral changes. When the first monolayer becomes completed, the way of molecules interaction with surface changed. Obviously, this happens at 1×10^{-6} M and, thus, produces the observed intensity drop and transformations of spectral profile. At sub-monolayer adsorption, ADMAS, as a bifunctional molecular linker, interacts simultaneously with two different nanoparticles by donation of nitrogens lone pairs. In such conditions, ADMAS molecules are located in the hot spots and its Raman scattering undergoes to higher enhancement. At multilayer adsorption, linking the nanoparticles via ADMAS becomes impossible that leads to the ordinary Raman enhancement.

The proposed hypothesis is consistent with the data obtained by scanning transmission electron microscopy for the same systems (fig 3). In the presence of AS at any concentration, the nanoparticles size and morphology do not change

significantly in comparison with the pure silver hydrosol. In case of ADMAS, the oblong agglomerates, which look like the glued nanoparticles, can be seen in the TEM images obtained for hydrosol with 1×10^{-6} M of modifier. For solution with 1×10^{-5} M of ADMAS, the TEM showed the small spherical nanoparticles as are typical for borohydride-reduced silver hydrosol.
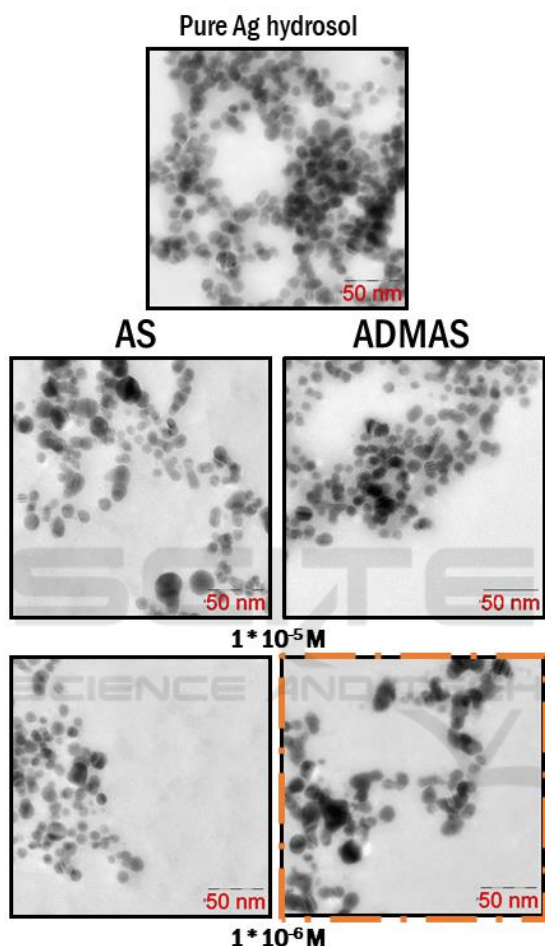

Figure 3: TEM images of Ag NPs modified by AS and ADMAS at different concentrations.

Thus, we can conclude that the methyl substitutes in one of two amino groups of ADMAS do not obstruct to its coordination with surface. Thereby, ADMAS has the same linking ability as DAS. Such results are quite surprising but they mean that a list of compounds, which can be used as molecular linkers, can be significantly expanded. The corresponding adsorption models are depicted at fig. 4.

The solutions of AS and ADMAS in silver hydrosol were further investigated in various environments to get a deeper insight into adsorption
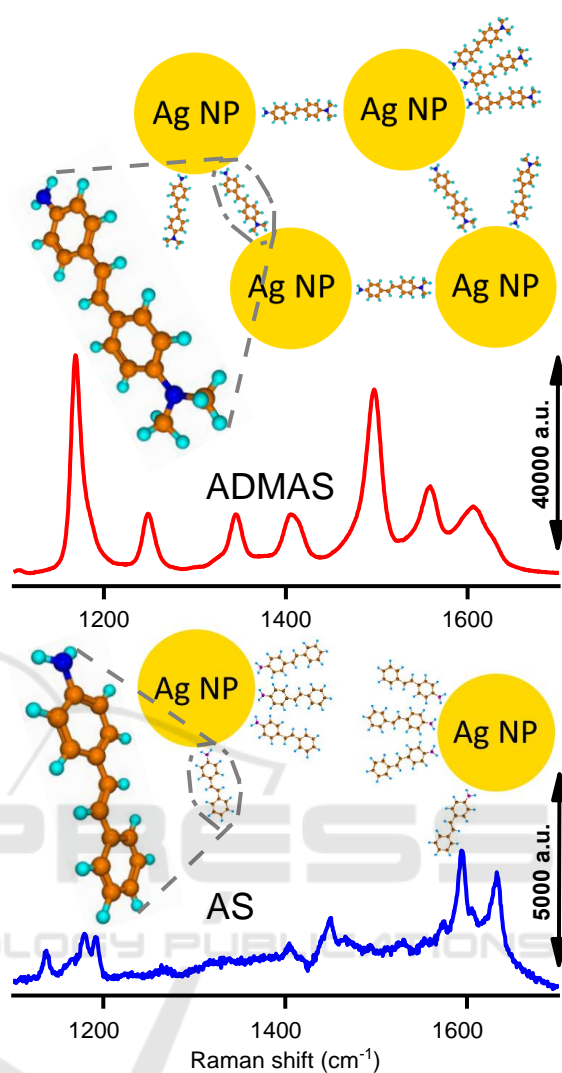

