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Adsorption orientations and interactions of methyl orange on negatively and positively charged colloidal silver particles

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Abstract

Both positively and negatively charged colloidal silver particles were prepared from chemical deoxidized methods. Then UV–visible absorption, fluorescence, and surface-enhanced Raman scattering of methyl orange adsorbed onto surfaces of these two kinds of particles were observed and compared with each other. The results indicate that dye molecules may adsorb onto these two kinds of silver surface in differing adsorption orientations with different interactions, which caused the different phenomena.

Keywords: Methyl orange; Silver particles; Adsorption orientation; Spectroscopy

1. Introduction

In recent years, extensive research has been carried out in the field of surface-enhanced Raman scattering (SERS) due to its potential applications in colloid chemistry, surface science, nanophase science, chemical analysis, and other fields [1–5]. When SERS experiments are conducted in aqueous solution for molecules adsorbed onto noble metal particles in a colloidal dispersion, a definite dependence of the enhancement on particle size and shape is ensured [6,7], as well as surface electrical properties [8–11] and so on. On the other hand, difficulties correspondingly arise in determining the adsorption orientation and enhancement mechanism due to different electrical properties, which leads to the nonreproducibility of the SERS spectra in many cases [3,8–10]. Since suitable electrical properties are crucial for obtaining large Raman enhanced intensities, control of the colloidal electric properties has to be achieved for SERS and also for other spectral signals.

In the present work, positively and negatively charged colloidal silver particles (PCCS and NCCS) were prepared; then UV–visible absorption, fluorescence, and surface-enhanced Raman scattering (SERS) of methyl orange (MO) adsorbed onto these two kinds of silver surfaces were investigated. The results showed many differences when MO was added to NCCS and PCCS, and these differences not only are important to the investigation of adsorption orientations of molecules on silver surfaces, but also yield new information for the study of mixing effects on spectral activity.

2. Experimental

2.1. Materials

Silver nitrate, tannin, and sodium citrate from Beijing Chemical Company were used as received, without further purification. All the other chemicals used in this work were analytical grade reagents, with deionized water used for solution preparation.

2.2. Preparation of silver colloids

The positively charged colloidal silver particles (PCCS) were prepared according to a modified procedure developed and established by Lee and Meisel [12]. A sample of silver nitrate (90 mg) was dissolved in 500 ml of deionized water and the resulting solution was heated to boiling. Then 9 ml of a 1% sodium citrate solution was added drop by drop to the boiling

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solution with vigorous stirring and held at boiling for a further 10 min with constant stirring. Finally, a green-gray silver sol was obtained, later found to be stable for several weeks, with a characteristic absorption spectrum showing a band centered at 420 nm (line a in Fig. 1A). These colloidal silver particles presented positive electricity, as determined from electrophoresis.

The negatively charged colloidal silver particles (NCCS) were prepared according to the method proposed by Si et al. [8]. A sample of silver nitrate (3 mg) was dissolved in 100 ml of deionized water at room temperature, 20 ml of 1% tannin solution was added, and then 0.5 ml of 1% potassium carbonate was added drop by drop with vigorous stirring to achieve a red-brown silver colloid, which presented negative electricity, as determined from electrophoresis. Their characteristic absorption spectrum also showed a band centered at 420 nm (line a in Fig. 1B).

