

Fluorescence quenching of 3,7-diamino-2,8-dimethyl-5-phenyl phenazinium chloride by AgCl and Ag nanoparticles

Smritimoy Pramanik^a, Subhash Chandra Bhattacharya^{a,b,*}, Toyoko Imae^b

^aDepartment of Chemistry, Jadavpur University, Kolkata 700 032, India

^bResearch Center for Materials Science, Nagoya University, Nagoya, Japan

Received 30 November 2005; received in revised form 19 May 2006; accepted 26 June 2006

Available online 8 August 2006

Abstract

Quenching of fluorescence of the dye 3,7-diamino-2,8-dimethyl-5-phenyl Phenazinium Chloride (Safranin T) has been investigated by AgCl nanoparticles in the W/O microemulsion medium at different $[H_2O]/[AOT]$ ratios (ω) and with Ag nanoparticles and Ag^+ in aqueous medium. A simple straightforward method has been introduced to prepare AgCl nanoparticles in well-characterized, monodispersed biomimicking nanocavities formed by sodium bis(2-ethylhexyl)sulfosuccinate (AOT) in heptane. Experimental results reveal that the size of the AgCl nanoparticles increases with increase in hydration. The results of the quenching experiment were analysed in the light of Stern Volmer equation. Quenching of fluorescence of the dye has been found to decrease with decrease in the size of the nanoparticles of AgCl and the variation of Stern Volmer quenching constants (K_{SV}) with particle size is different for two different size regimes.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Fluorescence; Quenching; Nanoparticles; Monodispersed; Microemulsion

1. Introduction

Fluorescence quenching of photosensitive dyes by neutral or charged species in organized assemblies has been frequently studied in order to characterize the medium [1–5]. The size selective synthesis of nanoclusters has stimulated researchers as the size provides an important control over many physical and chemical properties of the nanoscale materials [6–9]. The physical and chemical properties of the surfaces of solids are attracting increasing attention in catalytic chemistry. As the dimensions of the particles shrink into the nanometer range, there is a significant role of the surface in controlling the overall energy of the particles [6]. Solid clusters in the nanometer size show interesting size dependent chemical properties. These chemical properties help chemists in the functionalization of different size nanoparticles.

The photophysics and photochemistry of dyes in general are of considerable interest in the appreciation of various phenomena in pico to microsecond range, viz, fluorescence, phosphorescence, long- and short-range excitation energy transfer, electron transfer and various modes of quenching [10–16]. Interaction of a dye with the medium at the molecular level is reflected in its visible and fluorescence spectra [14–17]. Fluorescence quenching is a technique to understand the interaction within the medium in view of the special role of surfaces of the nanoclusters in guiding and modifying physicochemical processes.

Safranin T (ST) is a cationic dye. Both ground and excited state spectra of the dye are affected by solvents and quenchers [2,17–20]. The spectroscopic behaviour of the dye in different media with different quenchers have been studied by our group [2,3,18–21]. Silver halides have been used in photography for one and half centuries and their light sensitiveness forms the basis of modern photography. They are also used in photochromic glass [22]. However, it is difficult to use nanosized particles of silver halides in the photographic process because of their poor photosensitivity and stability. As the dimensions of the particles shrink

*Corresponding author. Department of Chemistry, Jadavpur University, Kolkata 700 032, India. Tel.: +33 2414 6223; fax: +91 33 24146584.

E-mail address: sbjuchem@yahoo.com (S.C. Bhattacharya).

into the nanometer range, there are significant changes in optical and electronic properties due to both quantum size effects and to the increasingly important role of the surface in controlling the overall energy of the particles [6]. Using both ionic and nonionic surfactants synthesis of silver halide nanoparticles have been reported [23,24]. Sensitizing dyes are used to extend the spectral property of silverhalide particles. As a kind of sensitive dye, the interaction of ST with AgCl nanoparticles is an important subject to be studied. Silver halides are generally used in photographic emulsion. Interactions of silver chloride nano particles with sensitizers are rare in literature. A comparative analysis of the results of quenching of ST by AgCl and Ag nanoparticles and Ag^+ ion has been presented. It has been seen that the probe molecules adsorbed on to the surfaces suffer strong quenching of their fluorescence.

