Catalytic Properties of Silver Nanoparticles Supported on Silica Spheres

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In this work, we investigate the catalytic properties of silver nanoparticles supported on silica spheres. The technique to support silver particles on silica spheres effectively avoids flocculation of nanosized colloidal metal particles during a catalytic process in the solution, which allows one to carry out the successful catalytic reduction of dyes. The effects of electrolytes and surfactants on the catalytic properties of silver particles on silica have been investigated. It is found that the presence of surfactants depresses the catalytic activity of the silver particles to some extent by inhibiting the adsorption of reactants onto the surface of the particles. Electrolytes either increase the migration rate of reactants in the solution resulting in an increase in the catalytic reaction rate or inhibit the adsorption of reactants onto the surface of the silver particles leading to a loss in the activity of the metal particles.

Introduction

Metal particles in nanoscales have become a subject of intense interest in various fields of chemistry and physics during past decades.[1−4] The interest in these particles stems from their unique optical,[5] electronic,[6] and catalytic[7] properties, which are different from their bulk counterparts and hence lead to novel applications in sensor,[8] catalysts,[9] nanoelectronic devices,[10] biochemical tagging reagents,[11] optical switches,[12] etc. It has been experimentally demonstrated that metal nanoparticles have high catalytic activities for hydrogenation, hydroformylation, carbonylation, etc.[13−18] However, in most cases, they would congregate during catalytic processes, because nanosized metal particles in the solution are active and prone to coalesce due to van der Waals forces and high surface energy unless they are protected. In this regard, surface modification using polymers, complex ligands, or surfactants are frequently used to stabilize metal catalysts.[15−17,19−21] However, this kind of stabilization will affect the catalytic activity of metal particles. These polymers or surfactants used as modifiers would interact with the catalysts and pack around the surface, which affects the accessibility of reacting molecules to the metal particles and even alters the mechanism of catalytic reactions. Therefore, to well understand the catalytic mechanism and investigate the effect of micro-environment on the catalytic properties of metal particles, it is necessary to explore novel techniques to stabilize the catalyst particles.

Recently, a new technique has been developed to immobilize metal nanoparticles onto a desired substrate from a colloidal solution, which is usually used to synthesize the materials with a core−shell structure.[22−26] The method using this technique can effectively prevent metal nanoparticles from forming agglomerate even in the presence of electrolytes. Here, we use this technique to prepare SiO_2/Ag core−shell particles and

investigate the catalytic properties of silver nanoparticles supported on silica spheres in a colloidal solution. The aim of this work is to study the catalytic properties of the supported silver nanoparticles and the effects of surfactants and electrolytes on the catalytic properties, which helps to understand the mechanism of the heterogeneous catalysis. Until now, much work has been done previously to investigate the catalytic properties of supported metal particles.[27] However, there are relatively few studies on the catalytic properties of supported metal catalysts in colloidal solution, as well as on the effects of the micro-environment on catalytic properties.

Experimental Section

Reagents. Silica spheres used as substrates, prepared by the Stöber−Fink−Bohn methods,[28] were functionalized with 3-aminopropyltrimethoxysilane (APTMS; 95+%).[22,23] Silver nitrate ($AgNO_3$; 99+%), sodium borohydride ($NaBH_4$; 97%), dyes (methylene blue, eosin, and rose bengal), and the electrolytes, cetyltrimethyammonium bromide (CTAB; 99+%) and sodium dodecyl sulfate (SDS; 97+%), were obtained from Beijing Chemical Reagents Co. Triton X-100 was purchased from Aldrich. All reagents were used as received without further purification.

Preparation of Silver Nanoparticles Supported on Silica Spheres. First, 1 mL of silica solution, produced as described above, and 5.7 mg $NaBH_4$ were added to 98 mL of deionized water under vigorous stirring. Next, 1 mL of 2.54×10^{-2} mol/L $AgNO_3$ aqueous solution was then injected, and the reaction was allowed to last for about 15 min. Silver particles supported on the silica sphere were used after 1 day.

Catalytic Reactions. A given amount of silver particles supported on silica spheres were mixed with one dye, and the volume of the mixture was adjusted to 9 mL with deionized water. After that, 1 mL of $NaBH_4$ solution was rapidly injected under stirring. The color of the mixture gradually vanished, indicating the reduction of the dye.

