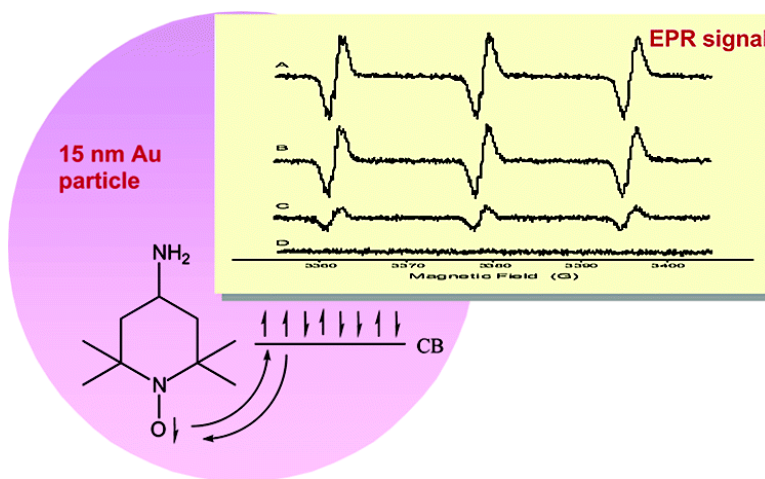


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## On the Interactions of Free Radicals with Gold Nanoparticles

Zhenyuan Zhang,<sup>†</sup> Alexander Berg,<sup>‡</sup> Haim Levanon,<sup>\*,‡</sup> Richard W. Fessenden,<sup>†</sup> and Dan Meisel<sup>\*,†</sup>

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**Abstract:** Electron paramagnetic resonance (EPR) spectroscopy was used to study the interactions between stable free radicals and gold nanoparticles. The nitroxyl free radicals used were TEMPO, TEMPAMINE, and TEMPONE. Two sizes of Au particles, 15 and 2.5 nm in diameter, were synthesized to investigate the interactions with the metallic particles. We find that the EPR signal is reduced upon adsorption of the radicals onto the 15 nm Au particle surface. Despite the strong adsorption of TEMPAMINE on the particles, the signal intensity recovers upon the introduction of a high concentration of ethanolamine to the solution. The signal reduction was proportional to the concentration of Au particles, and the signal totally disappeared at high concentrations of Au particles. Possible explanations of the signal reduction are discussed in this Article. We propose that the reduction in signal intensity arises from exchange interactions between the unpaired electrons of the adsorbed radicals and conduction-band electrons of the metallic particles. In addition, in the presence of oxygen, the adsorbed TEMPAMINE radicals are catalytically oxidized to the carbonyl derivative, TEMPONE. A mechanism for this unexpected catalytic reaction is proposed.

### Introduction

Nanoparticles are currently under intense investigation because of their unusual properties. It is generally anticipated, and verified in many instances, that materials in the nanosize regime yield size-dependent optical, electronic, and chemical properties advantageous in many applications.<sup>1–7</sup> As the size of a crystallite decreases to the nanometer range, a gradual transition from the bulk properties of the material to its molecular components is often observed.<sup>8</sup> For metals, for example, silver, it was shown that the redox potential of small metallic clusters is significantly more negative than the bulk metal and approaches the bulk value as the size reaches about 15 atoms.<sup>9</sup> On the other hand, magic numbers<sup>10</sup> of enhanced redox stability were observed for specific sizes. Unusually enhanced stability was recently reported for

Au<sub>55</sub>, which is particularly stable to oxidation.<sup>11</sup> As a consequence of the reduced size (and reduced dimensionality), the density of states and the spatial length scale of the electronic motion are also reduced.<sup>12</sup> The spectroscopic properties of metallic nanoparticles strongly depend on the identity of the species adsorbed on their surface.<sup>3,13–15</sup> The surface-plasmon band is particularly sensitive to the presence of electron donors and acceptors at the surface. Increasing the electron density in the particle surface leads to damping of the plasmon band and a blue shift in its energy. When a free radical is adsorbed at the particle surface, one may wonder whether the unpaired electron interacts with the metal conduction band and the consequences of such an interaction.

