# Photosensitized Growth of Silver Nanoparticles under Visible Light Irradiation: A Mechanistic Investigation

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*Received June 14, 2005. Revised Manuscript Received August 25, 2005*

By employing thionine as a sensitizing dye, we have succeeded in inducing silver nanoparticle formation in ethanol/toluene medium. The particle size increases with the duration of photolysis, thus providing a simple experimental parameter to control the particle size. The photoinduced transformations as probed by steady state photolysis and transient absorption spectroscopy provide an insight into the charge-transfer processes leading to the formation of nanoparticles. Under visible light illumination, dye thionine undergoes self-quenching of the excited triplet to produce electron-transfer products in toluene/ethanol (1:1) mixture. The quenching of triplet excited dye by the ground state dye molecules ($k = 4.9 \times 10^9$ $M^{-1}$ $s^{-1}$) occurs at a much faster rate than the quenching by $Ag^+$ ions ($k = 1.30 \times 10^6$ $M^{-1}$ $s^{-1}$). Semithionine acts as a mild reductant to initiate reduction of silver ions ($k = 7.26 \times 10^7$ $M^{-1}$ $s^{-1}$) and form silver seeds. These seeds grow with autocatalytic reduction of $Ag^+$ ions and by Ostwald ripening to produce larger size particles (10−30 nm diameter).

## Introduction

Synthesis of extremely small metal particles of diameter <10 nm are of great interest because of their unusual catalytic and optical properties.[1−11] Quantized charging[12,13] and conductance[14] properties of gold nanoparticles and their role in enhancing catalytic[15] and photocatalytic[16] properties have already been recognized. When in contact with a semiconductor nanostructured material, the metal nanoparticles undergo charge equilibration under photoexcitation and shift the Fermi level of the composite closer to the conduction band of the semiconductor.[16−19] $TiO_2$-capped silver particles have been shown to store photogenerated electrons and discharge them on demand.[20,21] In addition, application of such metal nanoparticles in optics, microelectronics, catalysis, sensors, information storage, and energy conversion have been explored.[8,10,11,22−32]

The common methods for the synthesis of metal nanoparticles include the chemical reduction of metal salts using various reducing agents in the presence of stabilizers.[33−35] The growth of particles depends on the nature of the reductant and the medium in which the reduction is being carried out. Photolytic and radiolytic methods often provide a convenient means to produce size- and shape-controlled metal nanoparticles.[36,37] For example, prism-shaped silver and rod-shaped gold nanostructures can be prepared using a photolytic method.[38] Yonezawa et al.[39] have found that the

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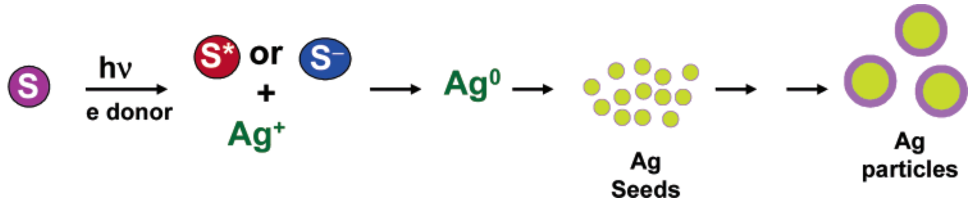
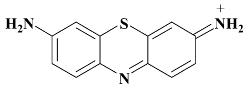
(1) Kamat, P. V. *J. Phys. Chem. B* **2002**, *106*, 7729.
(2) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.
(3) Kalyanasundaram, K.; Graetzel, M.; Pelizzetti, E. *Coord. Chem. Rev.* **1986**, *69*, 57.
(4) Mulvaney, P. *Langmuir* **1996**, *12*, 788.
(5) Pileni, M. P. *New J. Chem.* **1998**, 693.
(6) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.
(7) Hodak, J.; Henglein, A.; Hartland, G. V. *J. Phys. Chem. B* **2000**, *104*, 9954.
(8) El-Sayed, M. A. *Acc. Chem. Res.* **2001**, *34*, 257.
(9) Toshima, N.; Yonezawa, T. *New J. Chem.* **1998**, *22*, 1179.
(10) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 668.
(11) Schmid, G.; Corain, B. *Eur. J. Inorg. Chem.* **2003**, 3081.
(12) Chen, S.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvarez, M. M.; Whetten, R. L. *Science* **1998**, *280*, 2098.
(13) Chen, S.; Murray, R. W. *J. Phys. Chem. B* **1999**, *103*, 9996.
(14) Li, J.; Yamada, Y.; Murakoshi, K.; Nakatoa, Y. *Chem. Commun.* **2001**, 2170.
(15) Haruta, M. *Catal. Today* **1997**, *36*, 153.
(16) Subramanian, V.; Wolf, E. E.; Kamat, P. V. *J. Phys. Chem. B* **2003**, *107*, 7479.
(17) Wood, A.; Giersig, M.; Mulvaney, P. *J. Phys. Chem. B* **2001**, *105*, 8810.
(18) Jakob, M.; Levanon, H.; Kamat, P. V. *Nano Lett.* **2003**, *3*, 353.
(19) Subramanian, V.; Wolf, E. E.; Kamat, P. V. *J. Am. Chem. Soc.* **2004**, *126*, 4943.
(20) Hirakawa, T.; Kamat, P. V. *Langmuir* **2004**, *20*, 5645.
(21) Hirakawa, T.; Kamat, P. V. *J. Am. Chem. Soc.* **2005**, *127*, 3928.
(22) George Thomas, K.; Kamat, P. V. *Acc. Chem. Res.* **2003**, *36*, 888.
(23) Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 8410.
(24) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709.
(25) Nie, S. M.; Emery, S. R. *Science* **1997**, *275*, 1102.
(26) Pileni, M. P. *J. Phys. Chem. B* **2001**, *105*, 3358.
(27) Katz, E.; Willner, I.; Wang, J. *Electroanalysis* **2004**, *16*, 19.
(28) Shipway, A. N.; Katz, E.; Willner, I. *Chem. Phys. Chem.* **2000**, *1*, 18.
(29) Goodson, T.; Varnavski, O.; Wang, Y. *Int. Rev. Phys. Chem.* **2004**, *23*, 109.
(30) Hartland, G. V. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5263.
(31) Cozzoli, P. D.; Comparelli, R.; Fanizza, E.; Curri, M. L.; Agostiano, A.; Laub, D. Photocatalytic synthesis of silver nanoparticles stabilized by TiO2 nanorods: A semiconductor/metal nanocomposite in homogeneous nonpolar solution. *J. Am. Chem. Soc.* **2004**, *126*, 3868.
(32) Imahori, H.; Kashiwagi, Y.; Endo, Y.; Hanada, T.; Nishimura, Y.; Yamazaki, I.; Araki, Y.; Ito, O.; Fukuzumi, S. *Langmuir* **2004**, *20*, 73.
(33) Henglein, A. *Isr. J. Chem.* **1993**, *33*, 77.
(34) de Cointet, C.; Mostafavi, M.; Khatouri, J.; Belloni, J. *J. Phys. Chem. B* **1997**, *101*, 3512.
(35) Pillai, Z. S.; Kamat, P. V. *J Phys. Chem. B* **2004**, *108*, 945.
(36) Henglein, A.; Meisel, D. *Langmuir* **1998**, *14*, 7392.
(37) Henglein, A. *Chem. Mater.* **1998**, *10*, 444.