For the study of the effect of surfactants and electrolytes on the catalytic properties, the surfactants or electrolytes were

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TABLE 1: Spectroscopic and Redox Properties of Dyes[29]

dye	color (λ_{max}) of the dye (oxidized form)	$E_{1/2}$ (V vs NHE) in different solvents[a]
rose bengal (RB)	red (550 nm)	−0.48 (a)
methylene blue (MB)	blue (665 nm)	−0.21 (w), −0.27 (a), −0.20 (t), −0.18 (s), +0.03 (c)
eosin (EO)	red (515 nm)	−0.53 (a)

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

injected into the mixture before the addition of dyes while all other conditions were kept unchanged. Three differently charged dyes such as methylene blue (MB), eosin (EO), and rose bengal (RB) were selected. In the working condition, MB becomes cationic, EO is anionic, and RB (due to the neutralization of anionic and cationic ions) is neutral. Spectroscopic and redox properties of the dyes used were shown in Table 1.

Instrumentation. UV−visible absorption spectra were measured at room temperature on a SHIMAZDU UV-1601PC UV−visible spectrometer. A quartz cuvette with 1-cm optical path length was used. Transmission electron microscopy (TEM) studies of the particles were performed with a JEOL JEM-CX200 microscope operating at 160 kV. The TEM samples were prepared by placing drops of sample on a Formvar coated copper grid (200 mesh; placed onto filter paper to remove excess solvent), and letting the solvent evaporate at room temperature.

Results

Role of the Silica Substrate. Silver nanoparticles with a small size are tethered to the APMTS-functionalized silica surface by virtue of the aminolphilic nature of the silver particles and the electrostatic interaction between a surface amidogen and metal particles.[22,23] The attachment is sufficiently strong so that the silver nanoparticles remain attached to the silica sphere during the catalytic reaction even in the presence of electrolytes, which can be verified by the TEM images of the silver particles supported on silica spheres before and after catalytic reactions (Figure 1). As shown in Figure 1, no discernible changes of the silver nanoparticles are observed, indicating that silver nanoparticles supported on the silica sphere are sufficiently stable and will not aggregate during the reaction.

Catalytic Properties of Silver Particles on Silica Spheres. In agreement with previous results,[15,29] the reduction of dyes, if it occurs at all, is insignificant in the absence of silver particles. However, in the solution containing silver particles, the reduction of the dyes by NaBH$_4$ is completed within a few minutes. The progression of the catalytic reduction of dyes can be easily followed by the change in optical density at the wavelength of the absorbance maximum (λ_{max}) of dyes. Figure 2 shows the evolution of the UV−visible spectra of dyes during their catalytic reductions at the silver nanoparticles supported on silica. Evidently, the absorbance at λ_{max} of the dyes gradually decreases with the reaction time, which is indicative of the reduction of dyes. As expected, the catalytic reduction of dyes proceeds successfully, and no deactivation or poisoning of the
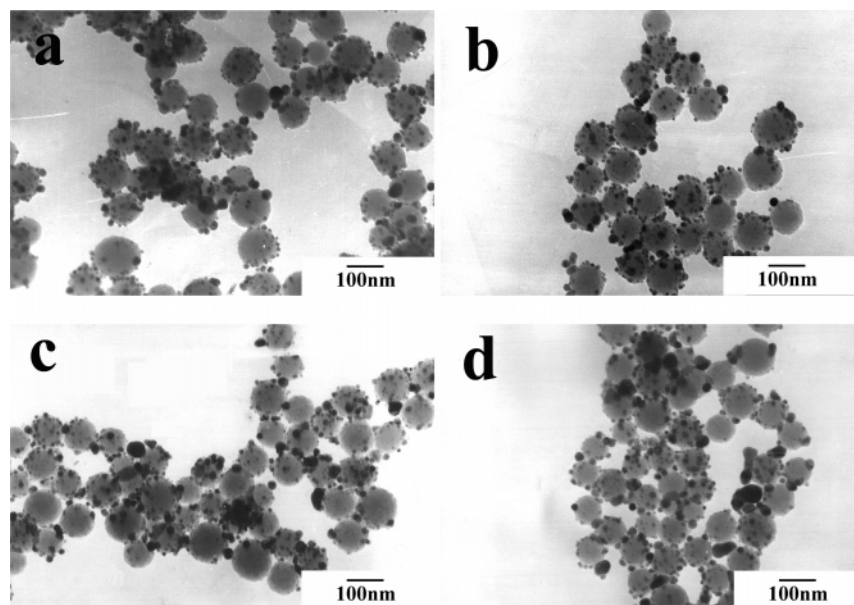