Despite the extensive studies of nanoparticles and the emphasis on optical and redox properties of the particles, data on the interactions of the particles with free radicals are rather scarce.<sup>16–18</sup> Electron paramagnetic resonance (EPR) spectroscopy can provide information on these interactions from measurements of the radical *g*-factors, its hyperfine interactions

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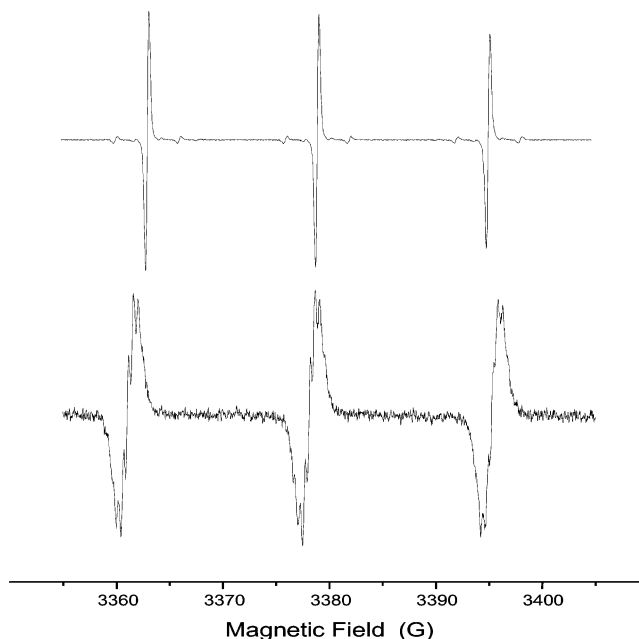
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with the surrounding atoms, and the line width of the transitions. This method may be utilized to study the physical and chemical properties of the nanoparticles themselves, as well as the processes that occur on their surfaces. Here we report on an EPR study of the interaction between stable nitroxyl radicals and gold nanoparticles of various sizes. The results show that radicals adsorbed on metallic nanoparticles escape EPR detection. This is attributed to signal broadening that results from the spin–spin exchange interaction between the unpaired electron on the radical and conduction-band electrons of the metallic particle. Moreover, and unexpectedly, we also discovered a catalytic oxidation reaction of the nitroxyl radical at the particle surface by molecular oxygen.

## Experimental Section

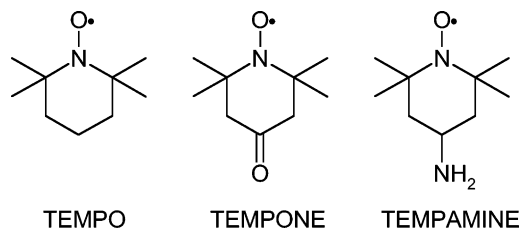
Large Au particles, 15 nm in diameter, were synthesized following the method of Turkevich and co-workers.<sup>19,20</sup> Briefly, 400 mL of water containing about 0.1 g of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (Aldrich) was heated to a boil, and 50 mL of 1% sodium citrate was added to the boiling solution under vigorous stirring. The solution was boiled for an additional 20 min, and the volume was adjusted to 500 mL after cooling. The obtained sol was concentrated by centrifugation to yield a suspension of  $3.4 \times 10^{-3}$  M Au. This stock solution was used to obtain the various concentrations of the large Au particles used in this study. Total Au concentrations used in these experiments were in the range  $(3.4\text{--}0.11) \times 10^{-3}$  M. The pH of all solutions was adjusted to 8.5–9.0 by dropwise addition of 0.05 M NaOH. After pH adjustment, the desired volume of  $(3\text{--}5) \times 10^{-3}$  M of the nitroxyl radicals, 4-R-2,2,6,6-tetramethylpiperidine, where R =  $\text{H}_2$  (TEMPO, from Aldrich), H and  $\text{NH}_2$  (TEMPAMINE, 97%, from Aldrich), O (TEMPONE, from Kodak), was added. All nitroxyl compounds were used as received. Because of the poor solubility of TEMPO and TEMPONE in water, solutions were prepared by first dissolving the radicals (but not TEMPAMINE) in ethanol and then adding water to yield  $\text{EtOH}:\text{H}_2\text{O} = 1:4$  by volume solutions. The pH of the solution was checked again and readjusted to 8.5–9.0 as needed by the addition of 0.05 M NaOH solution. The  $\text{pK}_a$  of TEMPAMINE is 9.5,<sup>21</sup> and thus a large fraction of the free amine in water is protonated in the experiments described here. Nonetheless, our experimental results demonstrate that TEMPAMINE strongly adsorbs at the particle surface despite the competing protonation. No change was observed in the plasmon band position of Au upon the addition of any of the TEMPO derivatives. The suspensions were saturated with the desired gas by bubbling air,  $\text{O}_2$ , or Ar for 10 min.