10.1021/cm0512777 CCC: $30.25 © 2005 American Chemical Society
Published on Web 10/04/2005

**Scheme 1. Photochemical Route of Synthesizing Ag Nanoparticles**



**Scheme 2**



Thionine ($TH^+$)

UV irradiation of aqueous solutions containing noble metal ions in a surfactant solution yields colloidal metal particles. Recently, photosensitized reduction of silver ions has been studied by irradiating a mixture of benzophenone and silver ions using UV laser pulses.[40,41] Photocatalytic reduction of metal ions on semiconductor particles has also been found useful in designing semiconductor−metal composite catalysts.[42−44]

The use of dye molecule as a photosensitizer can serve a dual purpose: the sensitizing dye can initiate the reduction of metal ions and it can bind with the metal surface to protect the particle and modify its optical properties (Scheme 1). In recent years many interesting efforts have been proposed to functionalize metal nanoparticles with photoactive molecules and use them in photochemical solar cells.[22,32,45−53]

In the present work, we have adopted a photochemical method for the synthesis of silver nanoparticles. The reduction of $Ag^+$ ions is initiated by the excitation of the dye thionine (Scheme 2) with visible light. The reduced dye formed during the self-quenching process initiates the reduction of $Ag^+$ ions to produce small Ag nanoparticles. Transient absorption spectroscopy measurements that provide mechanistic insights are presented here.

## Experimental Section

**Materials and Methods.** Silver nitrate was obtained from Aldrich. Thionine (Fluka) was purified over a chromatography column of neutral alumina.[54] All the solvents were of analytical grade and obtained from Aldrich. The toluene/ethanol solvent mixture containing a known amount of dye and $Ag^+$ ions were transferred to a quartz cuvette and deaerated by purging with nitrogen. Unless otherwise indicated, all solutions were subjected to visible excitation under $N_2$ atmosphere. The Ag particles were characterized using a JEOL JEM-100sx electron microscope.

**Optical Measurements.** Absorption spectra were recorded with a Shimadzu 3101 spectrophotometer. A 250 W xenon lamp was employed as the primary excitation source. Visible light filtered with a 530 nm cutoff filter was used for exciting thionine solution containing $Ag^+$ ions. Nanosecond laser flash photolysis experiments were performed with a 532 nm laser pulse (5 mJ, pulse width 6 ns) from a Quanta Ray Nd:YAG laser system. The experiments were performed in a rectangular quartz cell, and all the solutions were deaerated with high-purity nitrogen. The same laser setup was also used to study the dependence of silver particle size on the laser intensity.

## Results and Discussion

**Formation of Ag Nanoparticles with Visible Light Excitation of Thionine.** The changes in the spectral features observed upon visible light excitation of thionine dye (10 $\mu$M) and $AgNO_3$ (50 $\mu$M) solution in toluene/ethanol mixture (1:1) are shown in Figure 1A. The dye thionine exhibits strong absorption in the 550−630 nm region with a maximum at 598 nm. The filtered light of wavelengths >530 nm ensures selective excitation of thionine present in the solution. With increasing irradiation time, we observe a decrease in the absorption of the 598 nm band and an increase in the absorption around 410 nm. These spectral features are retained even after exposing the solution (visible light irradiated) to air or oxygen (Supporting Information Figure S1). The Ag nanoparticles formed during photolysis can be separated using centrifugation and can be resuspended in polar solvents such as ethanol.

