Growing Small Silver Particle as Redox Catalyst

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Growing small particles of silver have been observed to be more efficient catalysts than stable colloidal particles. These growing particles catalyze the borohydride reduction of several organic dyes. The rate of the reduction catalyzed by growing particles is distinctly faster compared to that of stable and larger silver particles, which are the final products of growing particles. Catalysis is due to efficient particle-mediated electron transfer from the BH_4^- ion to the dye. The catalytic activity of the particles depends on their size, $E_{1/2}$ of the dye, and the dye−particle interaction. The presence of surfactant influences the catalytic property of the particles by controlling their growth, by inhibiting adsorption of reactants/products onto the particle surface, and by specific dye−surfactant interaction.

Introduction

The intermediate stages of growing small metal particles still remain neglected, though properties of stable and larger particles at their final stage of growth are an intense field of research.[1−4] Studies on the properties of such growing particles will, no doubt, help to unravel some problems of fundamental importance such as evolution of bulk properties, origin of size effects in catalysis, etc. These subcolloidal particles are formed as short-lived intermediates during reduction of metal ions and act as seeds for the growth of metal colloids.[3−7] At the initial stage of colloid formation metal atoms are produced which subsequently agglomerate to form subcolloidal particles. Then growth may take place by reduction of excess Ag^+ ions adsorbed at the surface of such subcolloidal particles and/or by their further agglomeration. If in a solution both a particulate of a metal and its ions are present together, then a typical metal electrode equilibrium can be expressed as follows:

$$M_{n-1} + M^{x+} + xe^- = M_n \qquad (1)$$
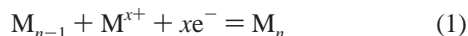
During the growth of such small scale particles their redox potentials vary continuously.[3,5−7] The redox potential of the particle for a particular metal depends on the value of agglomeration number, *n,* and the nature of associated ligand. When *n* = 1, i.e., for a free metal atom/ion (hydrated) system, the potential is much lower in value compared to that of the conventional electrode system, and it increases rapidly with increasing *n,* finally reaching the conventional electrode potential for *n* = ∞. For example, the redox potential is as negative as −2.7, −1.8, and −1.5 V (vs NHE) for *n* = 1 for copper, silver, and gold,[3,6,8] respectively. The potentials become more and more positive as the particles grow and ultimately reach their respective value of bulk electrode potential. As a matter of fact, these growing particles can take part in reactions where electrons are transferred across the particle−solution interface, similar to electrode reactions in electrochemistry.[3,6,7] To test the redox catalytic property of growing silver clusters, in this work the silver clusters are generated by the reduction of silver

ions in the presence of an electron acceptor dye. A reducing agent is used that can reduce simultaneously both the silver ions and the dye at the surface of growing clusters. The 3-fold advantages of these growing particles toward redox catalysis are (i) extraordinary large surface area for catalysis, (ii) continuously renewable microelectrode surface, and (iii) continuous variation in the potential values of the microelectrode without any need of external circuits. Our focus of attention is on silver particles for the following reasons. First, silver particles have a strong and sharp plasmon band in the visible region whose shape and position are very much susceptible to surface adsorption.[7] Therefore, formation of particles and any adsorption effect on it can be followed spectrophotometrically. Second, a method for in situ reversible formation and dissolution (oxidative) of silver nanoparticles in aqueous surfactant media has been recently developed by us,[9] which allows repetitive generation of new catalyst surface whenever necessary.

Unlike growing metal particles, metal sols have been and are being used as a model catalyst due to their better stabilities and well-understood physicochemical properties.[4,10−12] Such systems are macroscopically homogeneous but microscopically heterogeneous. This is the most important and interesting aspect that provokes such microheterogeneous systems to be explored as catalysts with the advantage of exploiting both their homogeneous and heterogeneous catalytic properties. Their solution remains optically transparent, allowing convenient analysis of the elementary steps involved in the catalytic process. Thus, they are very important for mechanistic studies of the heterogeneous catalysis. In comparison, the use of growing small particles as catalysts is limited due to their short lifetime.[3,6,13] Sometimes, they have been stabilized in suitable solid matrix[14] or by surface modification using appropriate ligands[4,12] or polymers[15] and have been used in heterogeneous catalysis. This type of stabilization always leads to loss of catalytic activity to a greater extent. Solid matrices/ligands strongly interact with surface atoms occupying a good number of active sites of the catalyst. For polymers, though their interaction might not be so strong with the catalyst surface, steric effects from these bulky species come into play in the vicinity of the catalyst surface.[16] In this regard, surfactants are recommended as a viable alternative.[17] Their loose packed but

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dynamic structure around the catalyst surface stabilizes the particles but hardly affects the accessibility of the particles to reacting molecules. Moreover, surfactants leave a control over the rate of synthesis and particle size as well, without unduly diminishing the active surface area of the catalysts.

We have produced silver particles in aqueous surfactant media and have studied their catalytic properties toward the reduction of a number of dyes as test reactions. The dyes used are methylene blue (MB), phenosafranin (PS), fluorescein (F), 2,7-dichlorofluorescein (DCF), eosin (E), and rose bengal (RB). Choice of dyes is based on the following three factors. First, the reductions of all the dyes are thermodynamically favorable but not kinetically. Second, these dyes have different colors in their oxidized and reduced states, and their major spectral bands do not overlap with the plasmon band of silver. Third, $E_{1/2}$ values of the dyes vary over a wide range, which is helpful in examining the catalytic activity of the growing particles for a wide range of $E_{1/2}$ values of the electron acceptor dyes.