Figure 1. TEM images of silver nanoparticles supported on silica before (a) and after (b) the catalytic reaction in the absence of electrolytes; (c) after the catalytic reaction in the presence of KNO$_3$; (d) after the catalytic reaction in the presence of Na$_3$PO$_4$.
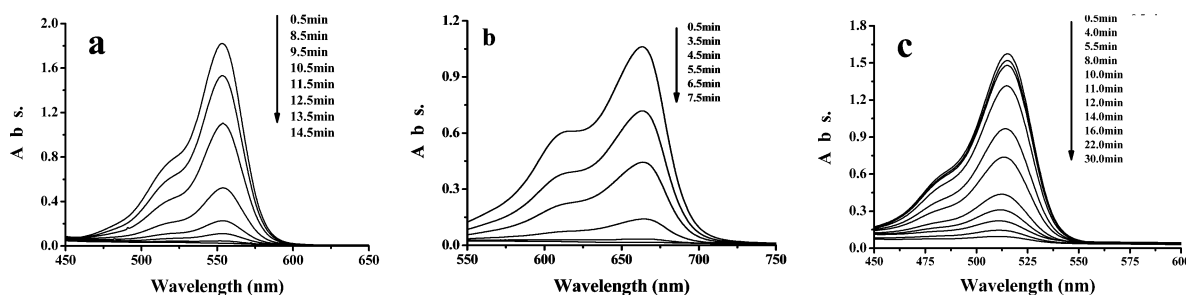

Figure 2. UV−visible spectra of (a) RB, (b) MB, and (c) EO during the reduction catalyzed by silver nanoparticles on silica spheres, [NaBH$_4$] = 1×10^{-2} mol/L and [RB] = [MB] = [EO] = 2×10^{-5} mol/L. The arrows mark the increase of the reaction time.
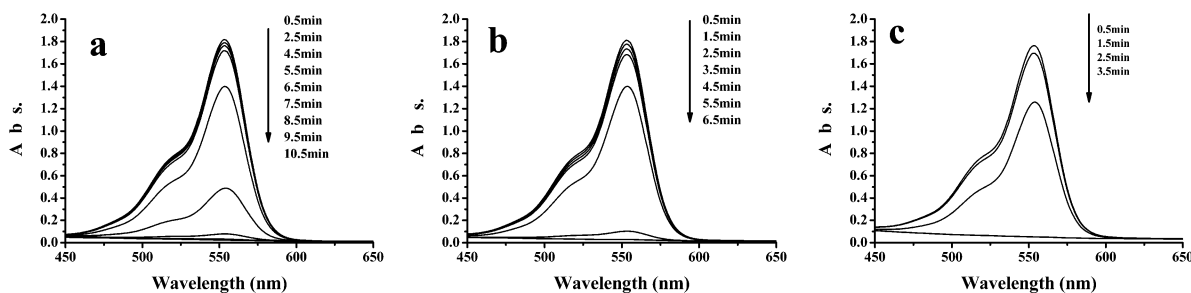
Figure 3. UV−visible spectra of rose bengal during the catalyzed reduction varying the concentration of silver nanoparticles. [RB] = 2×10^{-5} mol/L, [NaBH$_4$] = 1×10^{-2} mol/L, (a) [Ag]$_0$ = 3.75×10^{-5} mol/L, (b) [Ag]$_0$ = 5.0×10^{-5} mol/L, (c) [Ag]$_0$ = 6.25×10^{-5} mol/L. The arrows mark the increase of reaction time.
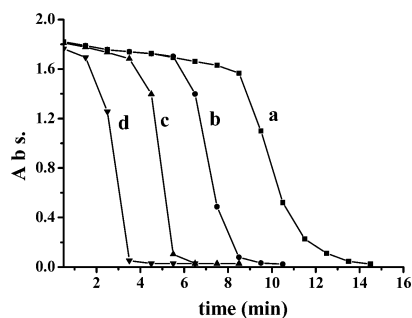

Figure 4. Plot of the absorbance at λ_{max} of RB versus time at different concentrations of silver nanoparticles. (a) [Ag]$_0$ = 2.5×10^{-5} mol/L, (b) [Ag]$_0$ = 3.75×10^{-5} mol/L, (c) [Ag]$_0$ = 5.0×10^{-5} mol/L, (d) [Ag]$_0$ = 6.25×10^{-5} mol/L.
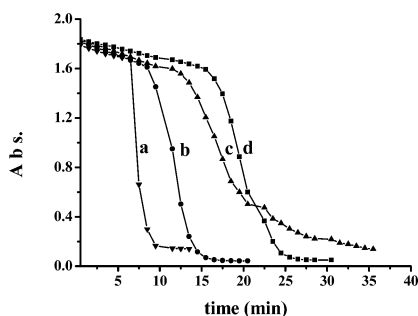

Figure 5. Reduction kinetics of RB catalyzed by silver nanoparticles supported on silica spheres in the presence of different surfactants: (a) no surfactant, (b) CTAB, (c) SDS, (d) Tx-100.

catalyst is observed. The rate of the catalyzed reduction of the dyes increases with an increase in the concentration of the silver supported on silica (Figure 3).