The increase in the absorbance seen around 410 nm is the characteristic of Ag nanoparticles that arise from the surface plasmon absorption. The steady increase of the 410 nm absorption band is representative of growth of Ag nanoparticles. It is also interesting to note that this increase in 410 nm absorption band parallels the decrease in the absorption of the dye at 598 nm. The failure to observe recovery of the 598 nm band shows the irreversible phototransformation of the dye (∼25%) during the photochemical formation of Ag nanoparticles. These results confirm the participation of dye molecules in the formation and growth of Ag nanoparticles.

Figure 1B shows the growth of plasmon absorbance monitored at 410 nm at different concentrations of $AgNO_3$.

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(38) Jin, R. C.; Cao, Y. W.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G. *Science* **2001**, *294*, 1901.
(39) Yonezawa, Y.; Sato, T.; Ohno, M.; Hada, H. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 1559.
(40) Kometani, N.; Doi, H.; Asami, K.; Yonezawa, Y. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5142.
(41) Eustis, S.; Krylova, G.; Eremenko, A.; Smirnova, N.; Schill, A. W.; El-Sayed, M. *Photochem. Photobiol. Sci.* **2005**, *4*, 154.
(42) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4317.
(43) Bard, A. J.; Fox, M. A. *Acc. Chem. Res.* **1995**, *28*, 141.
(44) Kamat, P. V. *Pure Appl. Chem.* **2002**, *74*, 1693.
(45) Fox, M. A.; Wooten, M. D. *Langmuir* **1997**, *13*, 7099.
(46) Li, W. J.; Lynch, V.; Thompson, H.; Fox, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 7211.
(47) Makarova, O. V.; Ostafin, A. E.; Miyoshi, H.; Norris, J. R.; Meisel, D. *J. Phys. Chem. B* **1999**, *103*, 9080.
(48) Lahav, M.; Gabriel, T.; Shipway, A. N.; Willner, I. *J. Am. Chem. Soc.* **1999**, *121*, 258.
(49) Yu-Chen, M. M.; Katz, A. *Langmuir* **2002**, *18*, 8566.
(50) Kamat, P. V.; Barazzouk, S.; Hotchandani, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2764.
(51) Ipe, B. I.; George Thomas, K.; Barazzouk, S.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem. B* **2002**, *106*, 18.
(52) Barazzouk, S.; Kamat, P. V.; Hotchandani, S. *J. Phys. Chem. B* **2005**, *109*, 716.
(53) Kamat, P. V.; Lichtin, N. N. *J. Photochem.* **1982**, *18*, 197.
(54) Hasobe, T.; Imahori, H.; Kamat, P. V.; Fukuzumi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1216.