Experimental Section

Reagents. Silver particles were prepared by the reduction of AgNO$_3$ (BDH) solutions with NaBH$_4$/N$_2$H$_4$/ascorbic acid in the presence and absence of surfactant stabilizer. Surfactants used were cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS), purchased from Aldrich, USA. Dyes used were from Fluka, S.D. Fine Chemicals, and Sigma. Dye solutions ($\sim10^{-2}$ mol dm^{-3}) were prepared in distilled water. The NaBH$_4$ (10^{-2} mol dm^{-3}) solution was prepared in ice-cold distilled water. All other reagents used were of AR/GR grade, and distilled water was used for all purposes. Freshly distilled organic solvents were used for the cyclic voltammetric study.

Preparation of Silver Particles and Their Use in Catalysis. Ag particles were prepared by adding a reducing agent solution such as NaBH$_4$,[9] sodium ascorbate,[18] or N$_2$H$_4$[19] to AgNO$_3$ solutions. In this work we used NaBH$_4$ in most cases. When surfactant is used, AgNO$_3$ solutions were mixed with surfactant solutions, and then a NaBH$_4$ solution was added. All the stock solutions were purged with N$_2$ for 8–10 min before their use, to remove dissolved oxygen. In a typical experiment 0.03 mL (0.01 mol dm^{-3}) of an AgNO$_3$ solution was mixed with 3 mL (0.05 mol dm^{-3}) of CTAB solution. Then N$_2$ gas was purged again through the solution for 2–3 min, to remove all dissolved oxygen, and 0.2 mL (0.1 mol dm^{-3}) of a freshly prepared NaBH$_4$ solution was added to it. The color of the solution turns yellow within a few minutes due to the appearance of silver particles. For the study of growing silver particle catalyzed dye reduction, dye was added to aqueous surfactant solution before the addition of reducing agent solution. Dye concentration was varied between 10^{-5} and 10^{-2} mol dm^{-3}.

Stable and yellow silver sol, which was produced after the complete reduction of Ag$^+$ ions, was also used as catalyst. These sols contain larger silver particles which are the final products of growing particles. For the study of these larger silver particle catalyzed dye reduction, dye was added to aqueous AgNO$_3$–surfactant–NaBH$_4$ solutions after the complete reduction of Ag$^+$ ions, which was assessed by the stable plasmon band of silver that does not change with time. For the catalytic reduction of the dyes, the reducing agent used was 10–200-fold in excess.

The presence of surfactant stabilizes the metal particles from agglomeration even in the presence of dye. So in most cases we used surfactant media for the study of catalysis. In the absence of surfactant the particle aggregation as well as catalytic reduction of dye by aggregated and nonaggregated particles proceed simultaneously.

TABLE 1: Spectroscopic and Redox Properties of Dyes Used for Catalytic Reduction

dye	color (λ_{max}) of the dye (oxidized form)	$E_{1/2}$ (V vs NHE) in different solvents[a]
methylene blue (MB)	blue (665 nm)	−0.21 (w), −0.27 (a), −0.20 (t), −0.18 (s), +0.03 (c)
phenosafranin (PS)	red (525 nm)	−0.22 (a)
fluorescein (F)	yellow (490 nm)	−0.28 (a), −0.13 (w), −0.18 (t), −0.11 (s), −0.08 (c)
2,7-dichloro-fluorescein (DCF)	yellow (500 nm)	−0.10 (a), −0.10 (w), −0.08 (t), −0.11 (s), −0.03 (c)
eosin (E)	red (515 nm)	−0.53 (a)
rose bengal (RB)	red (550 nm)	−0.48 (a)

[a] w, in water; a, in acetonitrile; t, in aqueous TX-100; s, in aqueous SDS; c, in aqueous CTAB ($E_{1/2}$ depends on CTAB concentration).

Instrumentation. UV–visible spectra were measured in a Shimadzu UV-160 digital spectrophotometer (Kyoto, Japan) with 1 cm quartz cuvettes. Cyclic voltammetry of redox probe dyes was done using a combination of a PAR 173 potentiostat/galvanostat, PAR 273 interface, and EG&G PARC 175 universal programmer (Princeton, NJ). The reference electrode was Ag/AgCl ($E° = -0.222$ V (NHE)); counter and working electrodes were platinum wire and platinum electrode, respectively. A typical scan rate was 50 mV/s. NaCl was used as supporting electrolyte.

Results

Spectral and Redox Properties of the Dyes. For the investigation of the spectral properties of the dyes, we have studied the UV–visible spectra of each dye in water, micellar solutions, and also in surfactant stabilized stable silver particle systems. Table 1 summarizes the λ_{max} values of the oxidized form of each dye in water. Earlier studies showed that the λ_{max} might be blue- or red-shifted in aqueous surfactant solutions as compared to the λ_{max} values in water.[20,21] In this case a small red shift (0–5 nm) is observed when the dye and surfactant have opposite charge. This dye λ_{max} is not shifted further in the presence of stable silver particles. The reduced form of each dye is colorless.

The cyclic voltammetric study of the dyes showed that all the dyes (except fluorescein) gave reversible redox couples. We have determined $E_{1/2}$ values for each dye in water and in aqueous surfactant media. For some dyes, $E_{1/2}$ could not be determined in water or in aqueous surfactant media. In these cases acetonitrile has been used as a solvent. The study shows that although $E_{1/2}$ values in SDS systems are similar to the values in aqueous media, these values increase in CTAB media.