A plot of the absorbance at λ_{max} versus reaction time yields a sigmoidal curve when RB or EO is used as a probe (Figure 4), which indicates that the catalytic reaction had an induction period, the time required to begin the catalytic reduction. As shown in Figure 4, the induction period decreases with an increase in the concentration of the silver nanopaticles supported on silica.

Effect of Surfactants on the Catalytic Properties. The effects of surfactants on the catalyzed reduction of dyes are measured. The surfactants with different properties, such as CTAB, a cationic surfactant, SDS, an anionic surfactant, or TX-100, a nonionic surfactant, are used. Keeping all other conditions unchanged, a distinct decrease in the reduction rate of the dyes is observed after the addition of surfactants (Figure 5). A plot of the absorbance at λ_{max} versus reaction time shows that surfactants extend the induction period. In some cases, the reduction rate of dyes is decreased to a considerable extent and the reaction is even stopped after some initial progress in the presence of surfactants. This result indicates that surfactants can

deactivate or poison the catalyst by interacting with the surface and packing around it.

Effect of Electrolytes on Catalytic Properties. Electrolytes are found to have a profound impact on the catalytic properties of silver particles supported on silica spheres. It has been shown that electrolytes do not change the morphology and size of silver nanoparticles (Figure 1), indicating that the silver nanoparticles on silica are sufficiently stable even in the presence of electrolytes. Figure 6 shows the spectral evolution of the dyes during the catalytic reduction in the presence of different electrolytes, such as NaNO$_3$, Na$_2$SO$_4$, and Na$_3$PO$_4$. It seems that the catalytic properties of silver particles supported on silica spheres are closely dependent on the nature of electrolytes. As shown in Figure 6, NaNO$_3$ and Na$_2$SO$_4$ promote the catalyzed reduction of the dyes, and the catalyzed reduction rate of the dyes increases with an increase in the electrolyte concentration (Figure 7). Sodium phosphate, however, decreases the catalytic reduction rate to a considerable extent, and the reaction is totally inhibited when the concentration of Na$_3$PO$_4$ is increased to 0.05 mol/L. Actually, electrolytes, which can form insoluble salt with silver ions, such as halide ions, have strong interactions with silver nanoparticles and often change the morphologies of silver nanoparticles on silica in the solution.[22c] The likely reason that no distinct changes of silver nanoparticles are observed by TEM after exposure to electrolytes is a lower concentration of the electrolyte and a slight change of particles.

Discussion

It has been observed that the reduction of the dye by NaBH$_4$ did not occur to an appreciable extent in the absence of the metal nanoparticles. Moreover, the rate of the reduction for dyes gradually increased with the increase in the concentration of silver particles on silica (Figure 3). This indicates that silver nanoparticles play the role of a catalyst for the reduction of dyes. The catalytic process can be explained by an electrochemical mechanism, where silver nanoparticles-supported silica spheres serve as an electron relay for an oxidant and a reductant, and electron transfer occurs via the supported metal particles. Dyes are electrophilic, while BH$_4^-$ ions are nucleophilic in nature with respect to silver nanparticles. In general, a nucleophile can donate electrons to metal particles. In contrast, an electrophile would capture electrons form metal particles. Earlier work showed that BH$_4^-$ ions and dyes were simultaneously adsorbed on the surface of silver nanparticles when they were present together.[15,29] Therefore, the electron transfer from BH$_4^-$ ions to the dyes via silver particles is imaginable.

Evidently, the silica substrate plays an important role in avoiding the aggregation of the metal nanoparticles during the catalytic processes, which ensures the catalyzed reduction of dyes. In the absence of the silica substrate, the aggregation of metal particles and the reduction of the dyes catalyzed by
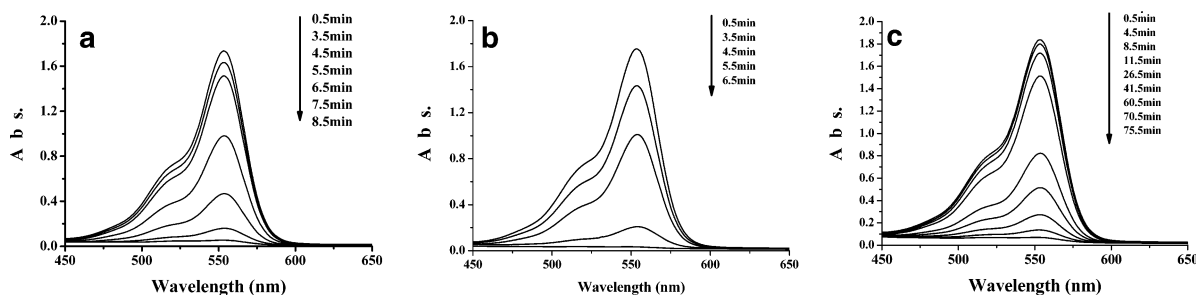
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Figure 6. UV−visible spectra of RB catalytically reduced by silver nanoparticles supported on silica spheres in different electrolytes. (a) [NaNO$_3$] = 0.050 mol/L, (b) [Na$_2$SO$_4$] = 0.05 mol/L, (c) [Na$_3$PO$_4$] = 0.005 mol/L. The arrows mark the increase of reaction time.
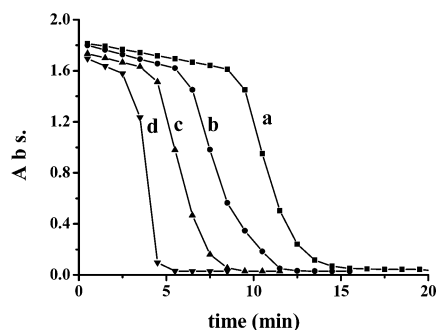