2. Experimental

ST (E. Merck) was crystallized thrice from ethanol–water mixture before use. The anionic surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was from Sigma and used without further purification. Spectroscopic grade *n*-heptane (E. Merck) was used after being dried according to standard procedure. AgNO_3 and KCl of E. Merck (Germany) were used without further purification. Deionized water was used throughout the work. The concentration of AOT in *n*-heptane was 0.5 M. The fluorescence spectra of the dye with Ag^+ ion, AgCl and Ag nanoparticles as quenchers were recorded using Spex Fluorolog F IIA spectrofluorometer with a slit width of 1.25 nm. The excitation and emission wavelengths were 531 and 565 nm, respectively. The concentration of ST used was of the order of 10^{-5} M. Absorption of the solutions was measured by a Shimadzu UV-1700 model spectrophotometer. Transmission electron microscopy (TEM) was carried out on a model Hitachi H-7000, 100 kW power at different time intervals. Samples were prepared by placing and drying a drop of solution on a copper grid coated with a thin amorphous carbon film.

2.1. Preparation of AgCl nanoparticles

To prepare AgCl nanoparticles, W/O microemulsion technique has been used: aqueous solutions of AgNO_3 (0.1 M) and KCl (0.1 M) were added separately into the reverse micellar solution of AOT in heptane with stirring. The reverse micellar solution of AOT containing KCl was titrated with the reverse micellar solution of AOT containing AgNO_3 to give a final molar ratio of water to surfactants, $\omega = [\text{H}_2\text{O}]/[\text{AOT}] = 16, 13, 10, 8, 6$ and 4 separately. Then AgCl and KNO_3 were formed by exchange reaction within the reverse micellar core as dispersed phase. Since AgCl is sparingly soluble in aqueous medium, it will remain in the dispersed phase. The microemulsion, which maintains AgCl at different concentrations within the water pool by proper choice of AgNO_3

concentration, was mixed with aqueous solution of ST with constant concentration. Although K^+ and NO_3^- were also formed within the water pool, they are unable to quench the fluorescence of ST.

2.2. Preparation of Ag nanoparticles

Ten mg of NaBH_4 was dissolved in 2 ml of water and was added slowly to 2 ml of AgNO_3 solution (1.00 mM) with stirring. The reaction mixture turned to a blackish colour within a few seconds after adding the first drop of NaBH_4 solution. Finally we obtained a blackish colloidal solution of Ag in the mixture. Different volumes of this solution have been used to quench the fluorescence of ST.

3. Results and discussion

Aqueous solution of the dye ST absorbs at 520 nm and emits fluorescence at 586 nm. In reverse micelles of AOT in heptane the $\lambda_{\text{max}}^{\text{abs}}$ has been shifted to 531 and $\lambda_{\text{max}}^{\text{fl}}$ to 565 nm. The nature and shape of the fluorescence spectra of the aqueous solution of ST in reverse micellar core remains the same, except for a change in intensity with change in ω . With increase in ω the fluorescence intensity increases. In the presence of AgCl colloids quenching of ST fluorescence is observed. Different sizes of silver chloride particles were employed to investigate the size effect of the AgCl nanoparticles on the emission profile of ST. The salient feature of physical significance is that fluorescence quenching increases significantly in progressing from lower ω to higher ω .

AgCl nanoparticles are formed by the collision and fusion of reverse micelles and exchange of reactant ions. Silver and chloride ions react and nucleate. Membranes of AOT reverse micelles restrict the growth of the formed nuclei. That is why nuclei grow to a limit of nanometric range and not beyond that. TEM micrographs of AgCl nanoparticles prepared in water–AOT–*n*-heptane, W/O microemulsion system at different ω , are given in Fig. 1. It has been shown that AgCl nanoparticles are spherical with average diameters of 10–18.5 nm at ω values 4–16.