The pH of the experimental solutions varied between 7 and 8, and accordingly the dyes used could be grouped as cationic (viz., MB and PS) and anionic (viz., F, DCF, E, and RB).[22]

Properties of Growing and Stable Silver Particles. Due to the almost instantaneous reduction of Ag$^+$ ion by NaBH$_4$ to Ag^0 and subsequent agglomeration of Ag^0 and/or growth by reduction of absorbed Ag$^+$ ions at the Ag$_n^0$ surface to form bigger particles, the lifetime of the growing silver clusters, measured by the absorbance increase, is generally a few seconds. However, the presence of surfactant increases the lifetime to several minutes.

The growing silver particles have a plasmon absorption band in the 350–550 nm region. Figure 1a shows the evolution of the UV–visible spectra for the growing particles in aqueous CTAB media. It shows that initially a broad plasmon absorption
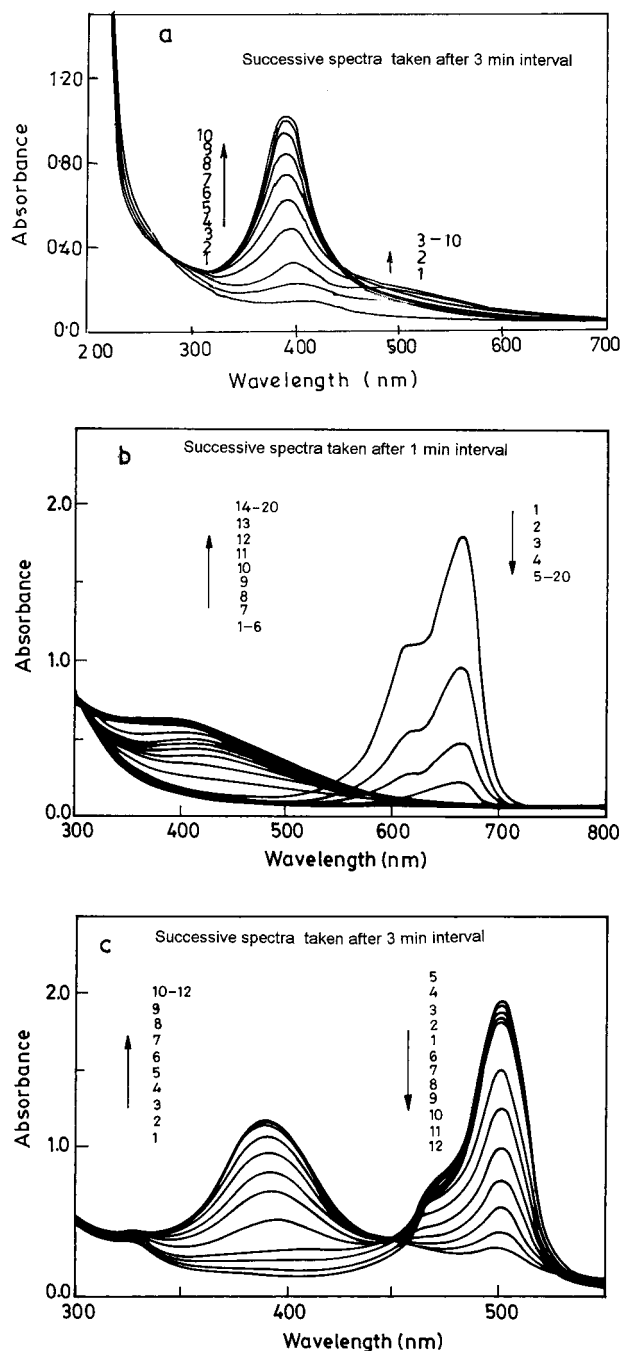
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Figure 1. Successive UV−visible spectra of (a) growing silver particles, (b) silver particle evolution and methylene blue (MB) reduction, and (c) silver particle evolution and fluorescein (F) reduction in aqueous CTAB solutions containing $[AgNO_3] = 10^{-4}$ mol dm^{-3}, $[CTAB] = 0.01$ mol dm^{-3}, $[NaBH_4] = 5 \times 10^{-3}$ mol dm^{-3}, and $[MB] = [F] = 5 \times 10^{-5}$ mol dm^{-3}. AgNO$_3$ and dye were used in near stoichiometric amount so that silver plasmon band was observable.

Figure 2. UV−visible spectra of silver plasmon band during fluorescein (F) reduction by stable silver particle in aqueous SDS solutions with $[AgNO_3] = 10^{-4}$ mol dm^{-3}, $[SDS] = 0.01$ mol dm^{-3}, and $[NaBH_4] = 5 \times 10^{-4}$ mol dm^{-3} for (a) and (b) and 5×10^{-3} mol dm^{-3} for (c) and (d); $[F] = 5 \times 10^{-5}$ mol dm^{-3}. (a) Plasmon band of stable silver particle, (b) plasmon band of stable silver particle in the presence of fluorescein (F), (c) plasmon band of stable silver particle in the presence of excess NaBH$_4$, and (d) plasmon band of stable silver particle taken during the induction period of fluorescein reduction.

hand, addition of dye into the stable particle solution leads to red-shifted (0−10 nm) plasmon bands. When both the dye and BH$_4^-$ ion are present together, the dye reduction reaction starts. Thus, it is difficult to see a blue or red shift when both reactants are present simultaneously. But in some cases an induction period is observed for the growing particle catalyzed dye reduction. In such cases a small blue shift is observed, which is the net effect of the larger blue shift and the small red shift caused by BH$_4^-$ ion and the dye, respectively (Figure 2).

