Capture of Charge Carriers at the Silica Nanoparticle−Water Interface

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Aqueous suspensions of methyl viologen, MV^{2+}, adsorbed onto silica nanoparticles were irradiated using pulse radiolysis, and the yield of the radical cation was determined. It is shown that the yield of MV^+ increases upon increasing the weight percent of SiO_2 in the sample. This increase parallels the increase in the yield of hydrated electrons that was previously observed to result from an increase in the absorbed dose by the silica particles. The increase in adsorbate abundance at the surface changes the surface-charge density, but it is shown that the increase in the yield is not merely due to changes in the surface potential; an acceptor state at the surface is required. However, the possibility that the presence of an acceptor at the interface affects charge separation within the particle cannot be dismissed.

Introduction

Radiation-induced chemical processes in the solid phase are reasonably well understood[1]. Ultrabandgap excitation of metal oxide materials, for example, generates electrons and holes, the majority of which rapidly recombine. The remaining charge carriers become localized in discrete energy levels within the bandgap. These traps are often identified as chemical impurities, lattice defects, or surface states. However, when the solid phase is a component of a heterogeneous system, another pathway becomes available to the charge carriers: migration across the interface into the neighboring phase. Systematic reports on this interfacial charge-transfer process are scarce.

Redox chemistry has been shown to occur in irradiated systems consisting of molecules adsorbed on high surface area metal oxides[2] These studies have been generally performed at solid−vacuum interfaces where charge transfer to surface-adsorbed molecules is believed to result from a reaction with surface-trapped charge carriers. This proposition can be verified by the fact that addition of adsorbates either before or after irradiation results in the formation of characteristic radical ions.

The solid−liquid interface offers an important, yet relatively unexplored, avenue for energy dissipation. Migration of charges, either kinetically hot carriers or thermalized free electron/hole carriers, into the liquid phase and their subsequent trapping by solvation may constitute a significant relaxation mechanism. In previous studies we reported on the production of hydrated electrons, e^-_{aq}, and hole products upon direct absorption of radiation by silica particles in heavily loaded aqueous suspensions of SiO_2 nanoparticles.[3,4] It was shown that the action of radiation energy on the nanoparticles is as efficient in generating e^-_{aq} as the absorption of energy by water. Electrons were observed to escape silica particles of up to 22 nm in diameter at loadings as high as 50 wt % SiO_2. On the other hand, holes were observed to remain trapped in the same particles down to 7 nm in diameter.

Aside from fundamental interest, the transfer of radiolytically generated charge carriers across a solid−liquid interface is of great technological concern. Applications include such issues as the radiation-induced catalytic transformation of pollutants in heterogeneous ecosystems, storage of high-level nuclear materials, and corrosion of solid surfaces in nuclear plant cooling systems.[5−7]

We report here on the capture of electrons as they escape into the aqueous phase at the silica nanoparticle−water interface. The electron that is initially generated in the particles is energetically very hot. Furthermore, the conduction band of silica is energetically very high, near the free electron vacuum level.[8] Therefore, a broad spectrum of electron energies in SiO_2 could allow their trapping as hydrated electrons in the aqueous phase, 1.6 eV below the vacuum level. However, highly energetic electrons are unlikely to be trapped by surface-adsorbed acceptor molecules. We show that all of the electrons that cross the interface can be captured at the particle surface. It is also demonstrated that the effect of surface charge density on electron escape yields is very small. Nonetheless, it is suggested that the presence of the acceptor at the interface may affect the escape probability.

Experimental Section

Pulse radiolysis experiments were performed using 2−3 ns pulses of 8 MeV electrons from the Notre Dame linear electron accelerator (TB-8/16-1S linac). Details of the linac, the spectrophotometric detection setup, and the computer-controlled data acquisition and detection systems are described elsewhere.[9] Irradiations were carried out at room temperature in quartz cells of 1 cm path length. The concentration of e_{aq}^- generated was $(2-3) \times 10^{-6}$ M per pulse as determined by the SCN^- dosimeter. Early experiments were performed at the linac of Argonne National Laboratory with substantially similar results.

