p-Benzosemiquinone Radical Anion on Silver Nanoparticles in Water

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Quinones are widely dispersed in plant and animal cells as coenzymes and act as electron acceptors in crucial biological processes such as photosynthesis and respiration.[1−5] Chemical systems comprised of quinones have been devised for inducing light-driven electron transfer and charge separation, with the objective of converting solar energy into chemical energy.[5] Aqueous silver clusters (Ag_n) are capable of transferring electrons to suitable acceptors.[6] Surface-enhanced Raman scattering (SERS) provides an extremely sensitive tool for investigating the structure and chemistry of the radical intermediates produced in this process. This communication reports the SERS observation of *p*-benzosemiquinone radical anion ($Ag_n^+Q^-$) produced by one-electron reduction of *p*-benzoquinone on aqueous Ag nanoparticles.

SERS studies have been performed previously on chemical transients produced by electrochemical methods on metal electrodes and by laser photolysis on solid metal surfaces.[7,8] The nanosize particles are reactive species with physicochemical properties quite distinct from those of the bulk.[6] The SERS observation of radical intermediates produced by electron-transfer reactions involving hydrated Ag nanoparticles is rare.

The resonance Raman (RR) spectra and structure of the *p*-benzosemiquinone radical anion[2−4,11] provide valuable references for identifying this radical by its vibrational characteristics in the SERS spectrum. The RR spectra of aqueous $Q^{-•}$ are characterized by a symmetric CO stretching vibration (Wilson mode 7a), observed at 1435 cm^{-1}, and a ring stretching (central CC bonds) vibration (Wilson mode 8a) at 1620 cm^{-1} (Figure 1A and B). The corresponding vibrations in *p*-benzoquinone are 1666 and 1639 cm^{-1},[4] respectively. Both vibrations are totally symmetric in $Q^{-•}$ (D_{2h} symmetry) and are strongly coupled to each other. The radical has another totally symmetric vibration in the 1000−1800 cm^{-1} region, a CH bending mode (Wilson mode 9a) observed at 1161 cm^{-1}. These three vibrations are strongly resonance enhanced on Raman excitation in resonance with the strongly absorbing 430 nm ($^2B_{2g} \rightarrow {}^2B_{3u}$) transition of the radical (Figure 1A). When excitation is in resonance with a weak electronic transition, $^2B_{2g} \rightarrow {}^2A_u$, absorbing in the 340−400 nm region, two nontotally symmetric vibrations at 1472 (ring stretch, Wilson mode 8b) and 1271 cm^{-1} (CH bend, Wilson mode 3) are also enhanced (Figure 1B) due to vibronic coupling between the excited $^2B_{3u}$ and ^2A_u electronic states.[2,3] Because of the high symmetry of $Q^{-•}$ and the distinct nature of the CO stretching frequency (∼1450 cm^{-1}), as compared to that in quinones (>1650 cm^{-1}) and hydroquinones (<1300 cm^{-1}),[4] the radical is readily distinguishable from the closed-shell molecules related to it.

The colloidal silver in aqueous solution was prepared using the standard citrate reduction method.[12] A 5 mM $AgNO_3$ solution in triply distilled, deionized water was heated to boiling. Sodium citrate at 4 mM concentration was added to the solution, and the mixture was heated for about 20 min and cooled while being stirred continuously. The prepared solution exhibited a broad absorption spectrum, with maximum absorbance at 420−440 nm. It should
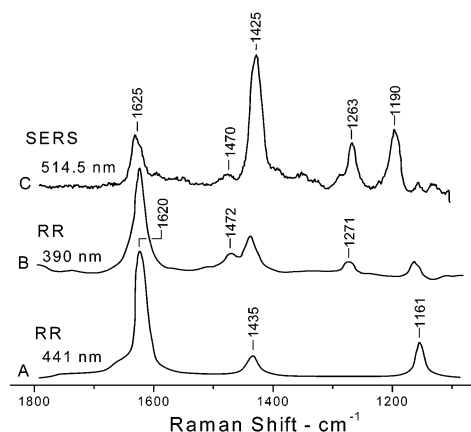
Figure 1. Time-resolved Raman spectra of *p*-benzosemiquinone anion radical prepared by pulse radiolytic oxidation of hydroquinone. (A) 441 nm excitation. (B) 390 nm excitation. (C) Surface-enhanced Raman spectrum of *p*-benzoquinone anion bound to silver nanosize clusters ($Ag_n^+Q^-$) in water.