Growing Silver Particles as Redox Catalysts and Influence of Reagents. If the dye solution is mixed with NaBH$_4$ solution, the color of the dye remains unaltered for 1−2 h, indicating that the dye reduction, if it occurs at all, is insignificant. However, reduction of the dye by borohydride occurs very fast in the presence of AgNO$_3$. Figure 1b,c shows the successive UV−visible spectra of the dye solution in the presence of AgNO$_3$ and NaBH$_4$ in aqueous CTAB media. The color of the dye gradually vanishes, which is indicated by the gradual decrease in absorbance value at the dye λ_{max}. But in the 350−500 nm region, absorbance gradually increases which ultimately gives a peak at ∼400 nm. This peak corresponds to the plasmon band of silver.

The progress of the catalytic dye reduction can be followed easily by the decrease in absorbance at the dye λ_{max} with time. Except for RB, the absorption band for all the dyes vanishes gradually without showing any change in its shape and position. For example, Figures 3 and 4 show the reduction of a cationic dye, PS in CTAB solution, and an anionic dye, DCF in SDS solution, respectively. In RB the λ_{max} first blue-shifts and then it vanishes. Very low concentrations of Ag$^+$ ions (one-tenth to one-fifth of the dye concentrations) were used to detect the catalytic activity. However, the plasmon band becomes very weak for $[Ag^+] < 10^{-5}$ mol dm^{-3} and is almost completely overwhelmed by the absorbance of the reduced dyes. Therefore, simultaneous evolution of the silver plasmon band along with the dye reduction cannot be followed when such a catalytic amount of silver is used. In most cases of catalyzed reaction, after some initial progress the dye reduction stops or the rate decreases to a considerable extent, when no surfactants were used. This fact is more prominent for growing particles as compared to stable ones.

at 400−550 nm appears slowly. Then a sudden jump of the absorbance in the 390−410 nm region occurs. A plot of the absorbance at λ_{max} vs time yields a sigmoidal curve, which suggests autocatalytic reaction kinetics.[23,24] An autocatalytic plot fitted satisfactorily, taking up to ∼30% initial absorbance values of the evolving plasmon band. The last ∼40% of absorbance values obey the first-order kinetics.

The plasmon λ_{max} of stable silver particles is at ∼410 nm. Addition of excess (the amount to be added for the reduction of dyes) BH$_4^-$ ions into the stable silver particle solution leads to a large (30 nm) blue shift of the plasmon band. On the other
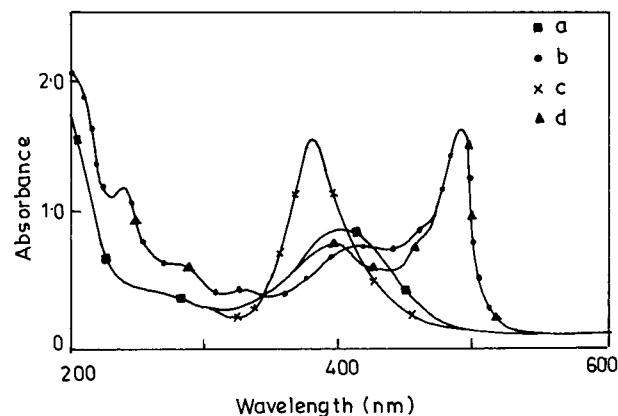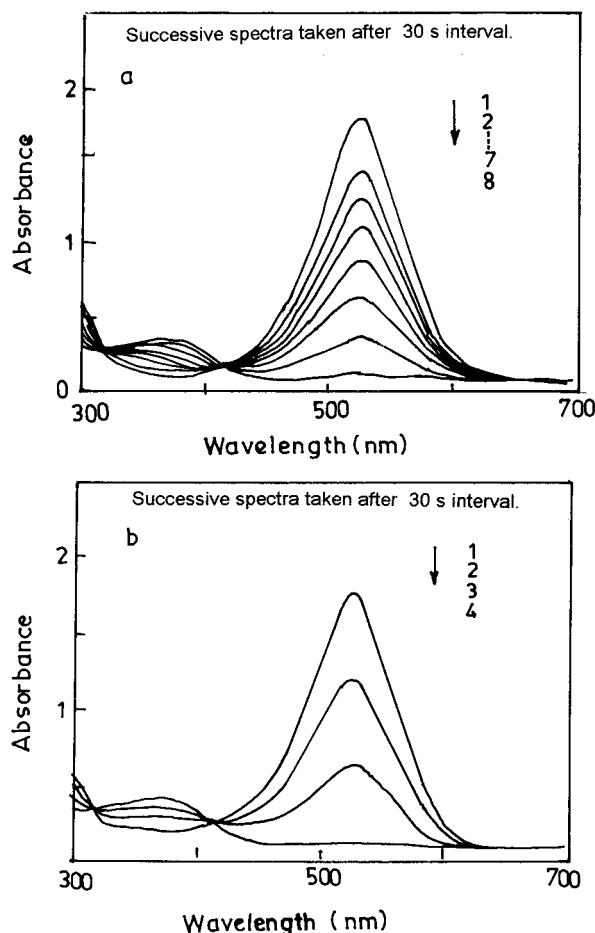
Figure 3. Successive UV−visible spectra of phenosafranin (PS) during its catalytic reduction by (a) growing and (b) stable silver particles in aqueous CTAB solutions containing $[AgNO_3] = 10^{-5}$ mol dm^{-3}, $[CTAB] = 0.01$ mol dm^{-3}, $[NaBH_4] = 5 \times 10^{-3}$ mol dm^{-3}, and $[PS] = 10^{-4}$ mol dm^{-3}.