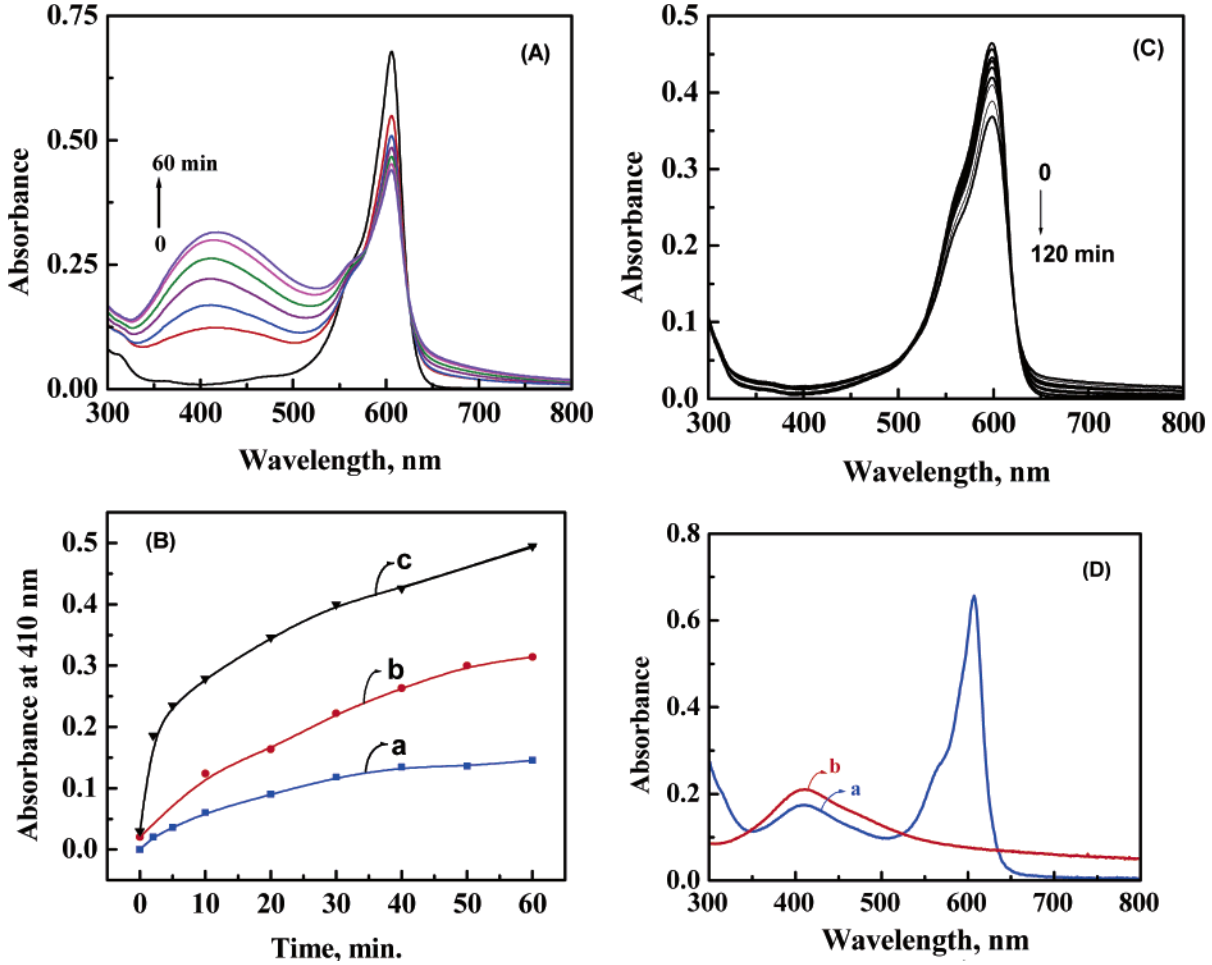

**Figure 1.** (A) Growth of the absorption spectra of Ag nanoparticles as a function of irradiation time in toluene/ethanol mixture (1:1). The spectra were recorded at 10 min intervals; [thionine] = 10 $\mu$M and [$AgNO_3$] = 50 $\mu$M. (B) Absorbance of sample at 410 nm containing (a) 25 $\mu$M, (b) 50 $\mu$M, and (c) 1mM $AgNO_3$ plotted as a function of time of irradiation; [thionine] = 10 $\mu$M. (C) Absorption spectra of thionine (10 $\mu$M) and $AgNO_3$ (50 $\mu$M) mixture in water as a function of irradiation time. Each spectrum was recorded at 20 min intervals. (D) Absorption spectra of silver nanoparticles prepared by (a) irradiation of thionine dye (10 $\mu$M) and (b) addition of $NaBH_4$ in toluene/ethanol (1:1) mixture. Concentration of $AgNO_3$ in both cases is 25 $\mu$M.

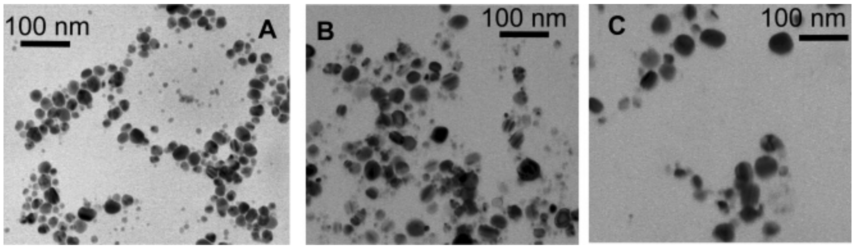

**Figure 2.** Transmission electron micrographs of silver nanoparticles obtained by visible light irradiation of 10 $\mu$M thionine dye containing 50 $\mu$M $AgNO_3$ in toluene/ethanol mixture (1:1) at different times: (A) 15, (B) 30, and (C) 90 min.

The plasmon resonance absorbance that represents Ag particle formation increases with continued visible photolysis. With increasing concentration of $AgNO_3$ we observe an increased rate of particle growth. When the concentration of $Ag^+$ was doubled (from 25 $\mu$M to 50 $\mu$M), the absorbance recorded after 60 min of photolysis was also doubled, thus indicating complete conversion of $Ag^+$ to $Ag^0$. However, when the concentration of $Ag^+$ was increased to 250 $\mu$M, the absorption growth became faster but the observed increase in the maximum absorbance was lower than expected. Since most of the dye (10 $\mu$M) is consumed at this high $AgNO_3$ concentration, the reduction of $Ag^+$ ions does not proceed to completion. Additional thionine is needed to promote the reduction of unreduced $Ag^+$ ions in solution. The spectral changes and transmission electron microscopic images of photolyzed samples with different $Ag^+$ concentrations are shown in the Supporting Information (Figure S2).

It is interesting to note that even with a 10 $\mu$M concentration of thionine we were able to reduce all the $Ag^+$ ions (25 or 50 $\mu$M) in 60 min. The complete conversion of $Ag^+$ ions was confirmed by comparing the absorption of silver nanoparticles formed by the reduction of silver nitrate using $NaBH_4$ as reducing agent. The absorbance of the 410 nm band was comparable in both cases (see Figure 1D). Whether we employ a direct reduction by $NaBH_4$ or a photochemical reduction method, we observe similar absorption changes. Furthermore, the results in Figure 1A show that only a small fraction of the dye is consumed in the formation of Ag seeds.

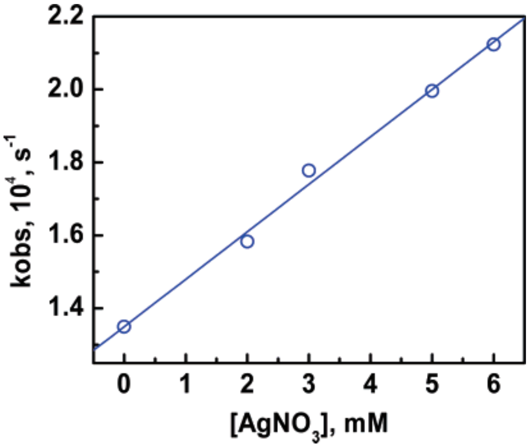

**Figure 3.** Dependence of pseudo-first-order decay rate constant of triplet thionine on $AgNO_3$ concentration in toluene/ethanol (1:1) containing $LiClO_4$ (5 mM) electrolyte.