be noted that this absorption is isoenergetic with the $Q^{-•}$ absorption (430 nm). The samples for recording the SERS spectra were prepared by adding 0.001−0.01 M of *p*-benzoquinone or quinhydrone to the colloidal solution. The addition of a small amount of NaCl (about 10 mM) to the sample facilitated the SERS observation. The pH was adjusted by an aqueous solution of NaOH, when desired. The procedure used here produces Ag clusters of 100−150 nm average size. The SERS spectra were excited by an argon ion 514.5 nm laser line operated at 25 mW power and detected with a Renishaw (RM1000) Raman spectrometer, equipped with a confocal microscope, a 2400 g/mm grating that gave a precision of ∼1 cm^{-1} in Raman peak positions, and a cooled CCD detector. The spectral calibration was repeatedly checked using known Raman lines of CCl_4 and toluene. The band positions were reproduced to within less than ±2 cm^{-1}.

The 514.5 nm Raman spectrum of an aqueous solution saturated with 10 mM *p*-benzoquinone, or a solution of quinhydrone (Q, QH_2), barely showed the 7a C═O stretching band at 1666 cm^{-1}. In quinhydrone solution, Q and QH_2 are in equilibrium with $Q^{-•}$ ($Q + QH_2 \leftrightarrow 2Q^{-•} + 2H^+$). However, the concentration of $Q^{-•}$ in solution is significant only in basic solutions, although the radical then becomes unstable.[11] The presence of $QH^•$ or $Q^{-•}$ could not be detected in the Raman spectrum of this solution excited at 514.5 nm. On addition of 2−10 mM *p*-benzoquinone or quinhydrone to the Ag colloid solution (pH 6.8), very intense bands appeared at 1625, 1425, 1263, and 1190 cm^{-1} (Figure 1C). These bands are not present in *p*-benzoquinone or its doubly reduced hydroquinone state. The observation of the same Raman signals with quinhydrone (intensity does not increase on addition of base) and *p*-benzoquinone shows that they do not arise due to the radical produced in solution that subsequently bonds with Ag_n on its surface. Raman measurements were made 10 min to 24 h after preparation of the samples,

with no change in observed spectral features. These signals were not seen when Raman spectra were recorded on a colloid solution containing >10 mM hydroquinone (QH_2), and on addition of a small amount of NaOH to the sample to raise the pH above 11. We failed to detect the Raman signals attributable to QH_2, Q^{2-}, or $Q^{-\bullet}$. It is evident that the spectrum in Figure 1C is due to a reaction product of Q adsorbed on the Ag particle surface.