Figure 4. Successive UV−visible spectra of 2,7-dichlorofluorescein (DCF) during its catalytic reduction by (a) growing and (b) stable silver particles in aqueous SDS solutions with $[AgNO_3] = 10^{-5}$ mol dm^{-3}, $[SDS] = 0.01$ mol dm^{-3}, $[NaBH_4] = 5 \times 10^{-3}$ mol dm^{-3}, and $[DCF] = 5 \times 10^{-5}$ mol dm^{-3}.

Two important observations of our experiments are (i) the time required to initiate the catalytic process and (ii) the comparative rate of catalysis by growing and stable particles. The time required to initiate the catalysis, generally termed the induction period, was found to be nil in aqueous stabilizer-free dispersions of silver particles. In other words, here the catalytic reduction started almost instantaneously after the addition of the reducing agent, BH$_4^-$ ion. But generally the reduction is associated with an induction period, if CTAB or SDS is added as stabilizer. The induction period varies from a few seconds to a few minutes depending on the nature and concentration of the dye, surfactant, BH$_4^-$, and Ag$^+$ ions. Where the catalytic reductions are very slow, as in anionic dye−cationic surfactant combination, it is difficult to determine the exact induction period. But it was observed that the induction period was generally larger in SDS than that in CTAB. An increase in [BH$_4^-$] or [Ag$^+$] decreases the induction period. On the other hand, it increases with increasing surfactant concentration. In some cases (PS in SDS and DCF in SDS) the induction period was observed for stable particles also. In general, the induction periods for stable particles were not found to be greater than those for growing particles.

The rate of the catalysis by growing particles depends on a number of factors: not only on the concentration of the reactants, catalyst-precursor ion, or the other reagents but also on the nature of the dye, surfactant, their electrical charges, etc. The rate of growing particle catalyzed reduction for a given dye
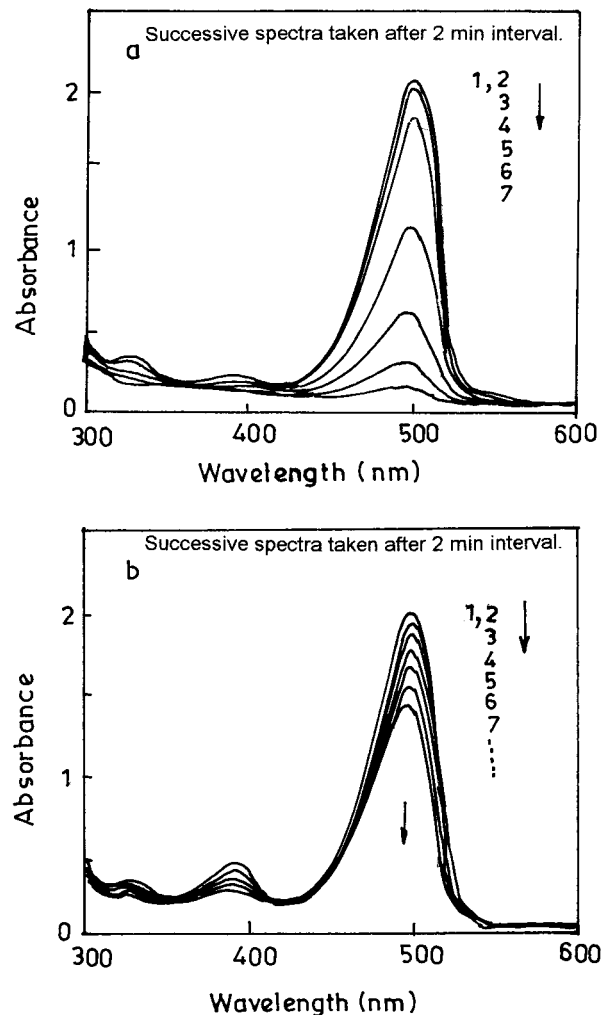
becomes slower if the stabilizer surfactant is of an opposite charge to that of the dye. For example, the rate of reduction of PS, a cationic dye with CTAB (Figure 3a), is faster than that with SDS (Figure 5a), and similarly the reduction of DCF, an anionic dye, is faster with SDS compared to CTAB.

The initial rates of reduction were determined for an anionic dye (F) with an anionic surfactant, SDS, and a cationic dye (MB) with a cationic surfactant, CTAB. It was found that the rate of reduction increases with the increase in [Ag$^+$], [BH$_4^-$], and [surfactant]. The rate has a first-order dependence with respect to [Ag$^+$] with SDS whereas with CTAB the order is <1. However, the rate of catalysis is appreciable only when [BH$_4^-$]/[Ag$^+$] > 10. The order with respect to [BH$_4^-$] was also found to be <1 irrespective of the surfactant used. To understand any special role of the reducing agent in the catalytic process, some other reducing agents such as hydrazine and ascorbic acid were used to reduce MB in the presence and absence of growing silver particles. MB has been chosen because its reduction by all the above-mentioned reducing agents is thermodynamically favorable. It was interesting to note that the growing silver particle catalyzed reduction of MB was possible only when BH$_4^-$ was used as reducing agent.