Figure 7. Plot of the absorbance at λ_{max} of RB versus reaction time; the concentration of NaNO$_3$ from a to d: (a) without NaNO$_3$, (b) [NaNO$_3$] = 0.025 mol/L, (c) [NaNO$_3$] = 0.05 mol/L, (d) [NaNO$_3$] = 0.075 mol/L.
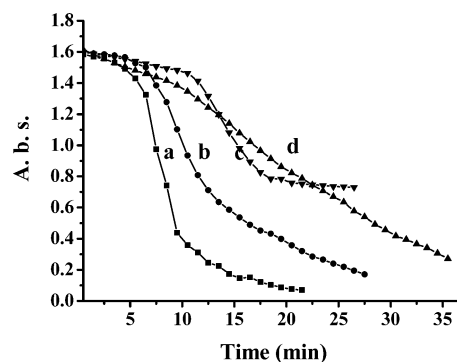

Figure 8. Reduction kinetics of EO catalyzed by silver nanoparticles supported on silica spheres in the presence of different surfactants: (a) no surfactant, (b) CTAB, (c) SDS, (d) Tx-100.

aggregated and nonaggregated particles would proceed simultaneously.[15,29] In some cases (especially in the presence of electrolytes), the catalyzed reduction of the dyes is stopped after some initial progress or the rate decreases to a considerable extent. Yet such phenomenon is not observed when silver nanoparticles supported on silica spheres are used as catalyst. This suggests that the silica spheres are necessary in stabilizing the silver nanopartcles. It is well known that the catalytic efficiency of a metal nanoparticle for an electron-transfer process is closely relate to the size-dependent redox properties that control its roles as an electron relay. As a general rule, the rate of a catalytic reaction should be determined by the concentration of the catalyst and the difference in potential between the reductant adsorbed metal particles and the oxidant used. As we know, the redox potential of a metal nanoparticle is dependent on the size, and it increases with the increase of the size.[1d,2] For a given concentration of silver nanoparticles, the smaller are the sizes of the particles, the more negative the potentials of silver particles are, which makes a larger potential difference between silver and dyes and hence a higher catalytic activity.[30] As for silver nanoparticles unattached to silica spheres, the size of the particles gradually increases due to aggregation, leading to the decrease of the number of particles and the difference in the potential between silver and dyes during the catalytic process. As a result, the catalytic reaction rate of the dyes decreases and even stops.

The effects of surfactants on the catalyzed reduction of dyes can be explained by the adsorption competition of dyes and surfactants. In most cases, surfactants would move to the surface of metal nanoparticles and pack around them, which affects the accessibility to the metal particles for the reacting molecules and leads to the loss of catalytic activity due to the predominant adsorption of surfactants. The ultimate reduction rate of a dye is related to the charge of the surfactant used. Usually, a larger decrease of the reaction rate is observed when the dye and the surfactant carry the same charge, while a smaller reduction of

the reaction rate results if the dye and the surfactant are oppositely charged. As shown in Figure 8, the reduction rate of EO is distinctly slower in SDS than in CTAB. This might be a result of the electrostatic interaction between the dye and surfactant. The accessibility of reacting molecules to the metal particles is probably more difficult for the dye when the surfactant carries the same charge due to electrostatic repulsion. The same result could be observed when RB is used. Although RB is generally considered a neutral dye in the present work, it carries negative and positive charge together. These charges will simultaneously interact with surfactants and result in the different reduction rate of RB. As shown in Figure 5, the use of a nonionic or anionic surfactant results in a large reduction of the reaction rate, while the use of a cationic surfactant results in a smaller reduction of the reaction rate. This result implies that the negative charge of RB shows stronger interactions with surfactants, which determines the ultimate reduction rate.