Small Au particles, 2.5 nm in diameter, were prepared following the radiolytic approach developed by Henglein.<sup>22</sup> An aqueous solution containing  $6 \times 10^{-4}$  M  $\text{NaAuCl}_4$  (99.99%, Alfa Aesar), 0.5 M methanol, and 0.01 M of the stabilizer poly(vinyl alcohol) (PVA, Mw 50 000–85 000, Aldrich) was deaerated by bubbling Ar, and then irradiated in a  $^{60}\text{Co}$ – $\gamma$  source for 25 min at a dose rate of  $9.3 \times 10^2$  krad/h. The desired amount of deaerated solution of the nitroxyl radicals was added to the Au sol, and the total concentration of the TEMPO or the other radicals was maintained at  $2 \times 10^{-6}$  M. The number of Au atoms per 15 and 2.5 nm particles is  $1 \times 10^5$  and 480, respectively. Thus, at complete adsorption of the nitroxyl, an average of 1.6 radicals adsorb on a small particle. In a few experiments, deaerated ethanolamine solution was added to deaerated Au–TEMPAMINE solution, and the suspension was sonicated for 5 min to displace the adsorbed radicals from the particle surface. The slow reappearance of the EPR signal was then monitored as a function of time.



**Figure 1.** EPR spectra of TEMPONE (upper) and TEMPAMINE (lower) nitroxyl radicals in Ar-saturated aqueous solutions. Microwave power 6 mW; amplitude modulation 0.205 G.

## Scheme 1. Structures of the Radicals Used in This Study



EPR spectra were taken on a Bruker ESP 380 spectrometer using a 50 kHz field modulation and 0.205 G amplitude modulation. EPR spectra were measured in 0.4 mm inner-thickness flat-quartz cells. UV–vis absorption spectra were taken on a Varian Cary 5 spectrophotometer. Particle size was determined by transmission electron microscopy as described previously.<sup>4</sup> The size distribution of the particles prepared here was  $\leq \pm 10\%$ .

## Results and Discussion

Formulas of the stable nitroxyl radicals used in this study are shown in Scheme 1. Figure 1 shows the spectra of the TEMPAMINE and TEMPONE radicals in the absence of gold with their well-documented magnetic parameters.<sup>23,24</sup> The  $g$ -factors of the various TEMPO derivatives in water are practically the same and equal to  $2.0055 \pm 0.0001$ .<sup>24</sup> The  $^{14}\text{N}$  hyperfine splitting values are 17.32, 16.13, 16.89 G ( $\pm 0.001$  G) for TEMPO, TEMPONE, and TEMPAMINE, respectively.<sup>23</sup> In air- or oxygen-saturated solutions, the EPR spectra were broadened due to exchange interactions of the radical with the paramagnetic oxygen, but their hyperfine splitting and  $g$ -factors did not change. Nonetheless, different results were obtained in the presence of  $\text{O}_2$  in the nanoparticle suspensions (see below).

