Experimental and theoretical evidence for the chemical mechanism in SERRS of rhodamine 6G adsorbed on colloidal silver excited at 1064 nm

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The evidence for the existence of a chemical mechanism in surface-enhanced resonance Raman scattering (SERRS) of rhodamine 6G (R6G) adsorbed on colloidal silver excited at 1064 nm is reported on the basis of experimental and theoretical analyses. A weak absorption peak at around 1060 nm for R6G-functionalized silver nanoparticles was observed, which is not present in the individual spectra of R6G or silver nanoparticles. Theoretically, the charge difference density reveals that this weak absorption is a metal-to-molecule charge transfer excited state. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: SERS; chemical mechanism; 1064 nm; charge transfer excited state

Introduction

Since the discoveries of surface-enhanced Raman scattering (SERS) and surface-enhanced resonance Raman scattering (SERRS), the mechanisms of electromagnetic (EM) and chemical enhancement via charge transfer (CT) have been widely accepted. The coupling of metals at suitable distances produces EM enhancements which give rise to SERS signal enhancements reaching values as high as 10^11. Because of the interaction between molecules and metals, the intensity of the signal can be enhanced by a factor of up to 10^4–10^6, when the wavelength of the radiation is close to an electronic excitation of the molecule–metal system, which is referred to as SERRS via CT between the molecule and metal. In fact, it is not easy to experimentally distinguish the CT mechanism from the EM mechanism in SERS or SERRS. In this article, we report experimental and theoretical evidence for the existence of chemical mechanisms in SERRS of rhodamine 6G adsorbed on colloidal silver excited at 1064 nm.

Experimental

The SERS-active silver colloid was prepared according to the process specified in Ref. [6]. The Ag particle concentration was estimated to be ~35 μM with an average diameter of around 100 nm. R6G (5 × 10^{-6} M) was dissolved in water and silver saline solution, respectively, and the absorption spectra were measured using a UV–VIS spectrometer (Cary 5000). A 50-μl volume of R6G (5 × 10^{-4} M) was added to a 5-ml silver saline solution (R6G in silver saline is 5 × 10^{-6} M) which was dropped and allowed to dry on a glass slide. The Raman spectra were obtained using an RFS 100/s Bruker NIR-FT spectrophotometer using an operating wavelength of 1064 nm. The maximum resolution of this instrument was 3 cm^{-1}, and a 180° geometry was employed.

All quantum chemical calculations were performed using Gaussian 03 suite. The detailed calculations and methods are described in the supporting information. The orientation of CT was visualized with charge difference density.

Results and Discussion

Figure 1(a) and (b) shows the experimental normal Raman spectrum of R6G powder and the SERS spectrum of R6G adsorbed on the silver nanoparticles using an excitation wavelength of 1064 nm. It is found that these two profiles are similar. Experimentally, we measured the absorption spectra of R6G, silver colloid, and R6G with silver colloids, respectively, in the 250–1300 nm wavelength range (Fig. 2(a)). One can see that at around 1060 nm, there is a weak absorption peak for R6G-functionalized silver nanoparticles, which is not present in the individual spectra of R6G or silver nanoparticles. Thus we conclude that the weak absorption peak at around 1060 nm for R6G-functionalized silver nanoparticles arises from the interaction between silver and the N atoms of R6G, which is a new CT electronic excitation state. The Raman spectrum obtained from R6G adsorbed on silver nanoparticles using an incident light of 1064 nm should be SERRS enhanced by chemical mechanism via CT.

To confirm the experimental result shown above, the absorption spectrum of the R6G–Ag_2 complex was calculated using time-dependent density functional theory. Depending on the nature of the interaction between R6G and silver, new CT excited states can occur. The calculated optical absorption spectrum of R6G–Ag_2...
reveals the weak absorption peak at around 1064 nm (Fig. 2(b)). The charge difference density in the inset of Fig. 2(b) reveals that this excited state is a pure metal-to-molecular CT-excited state (electrons transfer from Ag_2 to R6G; see Fig. 2(b)), since all the holes and electrons are localized on the Ag_2 cluster and the R6G molecule, respectively. Because the electrons on the Ag_2 cluster are equally transferred to the xanthene group of R6G without any orientation using the incident light of 1064 nm, the profiles of the Raman spectra in Fig. 1(a) and (b) are almost the same.

**Conclusion**

We have provided experimental and theoretical evidence for the existence of chemical mechanism in SERRS of R6G adsorbed on colloidal silver excited at 1064 nm. The weak absorption at around 1064 nm was observed experimentally, and the charge difference density reveals that it is a pure metal-to-molecular CT excited state.

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**References**