The effect of electrolytes on the catalytic properties of silver nanoparticles is complicated. On one hand, the addition of an electrolyte promotes the migration of charges in the solution, which results in the increase of the catalytic rate. On the other hand, electrolytes adsorb onto the surface of metal particles and render the silver nanoparticles catalytically inert by blocking active sites due to preferential adsorption of the electrolytes. When electrolytes that interact weakly with silver nanoparticles, such as NaNO$_3$ and Na$_2$SO$_4$, are used, the effect that promotes the migration of charges predominates. As a result, the catalytic reduction rate of dyes is increased. Accordingly, the induction period of the catalyzed reduction is shortened (Figure 7). On the contrary, when sodium phosphate is used, which has a strong interaction with the supported silver particles, a fairly slow catalytic reaction rate is observed. To verify the effects of surface adsorption on the catalytic reaction, we chose the 1-phenyl-5-mercaptotetrezole (PMT) as an electrolyte, which has a strong adsorption on silver particles,[31] to investigate the catalytic properties of the supported silver nanoparticles. The result shows
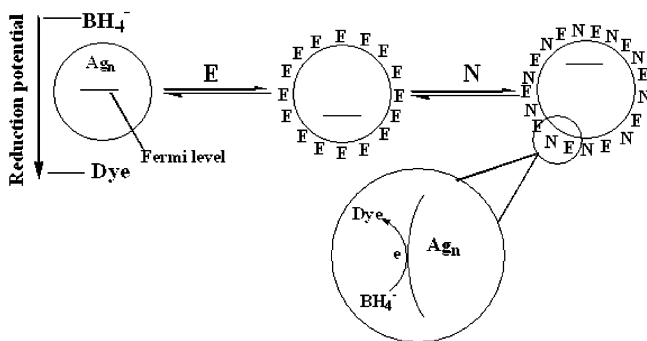
Figure 9. Schematic of the catalytic process occurring at silver nanoparticles supported on silica spheres and the change of the Fermi level during the reaction. E, electrophile (dyes); N, nucleophile (BH_4^- ions)

that the reaction is extremely slow and stops after a period of time when the concentration of PMT is 5×10^{-4} mol/L. The reaction is totally inhibited when the concentration of PMT is increased up to 5×10^{-3} mol/L. These results suggest that a physical connection between the catalyst and a precursor is necessary to ensure the reaction be successfully carried out. Any adsorbent that affects the accessibility to the particles for the reactants slows the catalytic reaction and even can render the silver nanoparticles catalytically inert.

The induction period is one of the most significant observations in this study. Pal et al.[15,29] suggested that surfactants might be responsible for the induction period in their investigation on the catalytic properties of stable silver particles. In their opinion, the encapsulation of stable particles by the surfactant functioned as a temporary barrier for the adsorption of BH_4^- ions onto the metal particles. Although the surfactants affect the induction period of the catalytic reaction in our experiments (Figure 5), it is evidently not a primary factor. As shown in Figures 3 and 4, the induction period persists whether the surfactant is present or not, which indicates that some other factors contribute to the induction period.

As mentioned above, the catalytic reduction rate of a dye is closely related to the difference in the potential between the metal particles and the dyes. The larger is the difference between the two potentials, the higher is the catalytic reaction rate. In the solution, the Fermi potential of a metal particle is related to the properties of micro-environment.[1a,32] An electrophile can lead the Fermi potential of the metal particles to a positive shift. In contrast, a negative shift in the Fermi potential will occur when a nucleophile is added. Figure 9 schematically illustrates the changes of the Fermi level of the supported metal particles during the catalytic process. In the initial stage of the catalytic reaction, silver nanoparticles are surrounded by dye molecules, and the Fermi potential of the silver particles is relatively high. After the addition of sodium borohydride, BH_4^- ions will gradually adsorb onto the surface of silver nanoparticles through competitive adsorption and the Fermi potential of the metal particles decreases. Therefore, in the initial stage of the reaction, the catalytic reduction rate of dyes is slow because of the lack of BH_4^- ions on the surface of silver particles and the small potential difference between the metal particles and the dyes. With increasing reaction time, a larger number of BH_4^- ions pack around the surface of silver particles, and the potential difference of the metal particles and the dyes is also increased. As a result, the reaction rate increases.