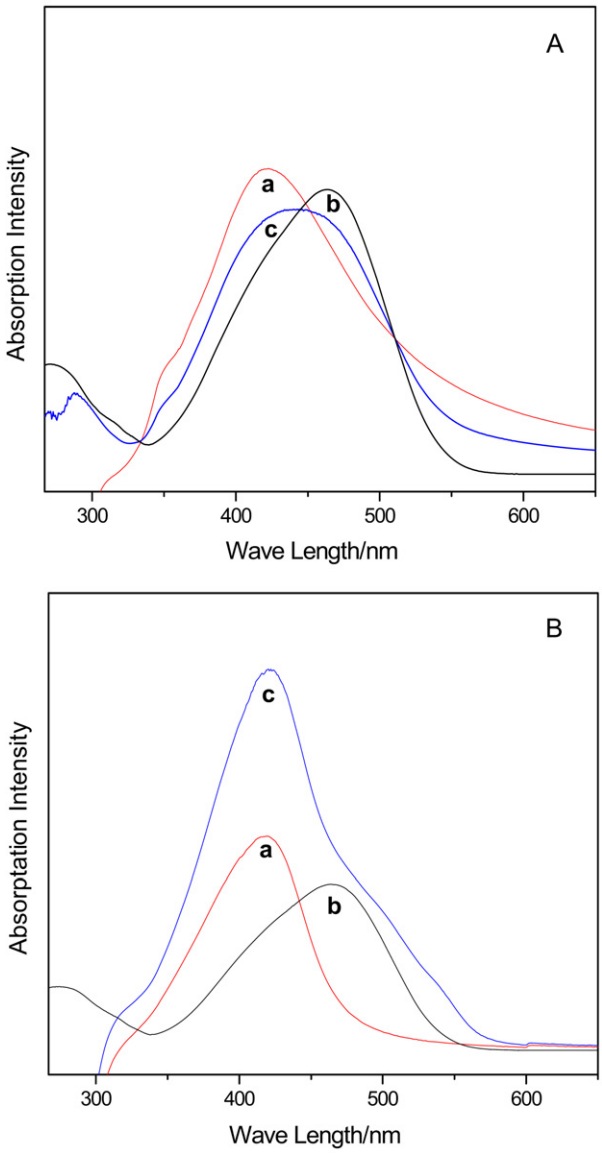

Fig. 1. Absorption spectra of PCCS (line a in (A))/NCCS (line a in (B)), MO (line b in both (A) and (B)), and PCCS–MO (line c in (A))/NCCS–MO (line c in (B)).

2.3. Apparatus and measurements

The Raman spectra were recorded by a microprobe Raman system (Renishaw H13325 spectrophotometer) with the excitation line at 514.5 nm (12 mW at the head) using an Ar ion laser. The use of a holographic notch filter coupled with a CCD detector results in extremely high detection sensitivity. Fluorescence and absorption spectra were recorded on a Fluorolog-3 spectrometer and a Shimandzu Model UV-2401PC UV–visible spectrometer, respectively.

All measurements were carried out at room temperature using a spectrophotometric 1×1 cm quartz cuvette. Fluorescence spectra were collected with the excitation wavelength fixed at 270 nm, which is the first absorption of MO molecules in aqueous solutions, and scanned from 300 to 800 nm with a WB 320-nm filter.

3. Results and discussion

Methyl orange, 4-[[4-(dimethyl amino)phenyl]-azo] benzenesulfonic acid, exists in a basic form (Fig. 2) when dissolved in aqueous solutions.

3.1. UV–visible absorption of MO in different colloidal systems

It is well known that the plasmon absorption at 420 nm (line a in Figs. 1A and 1B) is due to the dipole resonance of spherical monomeric silver particles in colloidal dispersion [13]; and its shape, intensity, and position will change with the change of external conditions. Because of the large specific surface of silver nanoparticles, the surface plasmon resonance absorption always appears strong when excited by anexternal optical field; and certainly, this surface plasmon resonance can easily be influenced by adsorbents [14].

Due to conventional plasmon absorption theories [13–15], the surface plasmon resonance frequency (ω_p) of a metal particle is in direct proportion to the 1/2 power of its surface free electron density N; that is, $\omega_p = K \cdot N^{1/2}$, and K is a constant correlated to metal. As a result, the surface plasmon resonance frequency of the metal colloid will be changed with the change of its surface electron density N. On the other hand, the penetration depth in the metal surface by external electromagnetic waves is just some atomic radius [15], which indicates a huge contribution of surface adsorption to the plasmon absorption of metal particles.

When MO anions adsorb onto PCCS with Coulomb attraction, surface electron density of particles may be decreased by electrical neutralization between anions and positively charged surfaces, and thus ω_p lowered, resulting in a red shift of its

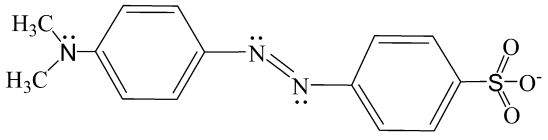

Fig. 2. The basic form of the MO molecule in aqueous solution.