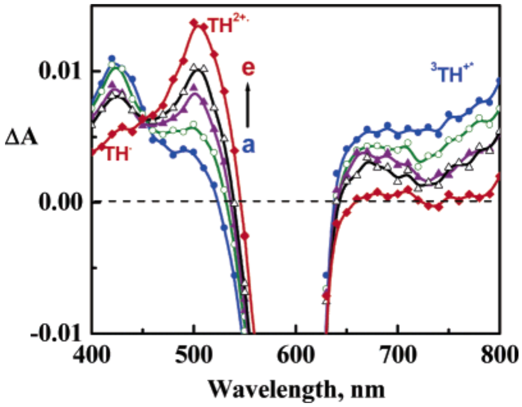

**Figure 4.** Time-resolved transient absorption spectra recorded (a) 5, (b) 10, (c) 15, (d) 20, and (e) 50 $\mu$s after 532 nm laser pulse excitation of deaerated toluene/ethanol (1:1) solution containing 10 $\mu$M thionine.

Further reduction of $Ag^+$ ions leading to the growth of the Ag particles is likely to be autocatalytic, perhaps ethanol acting as a sacrificial donor. The role of metal core in promoting the reduction of metal ions was discussed in earlier studies.[55−57]

We also carried out the steady state photolysis experiments in water, and to our surprise we failed to observe the formation of silver nanoparticles. The absorption spectra recorded at different photolysis times (Figure 1C) show only a small decrease in the dye absorption band. No evolution of plasmon absorption band could be seen even after photolysis of the sample for 2 h. Comparison of the results in Figure 1A,C show that the solvent polarity plays an important role in the dye-sensitized reduction of $Ag^+$ ions and formation of Ag nanoparticles. This important difference calls for further understanding of the photochemical processes leading to the formation of Ag nanoparticles.

**Transmission Electron Microscopy Characterization.** Silver nanoparticles formed during the visible excitation of the dye and $Ag^+$ ions (Figure 1A) were characterized by transmission electron microscopy (TEM). Figure 2 shows the TEM image of the silver nanoparticles formed at different photolysis times. The particles formed following 15 min of exposure are spherical in shape with 2−10 nm in diameter. The wide variation in the particle size distribution at early photolysis times is indicative of the formation of silver seeds during the early stages of photolysis. With increasing photolysis time we observe an increase in the particle size. The fully grown Ag particles after 90 min of photolysis exhibit a distribution of particles of ~20 nm diameter. Comparison of Figure 2A,C shows that the small Ag nanoparticles (<10 nm) are absent in long term photolyzed samples. The small particles formed in the initial stages of photolysis contribute to the particle growth via Ostwald ripening.

**Mediating Role of Excited Thionine.** As illustrated in Figure 1A, the formation of silver nanoparticles is initiated by the excitation of the dye with visible light. The excitation of thionine produces singlet and triplet excited states that are capable of undergoing electron-transfer reactions in the presence of electron donors or acceptors (reactions 1 and 2). For example, the reduction of excited thionine by amines has been shown to produce semireduced thionine.[58−60] The one-electron-reduction product further undergoes disproportionation to produce a stable two-electron-reduction product, leucothionine. On the other hand, if it is adsorbed on a semiconductor surface such as ZnO, the triplet excited dye is capable of injecting electrons and forming oxidized thionine.[61] In the absence of electron donor or acceptor, the dye triplet is also capable of undergoing self-quenching by ground state molecules. The ground state quenching occurs with a diffusion-controlled rate and proceeds with electron transfer in nonpolar media. The electron-transfer products (oxidized and reduced forms of thionine) formed in the self-quenching process (reaction 3) have been characterized in earlier studies.[54,62]

$$TH^+ + h\nu \rightarrow {}^1TH^+ \rightarrow {}^3TH^+ \quad (1)$$

$$^3TH^+ + D \rightarrow TH^{\bullet} + D^+ \quad (2)$$

$$^3TH^+ + TH^+ \rightarrow TH^{\bullet} + TH^{\bullet 2+} \quad (3)$$

In the present experiments, one can expect two different reaction pathways with which the dye excitation can result in the formation of silver nanoparticles. In the first case the $Ag^+$ ions can directly quench the triplet thionine and undergo reduction (reaction 4). In the second case, the anions formed in a self-quenching reaction can reduce the $Ag^+$ ions to produce $Ag^0$ (reaction 5).

$$^3TH^+ + Ag^+ \rightarrow TH^{\bullet 2+} + Ag^0 \quad (4)$$

$$TH^{\bullet} + Ag^+ \rightarrow TH^+ + Ag^0 \quad (5)$$

$Ag^0$ produced in either of these photoinduced processes can further grow to produce larger silver nanoparticles (Scheme

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(55) Janata, E.; Henglein, A.; Erschov, B. G. *J. Phys. Chem.* **1994**, *98*, 10888.

(56) Henglein, A. *Langmuir* **2001**, *17*, 2329.

(57) Shibata, T.; Bunker, B. A.; Zhang, Z. Y.; Meisel, D.; Vardeman, C. F.; Gezelter, J. D. *J. Am. Chem. Soc.* **2002**, *124*, 11989.

(58) Hatchard, C. G.; Parker, C. A. *Trans. Faraday Soc.* **1961**, *57*, 1093.

(59) Steiner, U.; Winter, G.; Kramer, H. E. A. *J. Phys. Chem.* **1977**, *81*, 1104.

(60) Bonneau, R.; Pereyre, J. *Photochem. Photobiol.* **1975**, *21*, 173.