Figure 4: Schematic models of adsorption for mono- and bifunctional stilbene dyes at 1×10^{-6} M conc. at Ag nanoparticles in hydrosol.

mechanisms and to evaluate the limits for practical applications of modified Ag NPs. The SERS spectra of stilbene derivatives at neutral and acidic pH are presented as Fig. 5. For ADMAS the effect of solution acidification is examined at various concentrations corresponding to two different adsorption modes. The most substantial influence of pH is observed for ADMAS at concentration of 1×10^{-6} M, when the molecules are attached to the two different nanoparticles. In this case, the intense SERS spectrum transforms to the spectrum of lower intensity, and the noticeable bands shifts can be seen also. It is should be noted that the profile of spectrum at 1×10^{-6} M ADMAS after acid addition converts to the profile similar with those observed

for 1×10^{-5} M ADMAS at pH 2. Apparently, molecules of ADMAS become disabled to «glue» the nanoparticles after protonation of amino (dimethyl) group. Protonated ADMAS molecules adsorb on the surface in the same way whether sub-monolayer or multilayer coverage. The changes in the spectral profile are caused by electron density redistribution. This is highlighted by the fact the most significant profile change is the intensity increase of modes near 1369 cm^{-1} relating to the deformational vibrations of double bond (Solovyeva, 2019). Probably, a reorientation of molecules induced by protonation also takes place.
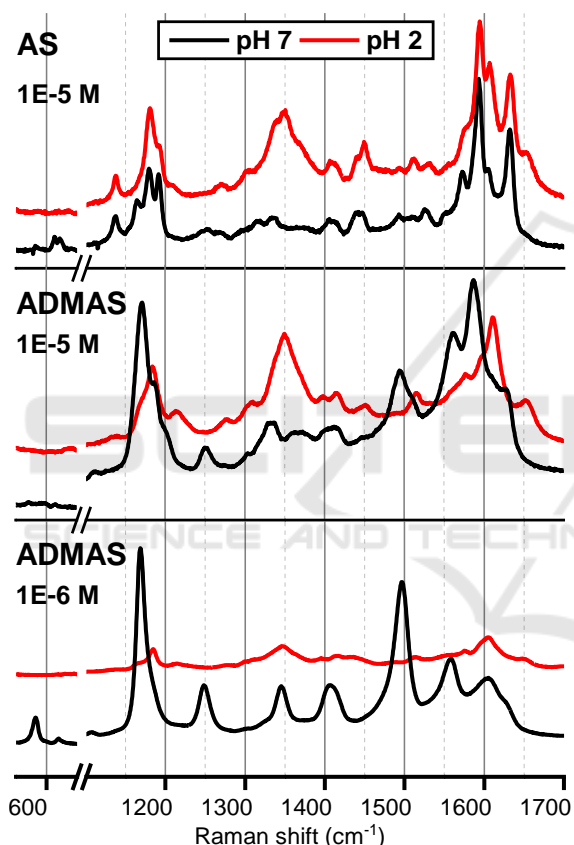
corresponding to sub-monolayer adsorption. In case of AS, as well as for ADMAS at multilayer adsorption, the addition of chloride ions is followed only by moderate increase of intensity and some bands transformations in their spectra. Apparently, chloride ions, embedding in the double electric layer, displace the ADMAS molecules from the first monolayer. This leads to the observation of ADMAS spectra characteristic for multilayer adsorption when the SERS signal is collected from several layers, including the top layers. It is should be mentioned, that the observations for ADMAS at protonation and chloride addition are the same with those that were revealed for DAS.
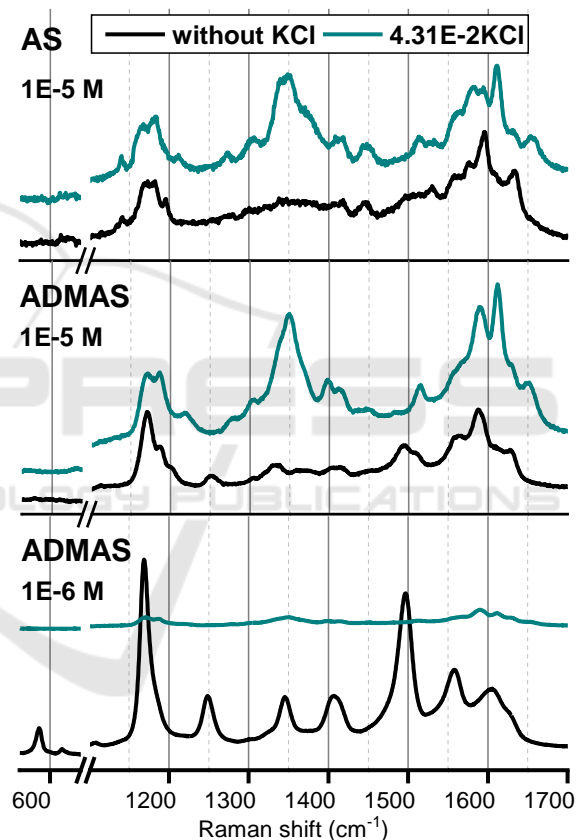