Under the experimental condition, it is important to note that the excitation wavelength of ST does not coincide with the absorption peak of AgCl at 253 nm (Fig. 2) and the AgCl particles do not exhibit any fluorescence. Moreover no such quenching of ST emission can be seen in the presence of KNO_3 . Compared to bulk water in micellar and reverse micellar medium of AOT, fluorescence intensity of ST is enhanced. So the quenching of ST (Fig. 3) indicates that the nanosize particles are responsible for this effect. The plot of F_0/F vs. $[\text{AgCl}]$ at six different sizes of the AgCl nanoparticles has been shown in Fig. 4. The plots obey Stern Volmer equation, $F_0/F = 1 + K_{\text{SV}}[Q]$, where F_0 and F , are the fluorescence intensities of ST in absence and presence of quencher (Q), respectively.

The linearity of the Stern Volmer plot indicates that only one type of quenching occurs in the system [15]. In the

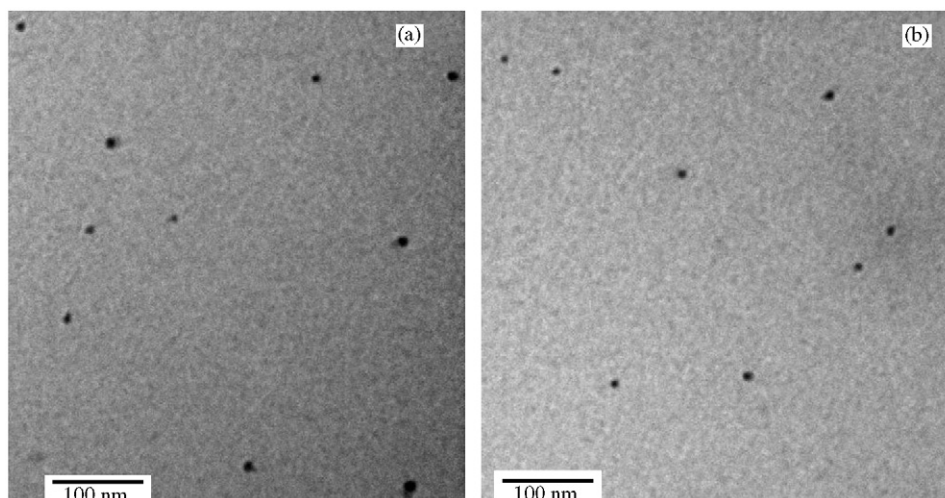


Fig. 1. TEM micrograph of AgCl nanoparticles prepared in AOT reverse micelle at (a) $\omega = 16$ and (b) $\omega = 8$.

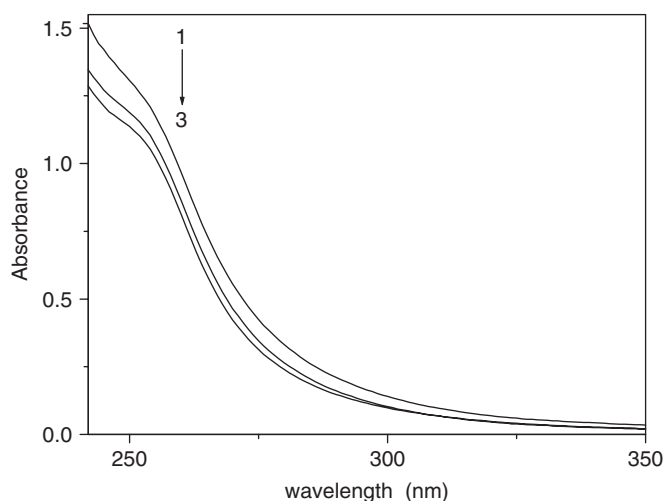


Fig. 2. Absorption spectra of AgCl nanoparticles at various water contents in AOT reverse micelle at (1) $\omega = 4$, (2) $\omega = 8$, (3) $\omega = 16$.

presence of quencher the absorption spectrum (which is not shown here) of ST remains unaltered. This indicates that static quenching does not occur [17]. In AOT reverse micelle, both the membrane of the surfactant AOT and AgCl nanoparticles are negatively charged [25] and the dye ST is a cationic dye. Therefore there was a competitive attraction effect of the dye to the AgCl nanoparticles or to the membrane of the AOT surfactant. When the numerical concentration, i.e., number of AgCl particles per cm^3 of the solution in RM, was the same, dye was adsorbed by AgCl nanoparticles, and there will be no obvious change in the absorption spectrum of the dye. The Stern Volmer quenching constants (K_{SV}) were evaluated and the values are given in Table 1. A plot of K_{SV} as a function of diameter of the particles has been shown in Fig. 5. The curve shows two distinct slopes for the two different size regimes, i.e., the quenching efficiency with particle size is different for the two different size regimes of the particles.