In addition, the nature of dyes (i.e., charge, hydrophobicity, presence of S/N donor atom, etc.) may also be an important factor influencing the induction period.[33] For a given concentra-

tion of silver nanoparticles, the induction period varies from dye to dye. For example, an induction period is always observed when RB and EO are used as probes, but no induction period is observed when MB is used. It implies that the induction period is dependent on the nature of the dyes. In general, a positively charged dye has a higher catalytic reaction rate than a negatively charged one due to electrostatic interaction. Metal particles would be cathodically polarized by BH_4^- ions though the following reaction[34]

$$BH_4^- + Ag_n + 3H_2O \rightarrow BO_3^{3-} + Ag_n^{8-} + 10H^+ \quad (1)$$
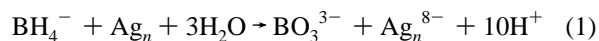
Therefore, the silver particles are more accessible to the positively charged dyes due to electrostatic interaction than the negatively charged ones. Accordingly, a relatively short induction period is observed for positively charged species.

Conclusion

The catalytic properties of silver nanoparticles supported on silica spheres have been investigated. Tethering silver nanoparticles onto silica spheres effectively protects metal particles from aggregation, thus avoiding deactivation and poisoning of the catalysts during the catalytic reaction. Surfactants and electrolytes have profound influences on the catalytic properties of metal nanoparticles on silica spheres. In most cases, the addition of surfactants leads to a distinct decrease in the catalyzed reduction rate of the dyes due to the reduced accessibility of the particle surface. The effects of electrolytes on the catalytic properties of the silver particles on silica spheres are complex. On one hand, electrolytes increase the migration rate of the reactants in the solution, which results in the increase of the catalytic reaction rate. On the other hand, the adsorption of the reactants may be inhibited due to the predominant adsorption of the surfactants leading to the loss of catalytic activity of the silver nanoparticles. Therefore, the catalytic reaction rate of dyes is closely dependent on the properties of electrolyte used.

References and Notes

(1) (a) Henglein, A. *J. Phys. Chem.* **1993**, *97*, 5457. (b) Michaelis, M.; Henleign, A. *J. Phys. Chem.* **1994**, *98*, 6212. (c) Linnert, T.; Mulvaney, P.; Henleign, A. *J. Phys. Chem.* **1993**, *97*, 679. (d) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.

(2) (a) Mostafavi, M.; Marignier, J. L.; Amblard, J.; Belloni, J. *Radiat. Phys. Chem.* **1989**, *34*, 605. (b) Huang, Z.-Y.; Mill, G.; Hajek, B. *J. Phys. Chem.* **1993**, *97*, 11542.

(3) (a) Mallin, M. P.; Murphy, C. J. *Nano Lett.* **2002**, *2*, 1235. (b) Métraux, G. S.; Cao, Y. C.; Jin, R.; Mirkin, C. A. *Nano Lett.* **2003**, *3*, 519.

(4) Ung, T.; Liz-Marzán, L. M.; Mulvaney, P. *J. Phys. Chem. B* **1999**, *103*, 6770.

(5) (a) Pastoriza,-Santos, I.; Liz-Marzán, L. M. *Nano Lett.* **2002**, *2*, 903. (b) Jin, R. C.; Cao, Y. W.; Mirkin, C. A.; Kelley, K. L.; Schatz, G. C.; Zheng, J. G. *Science* **2001**, *294*, 1901. (c) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*, Springer-Verlag: Berlin, 1995.

(6) Ung, T.; Liz-Marzán, L. M.; Mulvaney, P. *J. Phys. Chem. B* **2001**, *105*, 3441.

(7) (a) Adams, R. D.; Captain, B.; Zhu, L. *J. Am. Chem. Soc.* **2004**, *126*, 3042. (b) Schmid, G. *Clusters & Colloidal: From Theory to Application*; VCH: Weinheim, 1994.

(8) (a) Whetten, R. L.; Shafigullin, M. N.; Khoury, J. T.; Schaaf, T. G.; Vezmar, I.; Alvarez, M. M.; Wilkinson, A. *Acc. Chem. Res.* **1999**, *32*, 397. (b) Templeton, A. C.; Wuelfing, M. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.

(9) Wu, M. L.; O'neill, S. A.; Brousseau, L. C.; McConell, W. P.; Shultz, D. A.; Linderman, R. J.; Feidheim, D. L. *Chem. Commun.* **2000**, 775.

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(10) Greenwood, N. N.; Earnshaw, A. *Chemistry of Elements*, 2nd ed.; Butterworth-Heinemann: Oxford, 1997.

(11) (a) Glynou, K.; Ioannou, P. C.; Christopoulos, T. K.; Syriopoulou, V. *Anal. Chem.* **2003**, *75*, 4155. (b) Patolsky, K.; Lichtenstein, A.; Willner, I. *J. Am. Chem. Soc.* **2001**, *123*, 5194.