Growing Particle vs Stable Particle in Catalysis. The same initial concentration of Ag$^+$ ions was used to prepare growing

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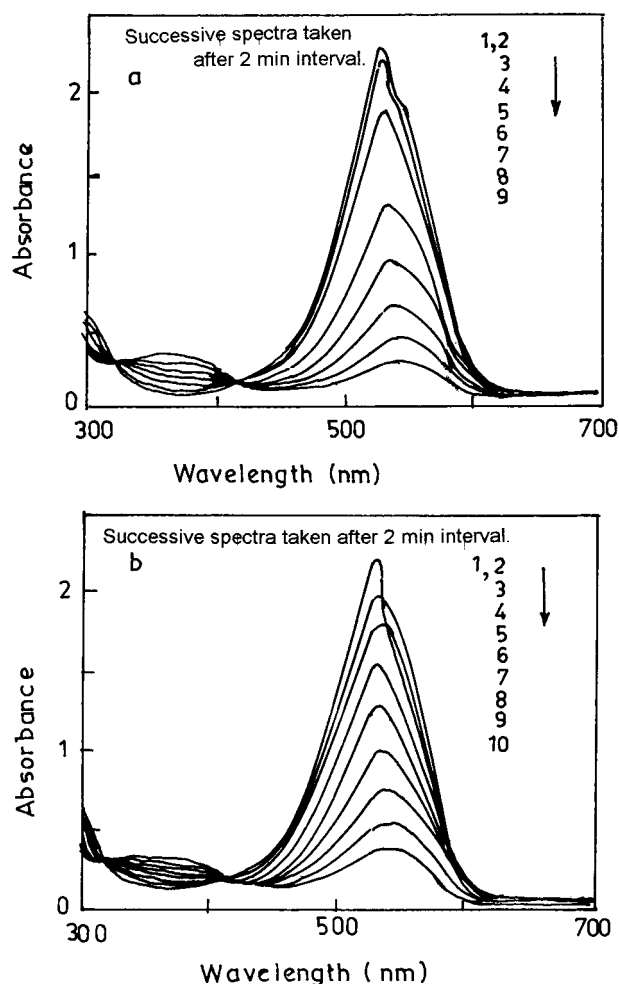*J. Phys. Chem. B, Vol. 103, No. 1, 1999* **119**

Figure 5. Successive UV−visible spectra of phenosafranin (PS) during its catalytic reduction by (a) growing and (b) stable silver particles in aqueous SDS solutions with $[AgNO_3] = 10^{-5}$ mol dm^{-3}, $[SDS] = 0.01$ mol dm^{-3}, $[NaBH_4] = 5 \times 10^{-3}$ mol dm^{-3}, and $[PS] = 10^{-4}$ mol dm^{-3}.

Figure 6. Successive UV−visible spectra of methylene blue (MB) during its catalytic reduction by (a) growing and (b) stable silver particles in aqueous CTAB solutions with $[AgNO_3] = 10^{-5}$ mol dm^{-3}, $[CTAB] = 0.01$ mol dm^{-3}, $[NaBH_4] = 5 \times 10^{-3}$ mol dm^{-3}, and $[MB] = 5 \times 10^{-5}$ mol dm^{-3}.

and stable silver particle for this rate comparison. The rate of the growing particle catalyzed reduction of anionic dyes was always faster than that of the stable particle catalyzed one in both aqueous and surfactant (CTAB and SDS) media. In fact, growing silver particles were found to be a superior catalyst in most cases. Exceptions were noted in the case of cationic dyes (PS and MB) (Figures 3 and 6). For MB, stable particle catalyzed reduction was faster in aqueous as well as in surfactant media, irrespective of the nature of surfactant. But interestingly, the performance of growing particles can be again improved over stable particles for PS in SDS (Figure 5a,b).

Surfactant-stabilized, aged stable silver particles have also been used as catalysts. These were prepared by using 2-fold excess of NaBH$_4$ compared to AgNO$_3$ and were used 5−10 h after its preparation. The aged stable particles have a plasmon λ_{max} at 420 nm; when excess NaBH$_4$ and dye are added, the plasmon λ_{max} is initially blue-shifted to ∼390 nm, and only after this has happened does dye reduction start. Here the induction period is longer than for freshly prepared stable particles, but the rates of reduction were comparable.

Discussion

The plasmon band position of stable silver particles is highly susceptible to the adsorption of the nucleophile or the electrophile onto the particle surface. If a nucleophile is adsorbed
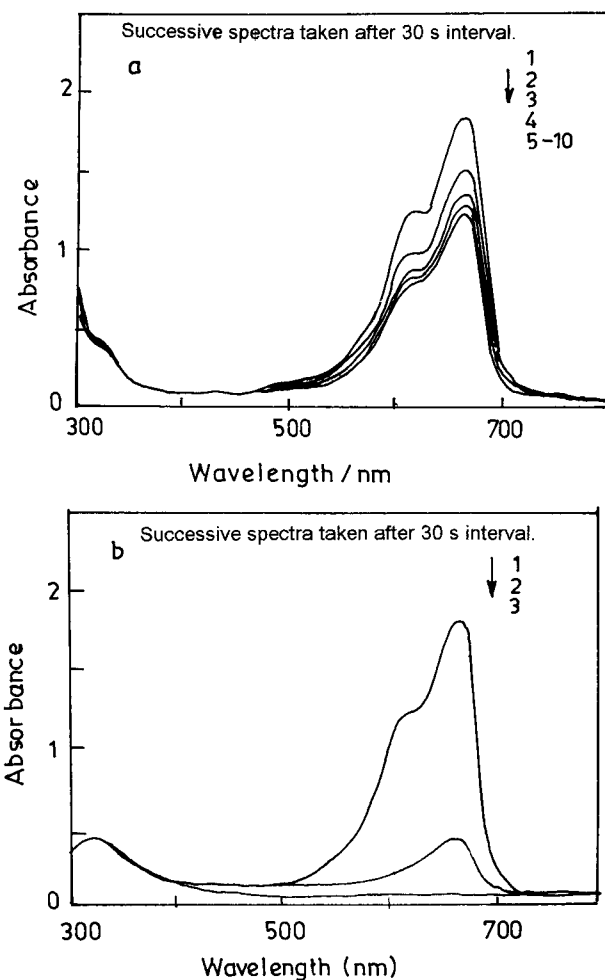
onto it, the plasmon band shows a blue shift due to a strong electron injection character. On the other hand, the plasmon band will be red-shifted due to the adsorption of an electrophile.[7] There are large blue shifts in the band position after addition of BH$_4^-$ ion and a comparatively small red shift upon addition of the dyes separately.[25,26] And a net blue shift is observed if they are present together. These facts prove that BH$_4^-$ ions and the dyes are not only adsorbed individually but also simultaneously on the particle surface. Second, they are nucleophilic and electrophilic in nature with respect to the particle, respectively. As a consequence, a partial electronic charge transfer can occur from BH$_4^-$ ion to the dyes via the particles.