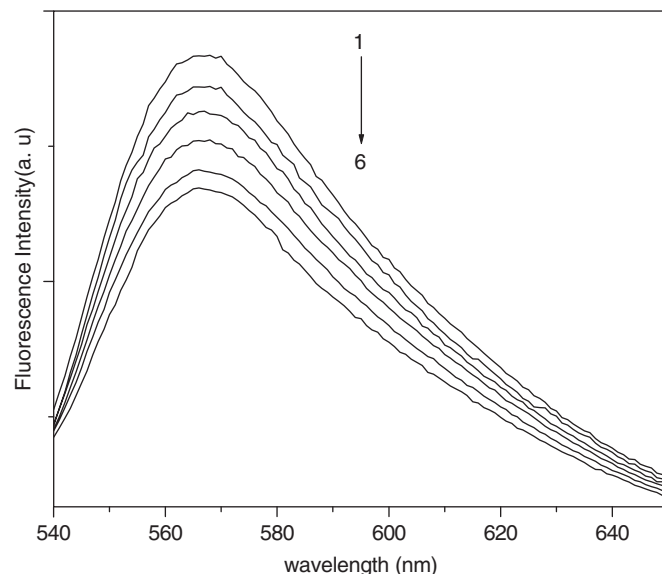


Fig. 3. Fluorescence quenching of the dye ST in AOT reversed micelle at $\omega = 16.0$ by AgCl nanoparticles. $[\text{AgCl}] = (1) 0, (2) 0.05, (3) 0.1, (4) 0.15, (5) 0.2, (6) 0.25 \text{ mM}$, $[\text{ST}] = 0.012 \text{ mM}$.

A plot of K_{SV} as a function of particle surface area has been shown in the inset of Fig. 5, from which two different slopes in two different size regimes of the particles are shown. K_{SV} increases with increasing particle size of the quencher. The size regime dependence of the AgCl particles on the fluorescence quenching process can be rationalized by the correlation of the structures of the nanoparticles in terms of size. Having the same fluorescent probe and nanoparticles of different sizes, we can realize the role of size and surface effect on the quenching. The bigger the particle, the larger is the surface area of the particles. The ST molecules added to the AgCl are in thermodynamic equilibrium between the surface and aqueous phase and the only fluorescent component is the free ST in the solution.

The fluorescence is due to unbound probe molecules in the system. As the size of the particles increases, the larger particles can accommodate a large number of ST molecules and therefore quenching increases. The difference in slope (Fig. 5) for two different size regimes of the particles indicate that there is a transition in quenching efficiency as the diameter decreases below 14.0 nm. This indicates that the AgCl molecule to surface area ratio increases as the particle size decreases below 14.0 nm. The results suggest that collisional quenching plays major role in the studied photophysical process in the presence of nanoparticles.

3.1. General comprehension

With increase in the concentration of AgCl nanoparticles, the dyes were adsorbed effectively and the fluorescence of the dye was quenched. The variation of K_{SV} with surface area of the particles (Table 1) is due to the adsorption of the dye on the surface of the particles. The quenching of the fluorescence of ST by metallic Ag nanoparticles in aqueous medium may also occur by the adsorption of the dye on the nanoparticles, where K_{SV} value is also high. The Stern Volmer quenching constant by Ag^+ ion in the aqueous solution is very low indicating absence of adsorption of the dye molecules on the quencher surface.

