Colloidal Silver as a Quencher for the Fluorescence of 2-Naphthalenesulfonic Acid

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Upon adsorption the fluorescence of 2-naphthalenesulfonic acid (NSA) is effectively quenched by colloidal silver indicating the occurrence of photoinduced interfacial electron transfer from the excited singlet of NSA to silver.

Interfacial charge-transfer processes at colloidal metals have been extensively investigated over the past decades because of their application in the catalysis of redox reactions.[1] The processes can broadly be classified into two categories: (*i*) electron injection into the metal particle from free radicals photogenerated by γ-radiation or UV-illumination,[2] and (*ii*) donation of the electron density from adsorbed reducing species molecules such as SH^-, CN^- and PH_3.[3] However, photoinduced interfacial electron transfer (PIET) from the excited state of the adsorbate to metal particles has attracted much less attention, even though it has been confirmed to be possible as established by surface enhanced Raman scattering (SERS).[4–6] Since colloidal metals have proved to be efficient electron transfer relays in catalysing redox reactions,[1,2] study of PIET is helpful in extending the application of colloidal metal catalysis in the conversion of light energy. The present communication reports for the first time the use of colloidal metal as a quencher for the fluorescence of adsorbates. It is found that the fluorescence of 2-naphthalenesulfonic acid (NSA) is effectively quenched upon the addition of an aqueous silver sol.

Colloidal silver was prepared as described previously,[7] from the reduction of $AgNO_3$ by $NaBH_4$. The preparation was carried out by a simple injection technique: 0.4 ml of a 0.1 mol dm^{-3} $NaBH_4$ solution was added rapidly under vigorous stirring to a 49.6 ml solution containing 2.0×10^{-4} mol dm^{-3} Ag^+ ions. This was then left to stand for about 30 min. The silver sol thus obtained was bright yellow with particle sizes in the range 10–15 nm, as determined by TEM.

The intense plasmon absorption band of colloidal silver in aqueous solution is very sensitive to the presence of nucleophilic reagents. Adsorption of a nucleophile on the particle surface often leads to reduction and shifting of the absorption band of colloidal silver.[3] By observing the changes in the shape of the absorption band, one can determine whether adsorption has occurred. Fig. 1 shows the absorption spectra of a 10^{-4} mol dm^{-3} silver sol before and after addition of 10^{-5} mol dm^{-3} NSA at pH 8.5. The 390 nm plasmon absorption band of silver sol is broadened, red-shifted and decreased in intensity. Similar phenomena were observed by Henglein's group[3a] using some nucleophilic ions, such as I^-, SH^- and PhS^-, as additives. It is believed that the changes in the shape of the absorption band are brought about owing to changes in the electronic properties of the silver particles caused by chemisorption of the nucleophiles.

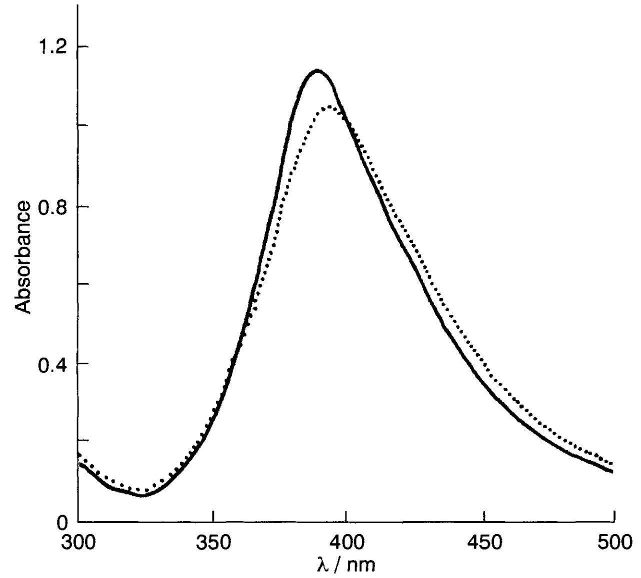

Fig. 1 Absorption spectrum of a 10^{-4} mol dm^{-3} silver sol before (solid line) and after (dotted line) addition of 10^{-5} mol dm^{-3} NSA

Addition of silver colloid to a NSA solution results in the quenching of its fluorescence emission. Fig. 2 shows the effect of increasing the concentration of silver colloid on the fluorescence spectrum of NSA. Nearly 80% of the emission of 10^{-5} mol dm^{-3} NSA can be quenched with 2.0×10^{-4} mol dm^{-3} colloidal silver. This quenching behaviour is similar to the previously reported fluorescence quenching of dyes by semiconductor colloids.[8] The quenching mechanism involves interfacial electron transfer from the excited singlet of NSA to the silver particle. CV indicates that the oxidation potential of NSA at pH 7 is +0.87 *vs.* SCE. With the absorption of a photon at 275 nm (4.5 V), the NSA molecule is now sufficiently energetic to transfer an electron to the silver particle, the Fermi potential of which is close to zero on the standard electrochemical scale when the particle is uncharged.[2]