(61) Patrick, B.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 1423.

(62) Kamat, P. V.; Lichtin, N. N. *J. Phys. Chem.* **1981**, *85*, 814.

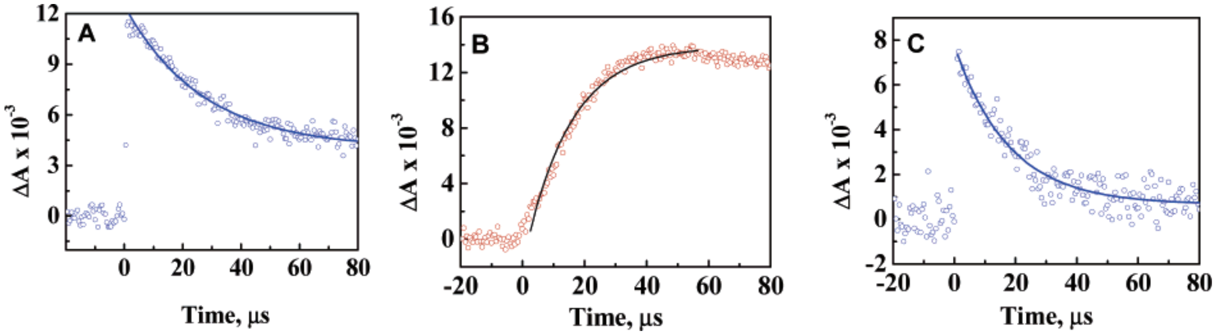

**Figure 5.** Absorption−time profile recorded at (A) 420, (B) 500, and (C) 700 nm following 532 nm laser pulse excitation of 10 $\mu$M thionine in toluene/ethanol mixture (1:1) medium.

1). Details on the growth of silver nanoparticles from silver seeds can be found in earlier studies.[35,63−65]

**Interaction of Dye Triplet with $Ag^+$ Ions.** To probe the direct interaction between the triplet excited thionine and $Ag^+$ ions, we excited the dye in the presence of $Ag^+$ ions. The triplet decay was monitored (700 nm) at different concentrations of $Ag^+$ ions. The reaction was carried out in the presence of $LiClO_4$ to maintain constant ionic strength. The $Ag^+$ at micromolar concentration level had little effect on the triplet excited state. Only a small decrease in the triplet lifetime is seen at millimolar concentration levels. The bimolecular quenching rate constant was determined from the dependence of observed pseudo-first-order decay on the concentration of $Ag^+$ using the relationship

$$k_{\mathrm{obsd}} = k_0 + k_q[\mathrm{Ag}^+] \tag{6}$$

The bimolecular quenching rate constant of reaction 4 as determined from the plot in Figure 3 was 1.30 (±0.06) × $10^6$ $M^{-1}$ $s^{-1}$. A relatively low triplet quenching rate constant of $Ag^+$ ions shows that the probability of reaction 4 is rather small in initiating the reduction process. Furthermore, the transient spectrum recorded at long times did not indicate formation of reduced dye. The absence of semireduced thionine ruled out the possibility of direct electron transfer from the triplet to $Ag^+$ ions (reaction 4) as the primary photochemical event leading to the formation of Ag nanoparticles.

**Self-Quenching Reaction of the Electron-Transfer Products.** Time-resolved transient absorption spectra of thionine in toluene/ethanol mixture (1:1) recorded after the 532 nm laser excitation is shown in Figure 4. The transient spectrum obtained 5 $\mu$s after the laser excitation shows absorption in the 400−450 nm region with a maximum centered at 420 nm and a broad band in the longer wavelength (<650 nm) region. The bleaching in the 600 nm region corresponds to the depletion of the ground state dye. These absorption changes which arise following laser pulse excitation are attributed to the triplet−triplet absorption of thionine. As the triplet absorption decays, new absorption bands emerge. The triplet absorption monitored at 700 nm decays completely within 50 $\mu$s, and the absorption band

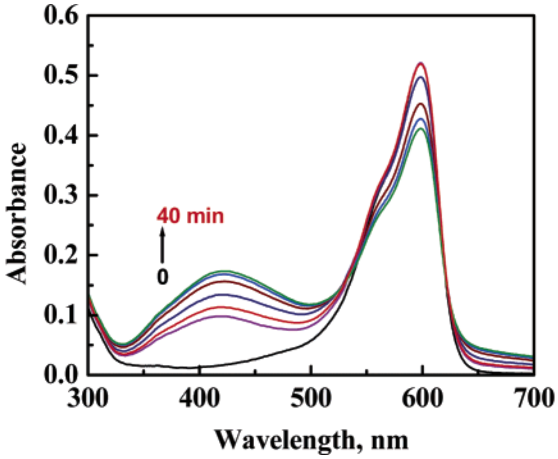

**Figure 6.** Formation of the silver plasmon band on irradiating aqueous solution of thionine dye (10 $\mu$M) containing $AgNO_3$ (50 $\mu$M) and TEOA (25 $\mu$M). The spectra were recorded at 5 min intervals.

corresponding to $TH^{\bullet 2+}$ at 500 nm grows during the same timeframe. In addition, a residual absorption at 420 nm is retained and this absorption is representative of the reduced form of thionine, commonly referred to as semithionine ($TH^{\bullet}$). These long-lived absorption features correspond to the electron-transfer products formed during the self-quenching of triplet excited thionine (reaction 3). The absorption−time profiles recorded at 420, 500, and 700 nm shown in Figure 5 represent the formation of these products during the decay of the triplet excited state.

