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# Intrinsic Fluorescence and Quenching Effects in Photoactivated Reactively Sputtered Silver Oxide Layers

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Nobel metal particles and clusters with nanometer dimensions have drawn considerable attention in the past due to their interesting optical and electronic properties. Besides their ability to promote surface enhanced Raman scattering[1] (SERS) they also emit fluorescent light in an intermittent manner. The latter effect was first shown for Ag and Cu clusters at cryogenic temperatures.[2] Further studies revealed similar characteristics at room temperature[3] when individual Au particles were investigated. The first two single molecule SERS reports on such particles were from Nie[4] and Kneipp.[5] Recently, Dickson et al.[6] reported intermittent fluorescence on Ag particles and showed applications of thin layers to optical data storage technology.

In this paper we report on sputtered silver oxide layers which play an important role in near-field optical data storage.[7,8] We show that such layers exhibit strong SERS activity and bright intermittent[9] fluorescence after photoactivation at 488 nm. The nature of the deposited films allows applications in a variety of solvents to investigate vibrational properties of substances, whereby the solvents used for immersion may be as diverse as water and benzene. Here, we show that the bright intermittent fluorescence emanating from an activated area on the silver oxide layers is effectively quenched in solvents such as 2-propanol and water. Upon addition of stronger Lewis bases to the solution, the fluorescence recovers under the simultaneous generation of an intense ligand SER spectrum. Furthermore, the degree of recovery of the fluorescence as well as the SERS intensity depends on the strength of the applied ligand as is demonstrated by displacement experiments. These results reveal that the SERS effect, as well as the fluorescence quenching, is clearly mediated by the same specific surface sites on the Ag particles.

We have used reactively sputter deposited AgO layers to demonstrate the effects described above. Films of 15 nm thickness were deposited on silver covered glass slides and investigated by means of a Raman spectrometer in backscattering geometry. Photoactivation was performed in situ by the 488 nm excitation line. A long working distance objective (50×, NA = 0.55) was used to give a diffraction limited spot at the sample surface. Details of the deposition conditions, as well as Raman equipment, have been described previously.[10] Fluorescence of AgO samples was measured in air with an integration time of 10 s. A spectral range from 200 to 6000 $\mathrm{cm}^{-1}$ was investigated. The time required to scan this spectral range was ≈45 s, and the power at the sample surface was 1.5 mW. The simultaneous activation leads to an immediate appearance of fluorescence. Figure 1 shows the temporal development of the fluorescence intensity during a series of successively recorded scans, starting from $t_0$. Distinct peaks can be identified during the first few scans. Those peaks shift with time (while activation proceeds) and finally develop into an intense and stable background. The double peak between about 530 and 540 nm (1350 and 1590 $\mathrm{cm}^{-1}$) is not fluorescence but the SERS signal of amorphous or nanocrystalline carbon domains.[11] Such features have often been observed while performing SERS on silver substrates and have previously been investigated in detail.[12,13] In this study the source of the carbon impurities can be traced back to contaminations resulting from the sputtering process.

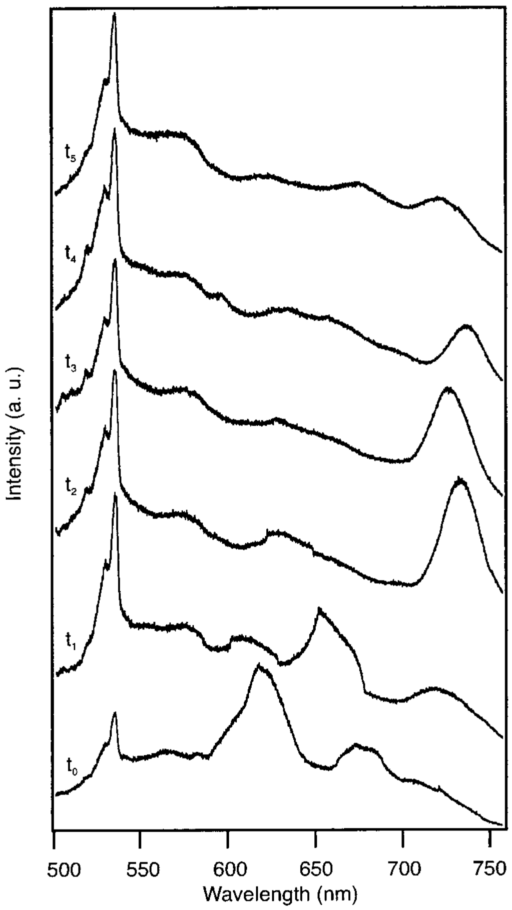

**Figure 1.** Temporal development of fluorescence of the AgO layers upon photoactivation at 488 nm starting from $t_0$.

Immersing the sample in 2-propanol and repeating the measurement under otherwise identical conditions gave the spectrum in Figure 2 a. The fluorescence is almost completely quenched.