TEMPAMINE was chosen for further experiments with gold suspensions because of the high affinity of the amine group to gold surfaces. In the presence of the gold particles, but in the

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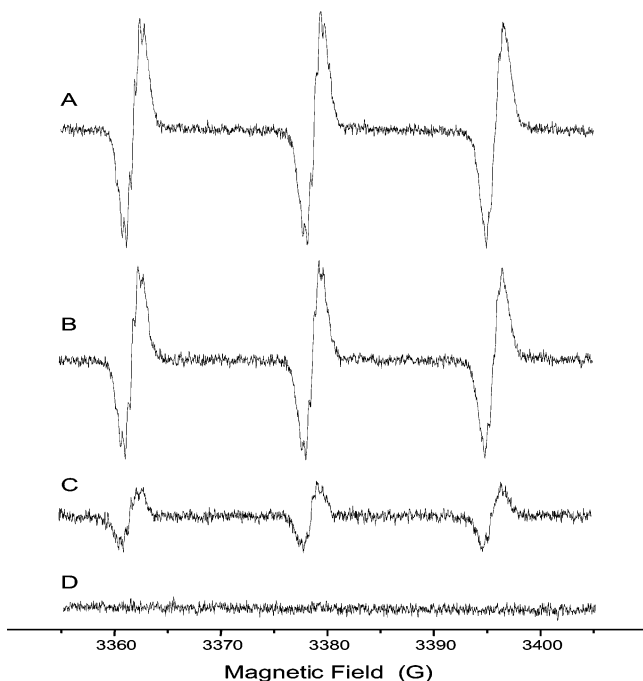
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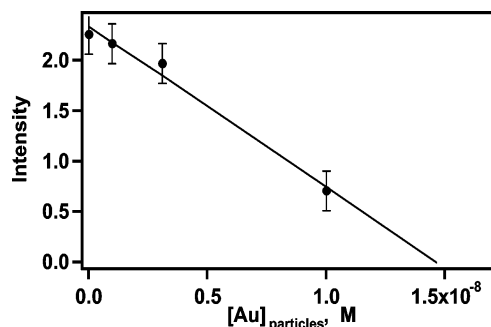
**Figure 2.** Effect of the concentration of 15 nm Au particles on the EPR spectra of TEMPAMINE ( $1.5 \times 10^{-5}$  M). (A)  $[\text{Au}] = 1 \times 10^{-4}$  M; (B)  $3 \times 10^{-4}$  M; (C)  $1 \times 10^{-3}$  M; (D)  $3 \times 10^{-3}$  M, in Ar-saturated solutions, under the same experimental conditions as those in Figure 1.

absence of oxygen, a significant reduction in the EPR signal amplitude of the radical was noticed. This reduction was proportional to the concentration of gold particles. At sufficiently high particle concentration, the EPR signal vanished altogether (Figure 2A–D). The possible destruction of the radicals at the particle surface by a chemical reaction was checked by addition of ethanolamine to the TEMPAMINE–Au solutions, as described in the Experimental Section (final concentrations:  $[\text{Au}] = 1.56 \times 10^{-3}$  M,  $[\text{TEMPAMINE}] = 1.35 \times 10^{-5}$  M,  $[\text{NH}_2(\text{CH}_2)_2\text{OH}] = 10^{-2}$  M). Approximately 95% of the signal intensity that was observed in the absence of gold was recovered. Therefore, the loss of signal intensity does not result from an irreversible reaction.

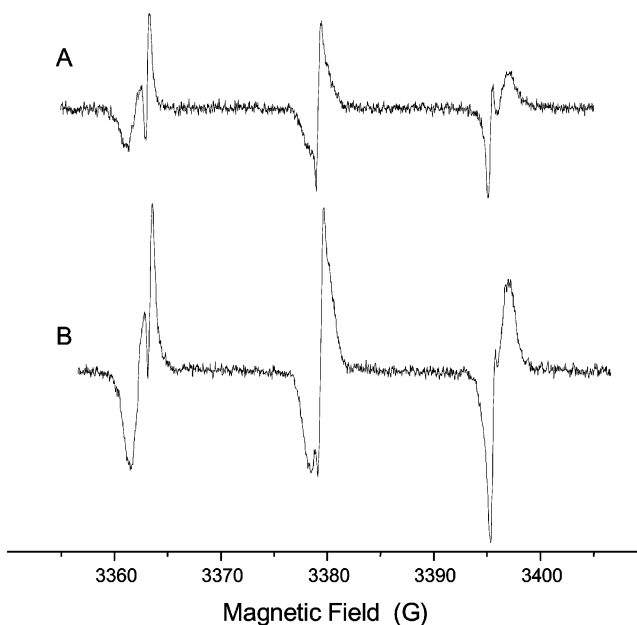
The adsorption of the radicals onto the particles is very strong. This is clear from the large amounts of ethanolamine needed to replace them. Assuming the adsorption–desorption equilibrium is strongly in favor of the bound state, the EPR signal intensity,  $I$ , is proportional to the concentration of particles according to eq 1:

$$I = I_o - \frac{s}{([\text{R}]_o/I_o)}[\text{Au}]_p \quad (1)$$

where  $s$  is the number of adsorption sites per particle,  $[\text{R}]$  is the concentration of the radicals, and the subscript  $o$  indicates the solutions in the absence of gold. The concentration of particles,  $[\text{Au}]_p$ , is calculated from the total gold concentration assuming the bulk density of the metal. Figure 3 shows the dependence of the EPR signal intensity on the concentration of particles. From the slope and intercept in Figure 3, one calculates  $s = 1050 \pm 75$  adsorption sites per particle. This constitutes approximately 10% of the Au-surface atoms in the 15 nm particles. From molecular models, we estimate the cross section of the radical to be approximately 0.31 to 0.14 nm<sup>2</sup> depending



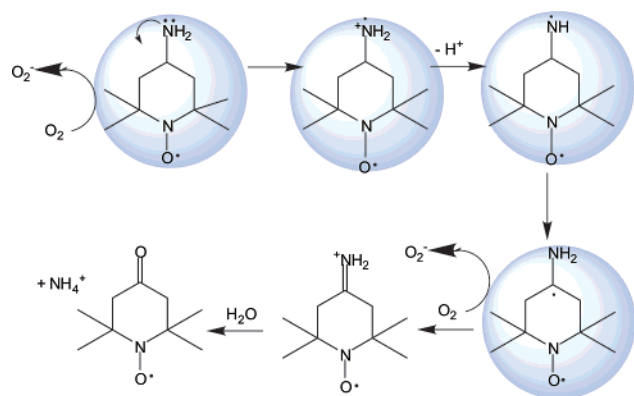
**Figure 3.** The dependence of the EPR signal intensity on the concentration of the 15 nm gold particles. Data points were taken from Figure 2.



**Figure 4.** EPR spectra of samples containing the following: (A) air-saturated solution containing  $1.5 \times 10^{-5}$  M TEMPAMINE and  $2.3 \times 10^{-3}$  M 15 nm Au particles; (B) air-saturated solution of  $1.5 \times 10^{-5}$  M TEMPAMINE and  $1.5 \times 10^{-6}$  M TEMPONE (no gold). Spectra were taken at the same experimental conditions as those in Figure 1.

on its orientation relative to the surface. Thus, up to 50% of the 15 nm particles surface area might be covered by the radicals.

In air-saturated solutions containing TEMPAMINE and gold particles, an additional EPR signal was generated along with the reduction in the signal intensity of the original radical. Figure 4A shows the appearance of this new radical a day after mixing TEMPAMINE with the suspension in the presence of air. The magnetic parameters of the new signal were identical to those of the well-documented TEMPONE radical.<sup>23,24</sup> The identity of the two radicals was confirmed experimentally by recording the spectra of a 10:1 mixture of TEMPAMINE and TEMPONE, without gold, under the same experimental conditions (Figure 4B). The similarity of these two spectra is apparent. Computer simulations of the experimental data showed that  $\sim 17\%$  of the initial TEMPAMINE in the suspension was converted to TEMPONE under the conditions of Figure 4A after 1 day. The simulation takes into account broadening of the radical signals due to O<sub>2</sub> in the presence of air, as well as the reduction of TEMPAMINE signal amplitude in the presence of the gold particles. It was verified that both oxygen and gold are required for this reaction to occur. The reaction does not take place in

**Scheme 2.** Proposed Autoxidation of TEMPAMINE on Gold Nanoparticles<sup>a</sup>

<sup>a</sup> The Au particle shown is meant to indicate the proposition that the radical adsorbs parallel to the surface via both the amine and the nitroxyl groups.