From the pseudo-first-order decay dependence (monitored at 700 nm) on the concentration of ground state dye, we obtained a bimolecular rate constant of 4.9 (±0.1) × $10^9$ $M^{-1}$ $s^{-1}$. This high rate constant shows that the self-quenching is the dominant process producing reduced dye, which in turn can initiate the reduction of $Ag^+$ ions (reaction 5). The $Ag^0$ formed in these reactions has an absorption in the UV region.[35] Because of the strong overlapping absorption in the UV region, we were unable to monitor this initial transformation of $Ag^+$ to $Ag^0$ in our laser flash photolysis experiments. However, as confirmed from the steady state photolysis (Figure 1B), the growth of Ag nanoparticles can be followed by the increase in the surface plasmon band in the steady state photolysis experiments. It should be noted that a fraction of the dye gets sacrificed during the formation of Ag nanoparticles. In the absence of $Ag^+$ ions the oxidized and reduced forms of the dye recombine in the millisecond timeframe with minimal degradation of the dye in the long

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(63) Gutierrez, M.; Henglein, A. *J. Phys. Chem.* **1993**, *97*, 11368.

(64) Ershov, B. G.; Janata, E.; Henglein, A.; Fojtik, A. *J. Phys. Chem.* **1993**, *97*, 4589.

(65) Henglein, A.; Linnert, T.; Mulvaney, P. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1449.

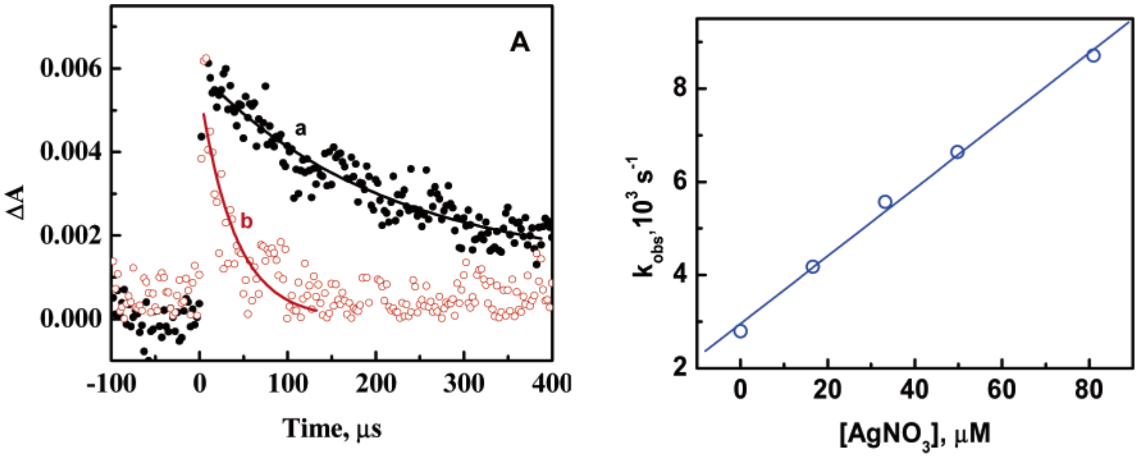

**Figure 7.** (A) Effect of $AgNO_3$ on decay of reduced thionine dye monitored at 420 nm. The semireduced dye was generated following 532 nm laser excitation of 10 $\mu$M thionine in the presence of 1 mM TEOA in aqueous solution (a) in the absence and (b) in the presence of 0.12 mM $AgNO_3$. (B) Dependence of $AgNO_3$ concentration on pseudo-first-order decay rate of semireduced thionine.

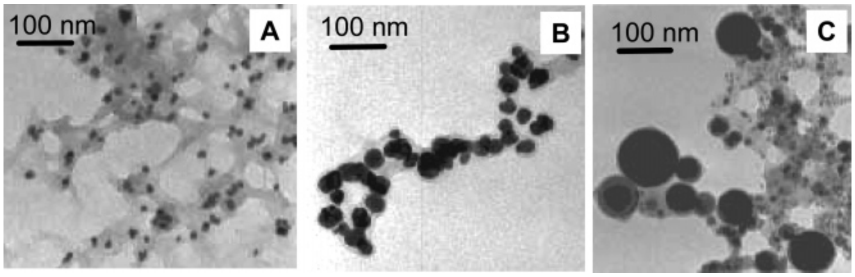

**Figure 8.** TEM images of Ag particles formed following 532 nm laser pulse excitation (10 Hz) of 200 $\mu$M thionine and 50 $\mu$M $AgNO_3$ in toluene:ethanol (1:1). The intensity of the laser pulse excitation was maintained at (A) 2, (B) 10, and (C) 20 mJ/pulse during the 90 s irradiation.

term irradiation experiments. When the $Ag^+$ ions are present the reduced dye transfers electrons, thus accumulating oxidized dye in the solution. This oxidized dye further undergoes irreversible changes as noted by the decreased absorption of thionine at 600 nm (Figure 1A).

When the same laser flash photolysis experiment was carried out in aqueous medium, the self-quenching process proceeded without the formation of electron-transfer products (see the comparison of transient spectra, Figure S3 in the Supporting Information). We observe only fast decay of the excited thionine triplet in aqueous solutions. As established in the earlier studies,[54,62] the electron-transfer yield of the self-quenching process is solvent polarity dependent and increases with decreasing solvent polarity. The absence of semithionine formation is the reason for not observing $Ag^+$ reduction in our steady state photolysis experiments.