It has been observed that the catalyzed reduction is not due to the effect of the organized assembly of the surfactants. Moreover, reduction of the dyes practically does not occur without the addition of Ag$^+$ ion to the system. Further, the rate of reduction is appreciably faster in the presence of only a small amount of Ag$^+$ ion. This indicates that Ag$^+$ ion or some product of it, which is formed under the reaction condition, catalyzes this dye reduction process. The catalytic reduction starts some time after the addition of the reducing agent in most cases and thus is often associated with an induction period. The use of the surfactant delays the initiation of the catalytic process, although Ag$^+$ ions were present in the reaction medium from the very beginning. Again, stable particles (where no Ag$^+$ ion

is supposed to be present in the presence of large excess of NaBH$_4$) can also catalyze the reduction. Furthermore, no catalyzed dye reduction is observed in the presence of the reducing agents, viz., ascorbic acid and hydrazine. All these facts indicate that the growing particle, not the Ag$^+$ ion, is the actual catalyst.

Unlike the growing particle catalyzed reduction, the stable particle catalyzed redox reaction and the mechanism of this type of catalysis are fairly well-known in the literature.[10,11] In the latter cases, catalysis proceeds through an electrochemical mechanism where electron transfer occurs via the particle. The catalytic efficiency of such particles for electron transfer processes is generally explained by their size-dependent redox properties which control their role as an electron relay. The required potential of the particle is intermediate between that of the electron donor and the acceptor. However, Henglein et al.[3,13] and Belloni et al.[5,6,27] have employed growing silver particles to catalyze the reduction of excess Ag$^+$ ions by a weak reductant present in the system. These systems could be described as follows. During the course of growth when the size of silver particle reaches a certain critical level, the electrochemical standard potential of the (silver particle/silver ion) system becomes less negative compared to that of the weak reductant. Then, the latter gives up electrons, reducing excess Ag$^+$ ion present in the system. Belloni et al.[27] also observed a simultaneous corrosion of silver cluster smaller than the critical level by the oxidized form of the dye which in the process gets reduced. In their experiments, the strong reducing agent is the solvated electron. In our case the reducing agent (viz., BH$_4^-$ ion) is also a strong one, and it can reduce simultaneously the Ag$^+$ ions and the dye. But the dye reduction is, however, kinetically not favored in the absence of silver particles. Therefore, here the growing silver particle plays the role of a true redox catalyst.

One of the important observations of this study is the induction period, the time required to begin the catalytic dye reduction. The existence of such an induction period has been observed recently by Watzky et al.[28] in the hydrogenation of cyclooctene in the presence of an Ir nanoparticle catalyst. Two possible factors might be responsible for the origin of the induction period, viz., a minimum concentration or a minimum particle size requirement of the growing particle for catalysis. It should be mentioned that the induction period is observed only when surfactants are used as particle stabilizers, and it depends on both the nature of surfactant and dye. As a matter of fact, the minimum concentration or the minimum size is determined by the dye, taking into the account the influence of the surfactant on the formation of the particles. Unlike CTAB, SDS, being an anionic surfactant, associates comparatively strongly with silver ions. So a large number of embryo silver particles are formed, leading to a higher number of particles. Zhai and Efrima[29] have reported similar types of effects of a number of surfactants and additives on the evolution and hence on the final size distribution of the particles. Therefore, for a given dye the required minimum concentration is first met with SDS due to the formation of more particles in this systems. As a consequence, induction periods would be smaller for SDS. Experimental results show that in general the induction period is larger in SDS systems than in CTAB solutions. This lends support to the critical size requirement for the catalyst. This type of size effect is commonly observed for silver in photographic processes.[5,30] Besides, it has already been established that a small, critical particle size of the catalyst is required for faster ethylene hydrogenation.[31]
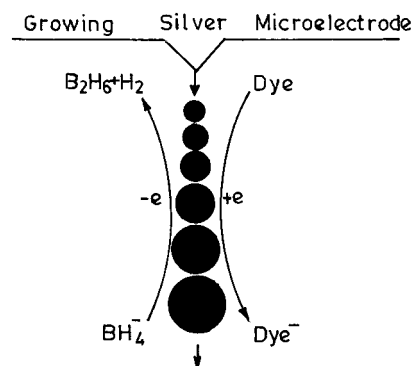

Figure 7. Scheme of growing silver particle catalyzed redox reaction.

For a given surfactant, the induction period again varies from dye to dye. It implies that it depends on the dye−particle specific interaction nature. Perhaps the surfactant plays a complex role in determining the nature of the dye−particle interaction which is not clear at present.