Ar-saturated gold–TEMPAMINE solutions or in air-saturated TEMPAMINE solutions that do not contain gold particles even after several days. Thus, it is concluded that the reaction is catalyzed by the gold particles. However, at this stage, it is not clear if adsorbed TEMPAMINE radicals or free radicals in solution are also involved in this catalytic reaction.

The observation of conversion of TEMPAMINE to TEMPONE was not reported previously. It requires conversion of the amine to carbonyl and release of the amine moiety from the piperidine ring. Similar reactions were observed for the autocatalytic oxidation of tertiary amines in aqueous solutions but at high oxygen pressures and elevated temperatures.<sup>25</sup> A similar mechanism may be proposed here (Scheme 2). Accordingly, the initial electron transfer to oxygen is catalyzed by the partial charge transfer from the amine to the metallic particle. This step initiates the radical reaction, which is the slow step in the absence of the catalyst.<sup>25</sup> Following release of a proton, a carbon-centered radical is formed. A second electron is then transferred to oxygen, which generates an iminium cation. Rapid hydrolysis of this group generates the ketone and releases an ammonium ion. Scheme 2 summarizes the proposed mechanism for autoxidation–dealkylation. The fate of the superoxide radicals that are generated along the mechanism has been discussed earlier.<sup>25</sup> In aqueous media, they probably proceed to produce hydrogen peroxide by well-established pathways. Reactions of superoxide with the rather reactive nitroxyl headgroup have been shown to regenerate nitroxyl radicals, both in oxidation and in reduction reactions.<sup>31</sup> Thus, it seems reasonable that only the amine headgroup is eventually oxidized. It should also be noted that, even though electron transfer steps are invoked in the reaction scheme, the reaction is rather slow, and the increase in charge density in the particles due to the reaction is not expected to be noticeable in the Au plasmon absorption band. Whereas the various steps of the above outlined mechanism are all well established, further verification of the

mechanism is beyond the scope of this study; other pathways may be invoked. Nonetheless, it is clear that the nanoparticles catalyze significantly the autoxidation reaction.

In addition to adsorbed TEMPAMINE, TEMPONE radicals are also adsorbed on the particle surface. A significant reduction (by  $\sim 60$  times) of the TEMPONE EPR signal was observed in the system containing  $1.5 \times 10^{-5}$  M of the radical and  $3.4 \times 10^{-3}$  M suspension of these Au particles. Under the same conditions, the TEMPAMINE signal entirely disappears. This observation suggests that, while adsorption of TEMPONE radicals does occur, the equilibrium constant in that case is smaller than that of TEMPAMINE. The adsorption of TEMPONE suggests that TEMPAMINE adsorbs flat parallel to the surface as shown in Scheme 2.

The reduction of the EPR signal of the radicals in the presence of Au particles (but in the absence of oxygen) requires some rationalization. Several mechanisms were considered in an effort to explain these observations:

(1) Immobilization of the radical on the particles can entirely broaden the EPR signal due to loss of the averaging free tumbling of the radicals at the surface. Several observations rule out this mechanism. TEMPO derivatives attached covalently to C<sub>60</sub> (diameter  $\approx 1$  nm) exhibit EPR signals even at low temperatures down to 100 K in toluene and dichlorobenzene glasses.<sup>26</sup> If the adsorption is via the amine group and the ring is perpendicular to the surface, then the nitroxyl end of TEMPAMINE is located  $\sim 0.75$  nm away from the gold surface and should not undergo stronger restriction of free rotation than in these cases. Moreover, the reduction of the EPR signal upon increasing the gold concentration is identical for all three hyperfine components of the spectrum. The hindered-tumbling broadening mechanism should affect the signal amplitude and line width of the various components asymmetrically.<sup>27,28</sup> Nitroxyl radicals attached to 1–3 nm Au nanoparticles coated with dodecanethiol do exhibit EPR spectra, albeit somewhat broadened.<sup>18</sup> Finally, if adsorption of the nitroxyl completely halts free rotation of the radical relative to the particles, the radical will rotate at the same speed as the particle. For the small particles described in the following section,  $r = 1.25$  nm, a rotational-diffusion time of 1 ns can be calculated from the Stokes–Einstein equation. This corresponds to approximately a 1 G line width according to the calculations and experimental observations of Freed and co-workers.<sup>29</sup> Because the line width of the radicals observed above is in the range from 0.3 (deaerated TEMPONE solutions) to 2.2 G (TEMPAMINE in the presence O<sub>2</sub>), broadening by this mechanism is not expected to mask the nitroxyl signal.