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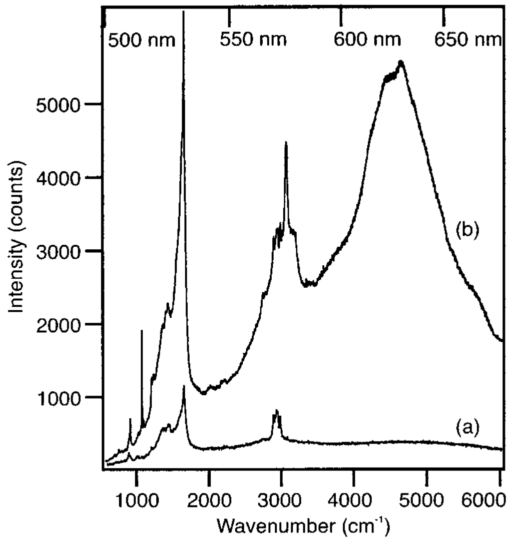

**Figure 2.** (a) Fluorescence quenching in 2-propanol and (b) fluorescence recovery upon addition of benzoic acid (absolute BA concentration: $10^{-4}$ M).

The dominant spectral features belong to 2-propanol and amorphous carbon, indicating that activation had occurred inside the layers. Upon addition of benzoic acid (BA) to a final concentration of $10^{-4}$ M the fluorescence recovered immediately. When a new (previously not activated) sample position was chosen for experimentation (Figure 2 b), similar temporal changes in the spectral distribution were observed to those shown in Figure 1. Rapid recovery of fluorescence is also observed at a previously unactivated position, but the spectra observed resemble those depicted in $t_5$ of Figure 1, and no longer changed noticeably with time. Additional experiments in water, ethanol, and methanol also lead to fluorescence quenching and a subsequent recovery upon BA addition.

We further found that the coupling of other ligands always leads to at least a partial recovery of the previously quenched fluorescence. The degree of recovery was dependent on the strength of the complex that formed between the active surface sites and the ligand. Whenever fluorescence recovery was observed, there was a simultaneous strong SERS signal developing from the coupled molecule. Watanabe[14] showed early that $Ag^+$ containing Ag clusters are necessary to promote SERS, suggesting the formation of charge-transfer complexes between a limited number of "hot" surface sites[15] and the SERS active molecule. According to the principle of hard and soft acids and bases[16] (HSAB), $Ag_n^+$ clusters can be classified as soft Lewis acids, hence they should form stable complexes with soft Lewis bases. In addition, it should be possible to replace weaker bases with stronger ones. Evidence for this assumption is given in Figure 3. The lower group of curves depict the temporal evolution of the SERS spectrum of a $2.5 \times 10^{-2}$ M pyridine (Py) in 2-propanol solution over 30 min. The initially sluggishly developing, but ultimately clear, Py peaks around 1000 cm$^{-1}$ disappear after the addition of methyl violet (MV) to a final concentration of $10^{-5}$ M (middle spectra in Figure 3) while the MV bands gain intensity.

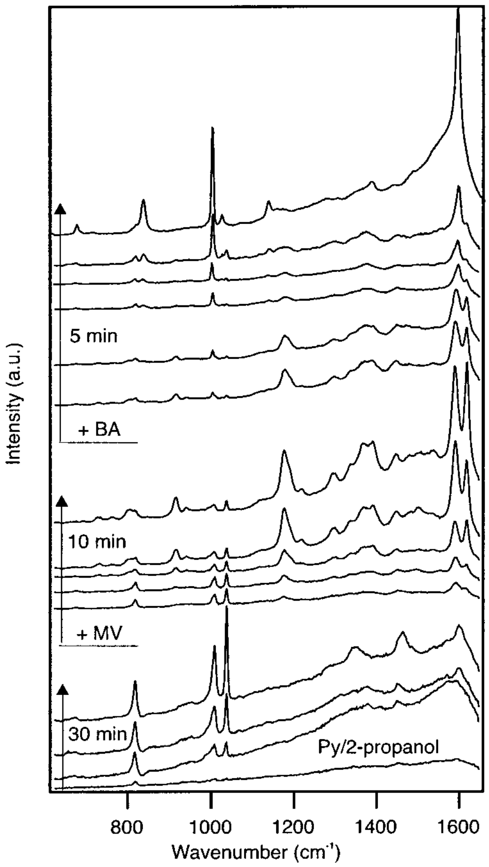

**Figure 3.** Superseding of ligands bonded to SERS active sites on the AgO surface. The bottom group of SER spectra show the temporal development of pyridine bands. The addition of methyl violet leads to an exchange at the surface as can be seen by the declining intensities and the developing MV spectra. Additional benzoic acid displaces the latter molecules, resulting in a prevailing BA spectrum.

Adding BA to a concentration of $10^{-4}$ M finally provokes a sudden displacement of the MV molecules at the SERS active sites on the silver particles leading to a dominant and clear BA SER spectrum. This behavior is in accordance with the increasing Lewis basicity and softness of the ligands in the row Py < MV < BA. The fluorescence recovers in all cases; in each case the degree of recovery is dependent upon the strength of the $Ag^+$–ligand complex and the resulting absolute number of occupied sites on the Ag clusters. The complete recovery upon BA addition demonstrates a quantitative and preferential bonding leading to a saturated surface. In comparison, the weak and hard bases 2-propanol, methanol, and water do not form stable bonds with the silver clusters.[17]

We conclude that the SERS inactive water and alcohol molecules are only physisorbed at the surface while stronger Lewis acids such as BA and other ligands occupy the active sites by forming stable covalent bonds. The formation of such bonds prevents the fluorescent Ag particles from transferring the excitation energy to the quenching molecules in the solution.

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[17] Further evidence is given by the observation that 2-propanol bands are only weakly enhanced by interacting with the silver surface.