Two stock Ludox colloidal silica suspensions (SM-30, 30 wt % SiO_2 suspension in water at pH 10.2 with an average particle diameter of 7 nm; HS-40, 40 wt % SiO_2 suspension in water at pH 9.7 with an average particle diameter of 12 nm; Aldrich) were used. All other chemicals, including methyl viologen (MV^{2+}) dichloride hydrate, were of highest purity commercially available and used as received. Ludox colloidal silica suspen-

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sions contain an organic stabilizer.[10] This impurity is reactive toward both OH radicals and hydrated electrons. The reactivity toward the primary radicals was confirmed by observing the production of MV^+ in an N_2O-saturated suspension, where all hydrated electrons are converted to OH. Several hours of dialysis against 0.175 M $NaClO_4$ solution at pH 10 eliminates this reaction completely, and further dialysis up to a week makes no difference. On the other hand, the half-life of e^-_{aq} in the deaerated suspensions is rather short ($\sim$300 ns [4]). Yet dialysis for over a week makes little improvement on its lifetime. Most of the reactions investigated in this study occur on a fast time scale ($<$200 ns) where neither reaction with impurities interferes. Therefore, most of the solutions described in this study were not dialyzed.

Various suspensions of SiO_2 concentrations were prepared by diluting the commercial stock solutions with water from a Millipore purification system. For labeling of the silica particles with the acceptor molecules, concentrated aqueous solution of the acceptor was added dropwise into the silica solutions under vigorous stirring at room temperature. Electrolytes were added to the suspensions in a similar fashion. Solutions were degassed by purging with high-purity nitrogen or nitrous oxide and sealed just prior to use.

Results and Discussion

Reduction of Methyl Viologen in Colloidal SiO₂. In water the reaction of e^-_{aq} with MV^{2+} to produce the corresponding radical cation has been thoroughly studied.

$$e^-_{aq} + MV^{2+} \rightarrow MV^+ \tag{1}$$

The rate constant is $k_1 = 6.7 \times 10^{10}$ M^{-1} cm^{-1} at pH 9.7.[11] As previously demonstrated, in the radiolysis of aqueous silica particles there are two sources for e^-_{aq}, the ionization of water and the ionization of SiO_2.[4] To analyze the interaction of those electrons escaping from the silica nanoparticles with surface-adsorbed MV^{2+}, it is necessary to distinguish between e^-_{aq} from these two origins. The experiments described below were designed to make that distinction.

Hydroxyl radicals (OH) have been shown to react with MV^{2+} to form a relatively stable OH adduct whose optical absorption peaks at 470 nm ($\epsilon \approx 14\,000$).[12,13] No evidence for this product could be found in solutions of MV^{2+} and aqueous colloidal silica, even in N_2O-saturated solutions. Apparently, OH radicals (or holes from SiO_2) do not react with MV^{2+} under the experimental conditions discussed here on the relevant time scale ($\leq$100 ns). The primary reason for the sluggish reaction of OH and its products with MV^{2+} is the reduced concentration of the latter in the bulk of the solution (vide infra). It was previously shown that the holes from silica could not oxidize water to OH radicals.[3] On the other hand, OH radicals that result from direct ionization of water are scavenged by the organic impurity that is present in the commercial product, as discussed above in the Experimental Section.

The hydrogen atom addition reaction to MV^{2+} has also been characterized in aqueous solution.[14,15] H addition is thought to take place at the nitrogen as well as the ring carbon atoms. The H adduct on the N atom of MV^{2+} exhibits the same absorption spectrum as MV^+. However, the rate constant for this reaction is 2 orders of magnitude slower than the electron-scavenging reaction and is not expected to interfere on the time scales ($\leq$100 ns) of interest here.
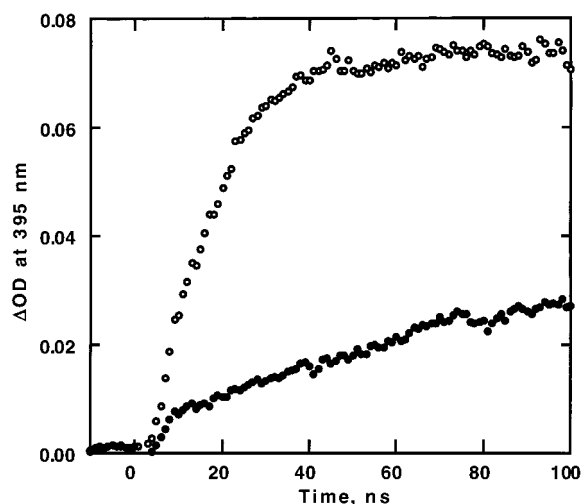

Figure 1. Transient absorbance of the methyl viologen radical cation in deaerated neat water (○) and a 36.8 wt % SiO_2 (●) aqueous suspension. $[MV^{2+}] = 1$ mM; particles are 12 nm in diameter.