Figure 5: Dependence of Raman signal from pH for ADMAS and AS 10^{-6} and 10^{-5} M solutions in Ag hydrosol.

Figure 6: Change of Raman signal for AS and ADMAS after addition of chloride ions in Ag hydrosol.

The halide anions have a high affinity to silver surface. The study of organics in metal hydrosols in their presence allows one to evaluate the processes of competitive adsorption. To this end, a potassium chloride was added to the prepared organometallic systems. Fig. 6 represents the effect of chloride anions on the SERS spectra of AS and ADMAS. As can be seen, the dramatic changes of SERS spectrum occur for ADMAS at low concentrations

A short time ago, we have investigated an ability to link the Ag nanoparticles for bifunctional DABB, which distinguishes from the stilbene derivatives by the structure of central fragment. In DABB, the benzyl rings are bonded with each other by the saturated ethane fragment instead of the double bond in stilbenes (see fig. 1).

Unexpectedly, the SERS spectra of DABB have demonstrated the monotonous dependence on the
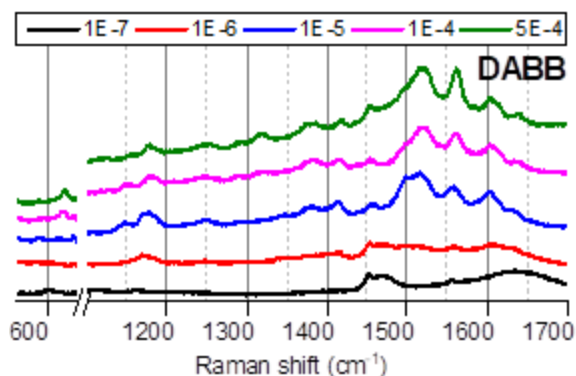
Figure 7: Dependence of SERS spectra of DABB on concentration (M) in silver hydrosol.

concentration similar with AS (fig. 7). This suggests that DABB do not link Ag NPs despite of two amino groups. No color change observed for the corresponding solutions of DABB in silver hydrosol also implies that the Ag nanoparticles save their size. This supports the previous assumption about inability of DABB to modify Ag NPs into agglomerates with hot spots. Obviously, the saturation of central fragment, defining a conjugation in the whole molecule, has a key significance for linking ability of studied aromatic amines. Revealing a role of central fragment structure in the interaction of molecules with the metal nanoparticles will be a subject of our future investigation.

4 CONCLUSIONS

Based on the obtained results, we proposed the models of adsorption for investigated stilbene dyes (fig. 4). At sub-monolayer adsorption, bifunctional aminostilbenes coordinate with the surface of two Ag nanoparticles simultaneously that leads to the formation of agglomerates with hot spots. The stilbene derivatives with one amino group adsorb on Ag nanoparticles by ordinary layer-by-layer way. The bifunctional stilbenes with the tertiary amines are also able to bind the metal nanoparticles, despite the fact that tertiary amines are less active electron density donors than primary ones.

Thanks to that, a list of photoactive compounds, which can be used as promising modifiers of plasmon substrates, can be significantly expanded. However, the efficiency of bifunctional stilbenes dyes as molecular linkers is lost in acidic solutions and at the presence of chloride ions. At the same time, the surface properties of single-particle

organometallic systems change due to the redistribution of potential energy. The comparative SERS study of bifunctional stilbenes and bibenzyls showed that a conjugation in the molecule is also significant for ability to link the nanoparticles.

The results of present study are able to find the application points in the broad range of modern research and development areas, connected to photoactive materials. The revealed SERS response of obtained organometallic composites dependent on the molecular structure and concentration of modifier as well on the environmental parameters gives the deeper insight into surface chemistry and practical possibilities of these and similar systems.

ACKNOWLEDGEMENTS

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