**Photochemical Reduction of $Ag^+$ Ions in the Presence of an Electron Donor.** To support the mechanism involving the reduced dye in the reduction of silver ions, we introduced triethanolamine (TEOA) as an electron donor in the aqueous medium. TEOA is capable of intercepting the triplet excited state to produce semithionine by direct electron transfer (reaction 7).

$$^3TH^+ + TEOA \rightarrow TH^{\bullet} + \text{products} \qquad (7)$$

If indeed $TH^{\bullet}$ is responsible for initiating the reduction process, we should be able to induce photochemical reduction of dye with TEOA and observe the formation of Ag nanoparticles in our steady state irradiation experiments. The absorption spectra recorded following visible excitation of thionine (10 $\mu$M), $AgNO_3$ (50 $\mu$M), and triethanolamine (25 $\mu$M) at different times are shown in Figure 6. With continued irradiation time, we see the growth of a surface plasmon band at 420 nm, confirming the formation of Ag nanoparticles. The spectral evolution corresponding to the formation of Ag nanoparticles in Figure 6 is similar to the one observed in ethanol:toluene solution (Figure 1A). The only difference is the presence of an electron donor TEOA to produce $TH^{\bullet}$ by direct electron transfer (reaction 7). Blank experiments carried out in the absence of thionine or visible light did not produce silver nanoparticles.

We further probed the reaction between $TH^{\bullet}$ and $Ag^+$ (reaction 5) in the laser flash photolysis experiment. On a long time scale (400 $\mu$s), $TH^{\bullet}$ is the only species absorbing at 420 nm. The transient absorption of the semithionine was monitored at 420 nm following a 532 nm laser excitation in the absence and presence of TEOA. Comparison of the two traces (Figure 7A) shows a fast decay of $TH^{\bullet}$ in the presence of TEOA, confirming thereby electron transfer to $Ag^+$ ions. The observed decay rate constant of $TH^{\bullet}$ increased with increasing concentration of silver nitrate, and the bimolecular quenching rate constant was determined to be $7.3\ (\pm 0.3) \times 10^7\ M^{-1}\ s^{-1}$(Figure 7B).

Although the rate constant for the electron transfer between $TH^{\bullet}$ and $Ag^+$ is rather small, the long life of $TH^{\bullet}$ and relatively high concentration of $Ag^+$ make this reaction proceed under both laser and steady state photolysis conditions.

**Silver Particle Formation under Visible Laser Excitation.** One way to accelerate the formation of silver nanoparticles is to use high-intensity laser excitation. The 2 mm quartz cuvette containing thionine and $AgNO_3$ in toluene/ethanol was subjected to 532 nm laser pulse excitation (10 Hz) for 90 s. The concentration of the sensitizing dye, thionine, was kept at relatively high concentration (200 $\mu$M) to avoid any loss of the dye during laser excitation. The particles formed at different laser intensities are shown in Figure 8.

At lower laser excitation intensity (2 mJ/pulse) we observe smaller particles similar to the one observed in steady state photolysis experiments. The only difference is the short duration (90 s) required to obtain small particles. With increasing laser intensity we see an increase in the particle size. The increased number of incident photons is expected to generate more reducing species, thus creating a greater number of silver seeds. The increased concentration of silver seeds would facilitate the ripening of particles, producing bigger particles. Additionally, laser-induced fusion of particle aggregates is likely to contribute to the formation of silver nanoparticles. Laser induced fusion and fragmentation processes have been described previously.[66,67] The laser excitation thus provides a simple way to attain different size particles in a very short time.

The results presented here show how dye photochemistry can be manipulated to initiate the reduction of $Ag^+$ ions and produce 2−20 nm diameter silver nanoparticles. Whereas the self-quenching reaction is the dominant process to produce $TH^\bullet$ in nonpolar solvents, an additional electron donor (e.g., TEOA) is required to generate the reduced dye in polar solvents. Both these reactions proceed with the initial excitation of the dye thionine with visible light, ultimately yielding the same product, viz., Ag nanoparticles.

## Conclusions

Photoinduced reduction of $Ag^+$ ions is a simple and convenient way to produce silver nanoparticles of less than 20 nm diameter. Steady state and laser flash photolysis experiments confirm the mediating role of thionine dye in the Ag nanoparticle formation. The photochemically generated semithionine, $TH^\bullet$, serves as the primary reductant as it transfers electrons to $Ag^+$ ions with a rate constant of 7.3 $(\pm 0.3) \times 10^7\ M^{-1}\ s^{-1}$. By controlling the production of $TH^\bullet$, it is possible to control the growth of these particles. The dye molecule, which acts as a photosensitizer, also serves as the capping agent to protect the silver nanoparticles.

**Acknowledgment.** The work described herein was supported by the Office of Basic Energy Sciences of the US Department of Energy. This is Contribution No. 4611 from the Notre Dame Radiation Laboratory.

**Supporting Information Available:** Effect of oxygen on the photolyzed sample of $Ag^+$ and thionine in toluene/ethanol (Figure S1), and effect of $Ag^+$ concentration on the particle growth (Figure S2) and transient absorption spectrum in water (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0512777

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(66) Kamat, P. V.; Flumiani, M.; Hartland, G. *J. Phys. Chem. B* **1998**, *102*, 3123.

(67) Fujiwara, H.; Kanemoto, M.; Ankyuu, H.; Murakoshi, K.; Wada, Y.; Yanagida, S. *J. Chem. Soc., Perkin Trans. 2* **1997**, 317.