However, the presence of an induction period for stable particle catalyzed dye reductions seems to contradict the concept of a minimum size requirement, since the size has already been attained in this case. But in no case was the induction period for stable particles greater than that for growing particles. This indicates that some other factor might be contributing to the induction period. Probably, the encapsulation of stable particles by the surfactant poses some temporary barrier for the adsorption of BH$_4^-$ onto the particle. Aged stable particles on which this surfactant layer becomes thicker[9] show a larger induction period as compared to that of the freshly prepared stable silver particles. Thus, the induction period may result from different causes for the growing and stable particles.

Increase in Ag$^+$ and BH$_4^-$ increases the number of reactants per organized assembly of surfactants, obviously leading to a faster growth process over the nucleation of the particles. On the other hand, increase in surfactant concentration has an opposite effect. Hence, the induction period decreases in the former two cases whereas it increases with increasing surfactant concentration.

To explain the rate of catalysis, we propose that electron transfer occurs via the growing particles, similar to (stable) colloid particle catalyzed redox reactions. The size-dependent redox potentials of the particles strongly depend on the medium too and govern the chemistry and catalytic activity of stabilized metal particles. Earlier work shows that the reduction potential of a silver wire decreases with the increase in BH$_4^-$ concentration in water due to the adsorption of BH$_4^-$ ion onto the electrode surface.[25] A similar effect is also expected in silver particles. However, the potential of growing particles containing BH$_4^-$ adsorbed on their surface, unlike that for stable particles, will gradually increase with the increasing size of the particle, because the inherent particle potential gradually increases with increasing nuclearity (size). The resultant potential of the particles with adsorbed BH$_4^-$ will obviously be anodic to the reductant (BH$_4^-$ ion) and cathodic to the oxidant (dye). Thus, an electron relay via particle to dye is possible. Figure 7 shows the scheme of this electron transfer, where the growing particle in its intermediate stage accepts electrons from BH$_4^-$ ions and conveys them to the dye.

The main focus of this report is the advantage of growing silver particles over stable silver particles as redox catalysts. It is very difficult to compare the catalytic property of growing and stable particles because of the difficulty in determining the concentration and surface area of the catalysts. However, their

Growing Small Silver Particle as Redox Catalyst

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catalytic property can be compared by taking the same initial concentration of precursor Ag^+ ions. In case of growing particles, some unreduced Ag^+ is always present. So the concentration of Ag^0 is always less in growing particles than the stable particles. In most cases growing silver particles are found to be superior catalysts as compared to the stable particles. This behavior of growing particles may be attributed to the following two properties: first, its continuously renewable surface and, second, its large negative electrochemical potential which arises owing to the very small size. As usual, the rate of catalytic reduction should be determined by the difference in potential of the BH_4^- adsorbed particle and the potential of the oxidant system. The smaller the size of the particle, the more is the potential difference leading to a higher rate of reduction.[32] Hence, the better catalytic activity of the growing particle is understood. Other reducing agents such as hydrazine and ascorbic acid were employed in this reduction. But only BH_4^- ions were found to be effective in this catalytic reduction, though all the other reducing agents reduce Ag^+ ions. In fact, the efficiency of the BH_4^- ion is associated with its high electron injection capacity. Thus, it emphasizes the importance of the size-dependent redox potential of the catalyst particles. Lesser nucleophilic reducing agents could, in principle, reduce the dyes only by their adsorption onto the particle at its early stages of formation. At a later stage, the electron injection capacity of these lesser nucleophilic reagents is insufficient to make the particle potential less negative than the potential of the dye to be reduced.

Other factors also play a role in determining the rate, viz., dye−surfactant and dye−particle interactions, difference in the catalyst concentration, and the fraction of surface atoms, etc. For example, the very slow rate of reduction, when the dye and surfactant are of unlike charges, indicates the influence of the dye−surfactant interactions. Again, stable particles are superior catalysts when compared to growing particles for MB reduction, whereas for PS it is true in CTAB only, but in SDS growing particles are again superior catalysts over stable particles. Perhaps the strong interaction and adsorption of these two dyes (due to the presence of sulfur and nitrogen in the molecular skeleton) at the silver surface poison the growth of the particles in the embryo stage before attaining the required minimum size for the catalysis. As the stable particles are already formed, the question of such poisoning does not arise for them, which imparts the stable particles a better performance here. This also explains why the growing particle catalyzed dye reduction stops after some time in most cases, particularly in the absence of any surfactant. In the presence of surfactant, the dye can be adsorbed on the micellar surface, and thus this restricts its adsorption on the particle surface in the embryo stage. Moreover, proximity, favorable orientation of the reactants relative to the hydrophobic surface of the particle, microscopic environment surrounding reacting molecules, the sensitivity of the surface structure etc., might have a direct bearing on the chemical reactivity.

Conclusion

A precise explanation of this catalytic effect is a difficult undertaking. It necessitates more experimental as well as theoretical studies. Nevertheless, this study has revealed that (i) at a certain point of their growth the particles become catalytic, (ii) the growing particles are more catalytic than stable particles, and (iii) strong catalyst surface−substrate interaction is essential for an effective catalytic process. However, the nature of surfactant and the reducing agents too influence the catalytic property of growing particles. Judicious selection of a surfactant may result in its enhanced or suppressed catalytic efficiency for a given reactant (dye). This report also indicates that choice of a proper nucleophilic reducing agent for a particular metal could give unique catalytic selectivity. Thus, growing metal particles emerge as a new generation catalyst with their distinct advantages over stable final particles.

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