The quenching of the fluorescence of ST by Ag^+ in aqueous medium also suggests that the electrostatic effect between the cationic dye and cationic quencher (Ag^+) may be responsible for the reduced quenching. The process has been found to be less efficient (with significantly low K_{SV} values) in the aqueous medium. The interfacial barrier and regional fluidity have a role on the photophysical process involving the fluorophore and quencher. In the present system both the fluorophore and the quenchers resided in the interior of the water pool of the microemulsion, so that the interaction property was essentially guided by the fluidity of the core water, which increased with increasing ω , resulting in a concomitant increase in K_{SV} . At low ω , the solution of interfacially adsorbed AOT molecules in the water pool fairly decreased the pool fluidity and hence reduced K_{SV} values.

4. Conclusions

$[H_2O]/[AOT]$ ratio plays an important role on the size of the AgCl nanoparticles. The process of fluorescence quenching of ST by AgCl and Ag nanoparticles and Ag^+ ion indicates that the collisional quenching occurs and the quenching depends on the particle size of quencher.

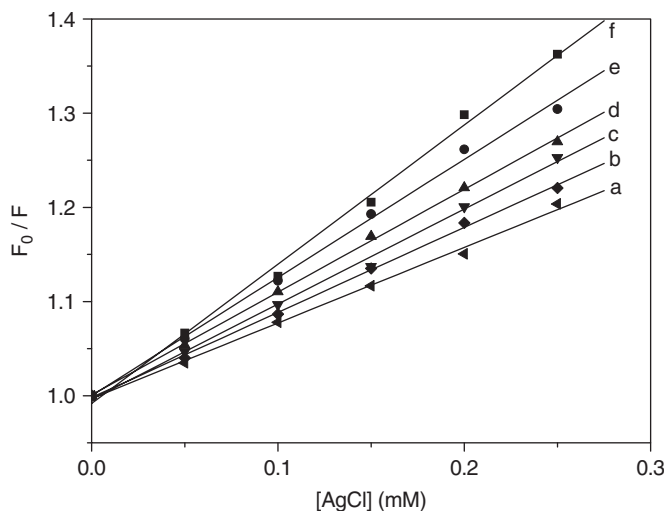


Fig. 4. Plot of F_0/F vs. $[AgCl]$ for the dye ST at (a) $\omega = 4$, (b) $\omega = 6$, (c) $\omega = 8$, (d) $\omega = 10$, (e) $\omega = 13$ and (f) $\omega = 16$. $[ST] = 0.012$ mM.

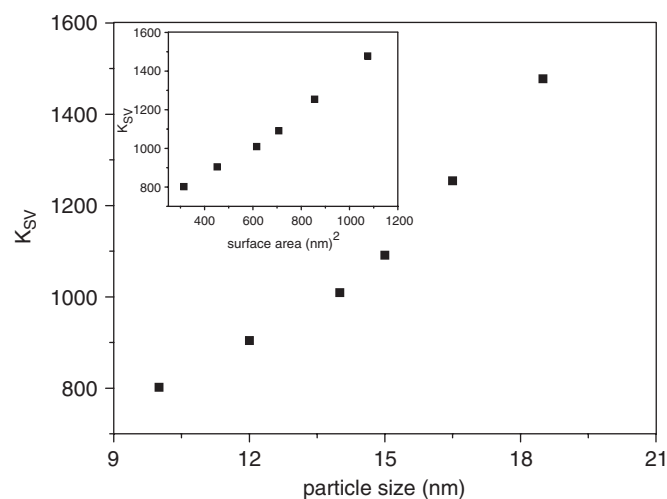


Fig. 5. Variation of K_{SV} with size of AgCl nanoparticles. Inset: K_{SV} as a function of the surface area of AgCl nanoparticles.

Table 1
Stern Volmer Quenching Constants by AgCl of different sizes, Ag nanoparticles and Ag^+ ion

Quencher	ω	Particle size (nm)	Surface area per particle (nm^2)	K_{SV} (M^{-1})
AgCl	16	18.5	1075.21	1478
AgCl	13	16.5	855.30	1254
AgCl	10	15.0	706.86	1091
AgCl	8	14.0	615.75	1009
AgCl	6	12.0	452.39	904
AgCl	4	10.0	314.16	802
Ag	—	9.7	295.59	218
Ag^+	—	—	—	9

The probe molecules are adsorbed on the surface of the nanoparticles and the fluorescence is quenched. Relative decrease in emission intensity is different for the two different size regime of the particles. For better action and to avoid oxidation it is better to use AgCl nanoparticles in microemulsion media for interaction with the sensitized dye.