(2) A spin–spin interaction between several radicals adsorbed on the same gold particle may completely broaden the signal. To check whether this mechanism is the cause for the decreased signal intensity, a similar experiment was performed with small particles of 2.5 nm diameter. No EPR signal was observed in the experiments, where a  $6 \times 10^{-4}$  M suspension of Au particles contained  $2 \times 10^{-6}$  M TEMPAMINE. In this case, an average of 1.6 TEMPAMINE radicals were present on a particle. Assuming a random distribution of the radicals among the particles, one can calculate the various populations of radicals per particle using the Poisson–Boltzmann statistics. At an average of 1.6 radicals per particle,  $\sim 32\%$  of the particles contain only one radical, while 26% of the Au particles contain

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two radicals, that is, at 2.5 nm apart on the average. Yet, in this system, where spin–spin interaction between the radicals is expected to be negligible, the EPR signal of TEMPAMINE is not observed. Therefore, this mechanism is also ruled out.

(3) An irreversible chemical reaction at the gold surface may eliminate the radicals. This possibility is ruled out, because the addition of ethanolamine results in essentially full recovery of the signal as described above.

(4) The EPR signals vanish because of an electronic interaction between the radicals and the particle. Because the absorption spectra of the Au surface-plasmon band remain unchanged upon adsorption of the radicals, the electron density at the surface remains essentially unchanged. Thus, partial transfer of the unpaired electron from the nitroxyl radical to the particle is not believed to be the cause for the observed signal loss. Freed and co-workers<sup>30</sup> observed loss of EPR signals from the nitroxyl radicals adsorbed on flat metallic surfaces and attributed it to exchange interactions between the unpaired electrons and conduction-band electrons of the metal. We propose a similar mechanism to rationalize the loss of EPR signals in the particle suspensions. This interaction probably contributes to the enhanced adsorption of the radicals relative to analogous molecules. Coating Au nanoparticles with protecting agents can insulate the radicals from the metal and prevent electron exchange between the spin labels and the conduction band. Under such circumstances, the EPR signal is observable.<sup>16,18</sup>

As mentioned above, addition of TEMPAMINE to a colloidal solution of 2.5 nm Au particles ( $[Au] = 6 \times 10^{-4}$  M and  $[TEMPAMINE] = 2 \times 10^{-6}$  M) resulted in complete loss of the EPR signal. Addition of ethanolamine (final concentration 0.01 M) to this solution changed its color from red into purple, indicating agglomeration of the particles. The EPR signal, however, did not recover even after 48 h and after 5 min of sonication. These findings imply stronger binding of the

TEMPAMINE radical to the small gold particles than to the larger ones. Nonetheless, introduction of air to this sample led to partial oxidation of the small (but not the large) particles. The radicals then were released back to the solution, and the EPR signal of TEMPAMINE reappeared. Similarly, no signals were observed in the samples containing either TEMPONE or TEMPO in the presence of the small gold particles. Thus, similar to the large particles, adsorption of the nitroxyl radicals onto the small particles occurs even in the absence of the amine group.

## Conclusion

Stable paramagnetic probes were used to study the interaction of gold nanoparticles and radicals. Adsorption of nitroxyl radicals occurs for all radicals studied here and results in loss of the EPR signal. It is suggested that the exchange interaction of the unpaired electrons with conduction-band electrons of the metallic particle completely eliminates the signal of the adsorbed radicals. In addition, it was discovered that a catalytic reaction in which TEMPAMINE is oxidized to TEMPONE occurs at the particle surface when oxygen is present in the solution.

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