There exists the possibility that the fluorescence quenching of NSA was caused by the trace Ag^+ ions generated by air oxidation. This is disproved by the experimental results as shown in Fig. 3. Addition of 2.0×10^{-4} mol dm^{-3} Ag^+ ions quenches only 34% of the fluorescence of 10^{-5} mol dm^{-3} NSA,

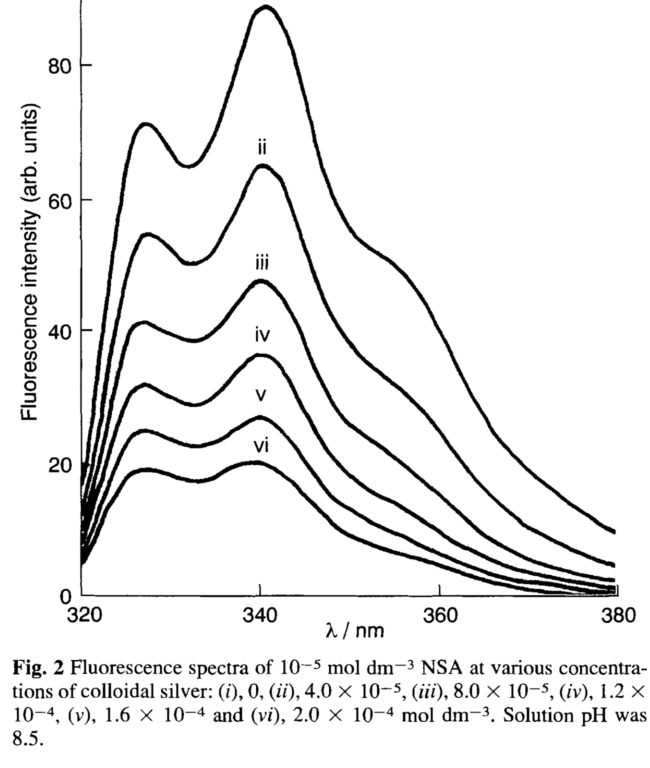

Fig. 2 Fluorescence spectra of 10^{-5} mol dm^{-3} NSA at various concentrations of colloidal silver: (*i*), 0, (*ii*), 4.0×10^{-5}, (*iii*), 8.0×10^{-5}, (*iv*), 1.2×10^{-4}, (*v*), 1.6×10^{-4} and (*vi*), 2.0×10^{-4} mol dm^{-3}. Solution pH was 8.5.

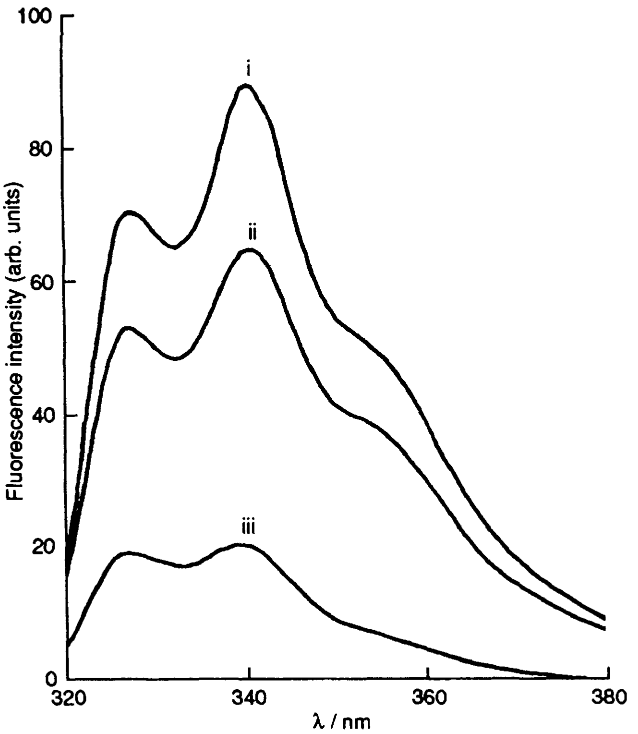

Fig. 3 Fluorescence spectra of 10^{-5} mol dm^{-3} NSA in the absence of colloidal silver (*i*), and in the presence of 2.0 × 10^{-4} mol dm^{-3} Ag^+ ions (*ii*), or 2.0 × 10^{-4} mol dm^{-3} colloidal silver (*iii*)

whereas nearly 80% of the fluorescence can be quenched in the presence of 2.0 × 10^{-4} mol dm^{-3} silver colloids. In view of the fact that in the aqueous silver sol the concentration of Ag^+ ions is much lower than that of colloidal silver, it can be concluded that the contribution from Ag^+ ions to the observed fluorescence quenching of NSA is negligible compared with that from silver colloids.

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