Comparison of the spectrum in Figure 1C with the RR spectra of aqueous $Q^{-\bullet}$ given in Figure 1A and B readily identifies the prominent SERS bands in Figure 1C with the surface-bound $Q^{-\bullet}$ ($Ag_n^+Q^-$). The similarities in the 514.5 nm SERS spectrum and the 390 nm RR spectrum are particularly striking. It is clear that the radical is produced on reduction of p-benzoquinone at the metal−water interface. The enhancement pattern in the 514.5 nm SERS spectrum is quite different from the 441 and 390 nm RR spectra of $Q^{-\bullet}$, given in Figure 1. It is the CO stretch that is very strongly enhanced in the SERS spectra (1425 cm^{-1} band, Figure 1C), while it is the 8a ring stretch (stretching of the central ring CC bonds) that represents the most prominent band (1620 cm^{-1}, Figure 1A and B) in the RR spectra. This contrast in enhancement pattern is quite significant from the perspective of the SERS mechanism. Resonance or preresonance Raman with the electronic transition involving a CT state is supposed to contribute toward SERS. While the origin of the CT state has been treated theoretically, it has been difficult to observe it directly. In the present case, the ground electronic state itself is a CT state. If a RR mechanism is contributing toward the SERS, the CO bonds in the resonant excited electronic state of $Ag_n^+Q^-$ must be drastically different from those of $Q^{-\bullet}$ (bond order $\approx$ 1.5); that is, they must be close to either double bonds, as in p-benzoquinone (Q), or single bonds, as in hydroquinone (Q^{2-}). The vertical energy difference between $Q^{-\bullet}$ (ground state $^2B_{2g}$) and Q ($^1A_{1g}$) is estimated to be <2.0 eV.[2] The low lying strongly allowed excited states of $Q^{-\bullet}$ (e.g, $^2B_{3u}/^2A_u$ states corresponding to 370−450 nm absorption) are higher than 2.0 eV and comparable with the plasmon excitation energy. Therefore, an efficient transfer of electron from $Q^{-\bullet}$ to Ag_n would occur on excitation of $Q^{-\bullet}$, Ag_n, or both. In other words, a resonant/preresonant excited state of $Ag_n^+Q^-$ can be readily visualized in which the adsorbed species is structurally similar to the ground electronic state of Q $\{Q^{-}(^2B_{3u}/^2A_u) \rightarrow Q(^1A_{1g}) + e^-\}$ (the $^1A_{1g}$ state need not be in its equilibrium configuration), and not to the $^2B_{3u}$ excited state of aqueous $Q^{-\bullet}$. Thus, the intensity pattern in the SERS spectrum of $Ag_n^+Q^-$ can be understood in terms of resonance Raman involving the ground and excited electronic states of $Ag_n^+Q^-$, which are similar to the ground electronic states of $Q^{-\bullet}$ and Q, two well-studied states of p-benzoquinone. We believe the experimental information presented in this work (SERS and RR) will be valuable for testing the quantitative theoretical predictions of the CT mechanism of SERS.

The 7a CO frequency in $Ag_n^+Q^-$ is 10 cm^{-1} lower and the 8a ring frequency 5 cm^{-1} higher than the corresponding frequencies in aqueous $Q^{-\bullet}$. The solvent interactions, such as hydrogen bonding on oxygen sites in water, decrease the 7a frequency and increase the 8a ring frequency as compared to frequencies in acetonitrile (1609 cm^{-1}).[4] Stronger chemical interactions than water, such as that of H_3O^+, further decrease the 7a frequency by 35 cm^{-1} and

increase the 8a frequency by 24 cm^{-1}, as compared to those in water.[3,13] The CO frequency of $Ag_n^+Q^-$ suggests that the chemical interactions experienced by the oxygen atoms are stronger than that of bulk water on $Q^{-\bullet}$, but weaker than that of protons. The CO frequency in $Ag_n^+Q^-$ is consistent with the oxygen atoms interacting with the silver surface via a positively charged Ag^+ counterion. The upward shift in the 8a ring frequency occurs due to mechanical coupling between the stretching motion of the central CC bonds of the ring and the CO bonds. The frequency of the 9a CH bending mode is very sensitive to the chemical environment of the radical (1143 cm^{-1} in acetonitrile; 1161 cm^{-1} in water). A significant increase in the frequency of this vibration in $Ag_n^+Q^-$, as compared to that of aqueous $Q^{-\bullet}$, is consistent with the stronger interaction on the radical in the surface environment.

The time-resolved SERS studies on radical intermediates produced by chemical, photochemical, and radiation-chemical methods are difficult to perform because of fragmentation of metal clusters by high power pulsed lasers and the redox reactions induced by the surface.[11,14] On the other hand, the tremendous detection-sensitivity attainable by SERS on molecular species adsorbed on 100−200 nm size metal clusters in water[9,10] should allow for the investigation of the reactive behavior of radical species at extremely low concentrations, often encountered in biochemical systems or in chemical and biochemical effects of low-level ionizing radiation. The redox potentials ($E°$) of Ag_n^+/Ag_n (0.79 eV) and $Q/Q^{-\bullet}$ (0.09 eV) couples[6,15] suggest a SERS detection sensitivity of better than $\sim$5 $\times$ 10^{-8} M for $Q^{-\bullet}$ bound to the surface of Ag nanoparticles in water in the present experiments.

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