Acknowledgement

S.C.B acknowledges the 21st Century COE Program (No. 14COEB01-00), Nagoya University, Japan, for the visiting professorship. S.P acknowledges Jadavpur University for providing financial assistance from Potential for Excellence Scheme.

References

- [1] M. Kadi, P. Hansson, M. Almgren, I. Furo, *Langmuir* 18 (2002) 9243.
- [2] S.K. Ghosh, P.K. Khatua, S.C. Bhattacharya, *J. Colloid Interface Sci.* 279 (2004) 523.
- [3] S.K. Ghosh, S.C. Bhattacharya, *Chem. Phys. Lipids* 131 (2004) 151.
- [4] N. Sarkar, K. Das, A. Datta, S. Das, K. Bhattacharya, *J. Phys. Chem.* 100 (1996) 10523.
- [5] S.K. Ghosh, P.K. Khatua, S.C. Bhattacharya, *J. Colloid Interface Sci.* 275 (2004) 623.
- [6] A.P. Alivisatos, *Science* 271 (1996) 933.
- [7] X. Wang, Y.G. Kim, C. Drew, B.C. Ku, J. Kumar, L.A. Samuelson, *Nanolett.* 4 (2004) 331.
- [8] I. Chakraborty, S.P. Moulik, *J. Disper. Sci. Technol.* 25 (2004) 849.
- [9] E. Hao, R.C. Bailey, G.C. Schatz, J.T. Hupp, S. Li, *Nanolett.* 4 (2004) 327.
- [10] S. Bhattacharya, S.C. Bhattacharya, M. Banerjee, *J. Phys. Chem. A* 108 (2004) 10783.
- [11] R.E. Riter, E.P. Undiks, J.R. Kimmel, N.E. Levinger, *J. Phys. Chem. B* 102 (1998) 7931.
- [12] M. Almgren, A. Ralstar, *J. Colloid Interface Sci.* 202 (1998) 222.
- [13] S.K. Ghosh, P.K. Khatua, J.K. Ghosh, S.C. Bhattacharya, *Spectrochim. Acta A* 61 (2004) 395.
- [14] J.B. Birks, *Photophysics of Aromatic Molecules*, Wiley Interscience, New York, 1970, p. 106 (Chapter 4).
- [15] J.R. Lackowicz, *Principle of Fluorescence Spectroscopy*, Plenum Press, New York, 1999, p. 243 (Chapter 8).
- [16] S. Chatterjee, S. Nandi, S.C. Bhattacharya, *J. Photochem. Photobiol. A: Chem.* 173 (2005) 221.
- [17] K.K. Rohatgi-Mukherjee, *Fundamentals of Photochemistry*, Wiley Eastern Limited, New Delhi, 1992, p. 101 (Chapter 4).
- [18] P.K. Khatua, S.K. Ghosh, S.C. Bhattacharya, *J. Mol. Liq.* 124 (2006) 45.
- [19] S. Nandi, S.C. Bhattacharya, *J. Mol. Liq.* 89 (2000) 223.
- [20] S. Nandi, S.C. Bhattacharya, *Colloid Surf. A* 186 (2001) 179.
- [21] S. Nandi, S.K. Ghosh, S.C. Bhattacharya, *Colloid Surf. A* 268 (2005) 118.
- [22] W.H. Armstrong, *Science* 144 (1964) 150.
- [23] R.P. Bagwe, K.C. Khilar, *Langmuir* 13 (1997) 6432.
- [24] S. Xu, Y. Li, *J. Mater. Chem.* 13 (2003) 163.
- [25] W.J. Moore, *Physical Chemistry*, Orient Longman, 1982, p. 502 (Chapter 11).