(12) (a) Francois, L.; Mostafavi, M.; Belloni, J.; Delouis, J.-F.; Delaire, J.; Feneyrou, P. *J. Phys. Chem. B* **2000**, *104*, 6133. (b) Mandal, S.; Selvakannan, P. R.; Pasricha, R.; Sastry, M. *J. Am. Chem. Soc.* **2003**, *125*, 8440.

(13) Zaera, F.; Gellman, A. J.; Somarajai, G. A. *Acc. Chem. Res.* **1986**, *19*, 24.

(14) Bonds, G. C. *Acc. Chem. Res.* **1993**, *26*, 490.

(15) (a) Pal, T.; Sau, T. K.; Jana, N. R. *J. Colloid Interface Sci.* **1998**, *202*, 30. (b) Pal, T.; Sau, T. K.; Jana, N. R. *Lamgmuir* **1997**, *13*, 1481.

(16) Fendler, J. H. *Chem. Rev.* **1987**, *87*, 877.

(17) Ahmadi, T.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-sayed, M. A. *Science* **1996**, *272*, 1924.

(18) Hercules, D. M.; Proctor, A.; Houalla, M. *Acc. Chem. Res.* **1994**, *27*, 387.

(19) Longenberger, L.; Mills, G. *J. Phys. Chem.* **1995**, *99*, 475.

(20) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709.

(21) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.

(22) (a) Zhong, Z.-J.; Liu, C.-Y. *J. Phys. Chem. B* **2003**, *107*, 12411. (b) Zhong, Z.-J.; Liu, C.-Y.; Liu, Y.; Zhang, Z.-Y.; Li, Y.-J. *Chem. Lett.* **2003**, *32*, 668. (c) Zhong, Z.-J.; Liu, C.-Y.; Li, Y.-J. *Chem. Lett.* **2003**, *33*, 498.

(23) (a) Westcott, S. L.; Oldenburg, S. J.; Lee, T. R.; Halas, N. J. *Langmuir* **1998**, *14*, 5396. (b) Oldenburg, S. J.; Averitt, R. D.; Westcott, S.

L.; Halas, N. J. *Chem. Phys. Lett.* **1998**, *288*, 243. (c) Jackson, J. B.; Halas, N. J. *J. Phys. Chem. B*, **2001**, *105*, 2743.

(24) Grbar, K. C.; Allison, K. J.; Baker, B. E.; Bright, R. M.; Brown, K. R.; Freeman, R. G.; Fox, A. P.; Keating, C. D.; Musick, M. D. *Langmuir* **1996**, *12*, 2353.

(25) Grabar, K. C.; Smith, P. C.; Musick, M. D.; Davis, J. A.; Walter, D. G.; Jackson, M. A.; Guthrie, A. P.; Natan, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1148.

(26) Blonder, R.; Sheeney, L.; Willner, I. *Chem. Commun.* **1998**, 1393.

(27) (a) Guzman, J.; Gates, B. C. *J. Am. Chem. Soc.* **2004**, *126*, 2672. (b) Claus, P.; Brückner, A.; Mohr, C.; Hofmeister, H. *J. Am. Chem. Soc.* **2000**, *122*, 11430. (c) Liu, Z.-P.; Hu, P.; Alavi, A. *J. Am. Chem. Soc.* **2000**, *124*, 14770. (d) Lopez, N.; Nørskov, J. K. *J. Am. Chem. Soc.* **2002**, *122*, 11262.

(28) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

(29) Jana, N. R.; Sau, T. K.; Pal, T. *J. Phys. Chem. B* **1999**, *103*, 115.

(30) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and application*; John Wiley & Sons: New York, 1980.

(31) (a) Gonnissen, D.; Hubin, A.; Vereecken, J. *Electrochim. Acta* **1999**, *44*, 4129. (b) Li, Y.-J.; Liu, C.-Y. *J. Electroanal. Chem.* **2001**, *517*, 117.

(32) (a) Mulvancy, P.; Linnert, T.; Henglein, A. *J. Phys. Chem.* **1991**, *95*, 7843. (b) Blatchford, C. G.; Siimon, O.; Kerker, M. *J. Phys. Chem.* **1983**, *87*, 2503.

(33) Jana, N. R.; Pal, T. *Langmuir* **1999**, *15*, 3458.

(34) (a) Ung, T.; Liz-Marzán, L. M.; Mulvancy, P. *J. Phys. Chem. B* **1999**, *103*, 6770. (b) Schlesinger, H. I.; Brown, H. C.; Finholt, A. E.; Gilbreath, J. R.; Hoekstra, H. R.; Hyde, E. K. *J. Am. Chem. Soc.* **1953**, *75*, 215.