Time-resolved absorption measurements of MV^{2+} reduction in aqueous colloidal silica, following pulsed irradiation, result in spectra that are identical to those obtained from neat aqueous MV^{2+} solutions.[16,17] They are the same as those reported in the literature, but the radical is obtained from the adsorbed molecule. The presence of SiO_2 particles significantly slows the rate of the reaction between MV^{2+} and e^-_{aq}. Figure 1 demonstrates this strong attenuation effect in a solution containing a high concentration of silica particles. Whereas the reaction rate is significantly lower, the final yield of MV^+ at the end of the reaction of e^-_{aq} (not shown) is higher in the silica-containing suspensions than in neat water solutions. The larger MV^+ absorbance in the solution containing colloidal SiO_2 results from the increased concentration of e^-_{aq} in the radiolysis of the suspensions compared to water as previously reported. We show below that the rate of the reaction is controlled by the approach of e^-_{aq} to the particles and not by release of MV^{2+} to the bulk.

At high pH values aqueous colloidal silica particles are negatively charged.[18] Because of the high negative surface charge density, positively charged species are strongly adsorbed to the surface of the particles via Coulomb attraction. Previously reported binding studies, performed on systems of 4 nm silica particles with cationic electron acceptors, suggest that the number of binding sites is $\sim$0.6−1.3 per nm^2 at pH values between 9 and 10.[19,20] Since the charge density on SiO_2 is independent of particle size at a given pH, 200 and 580 binding sites can be estimated for the 7 and 12 nm particles, respectively.[21] At the largest ratios of $[MV^{2+}]/[SiO_2]_p$ employed in this study, where $[SiO_2]_p$ represents the concentration of silica particles, less than 30% of the available sites would be taken by MV^{2+}. Attempts to obtain a higher loading of the silica with MV^{2+} result in unstable sols that easily gel.

Figure 2 shows the effect of $[SiO_2]$ and $[MV^{2+}]$ on the rate of reaction 1 in the colloidal solution. For comparison the rate in the absence of the colloid is shown as a dashed line. The rate increases upon increasing concentration of either SiO_2 or MV^{2+}. The former dependence indicates that all of the MV^{2+} ions are adsorbed on the particles even at the lowest $[SiO_2]_p$ studied. Any significant equilibrium concentration of MV^{2+} in the bulk aqueous phase would decrease upon increasing concentration of the particles, and consequently, the rate would have decreased. Furthermore, because the rate increases upon increasing $[SiO_2]_p$, one concludes that the rate-determining step in reaction 1 in the presence of the particles is the rate of
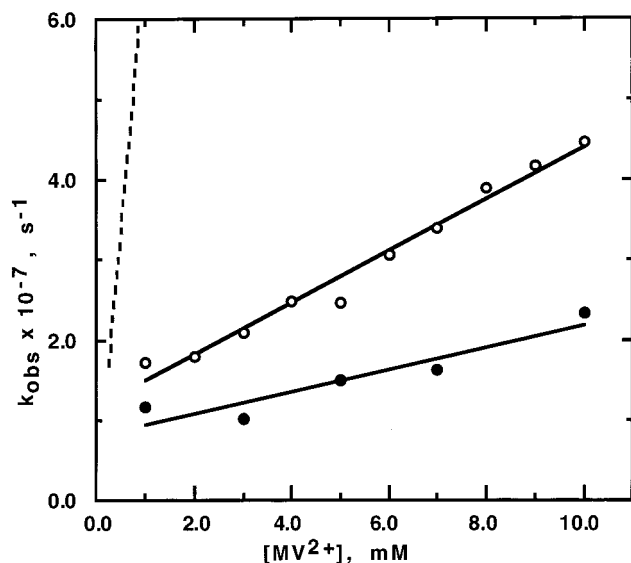
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Figure 2. Dependence of the pseudo-first-order rate constant for e^-_{aq} + MV^{2+} on the concentration of MV^{2+} in deaerated solutions containing 18.2 wt % SiO_2 (●) or 36.8 wt % SiO_2 (○) colloidal particles. Silica particles are 12 nm in diameter. Dashed line is calculated from the known rate constant in neat water.

Figure 3. Transient absorbance of the methyl viologen radical cation in deaerated 36.8 wt % SiO_2 aqueous suspensions in the absence (●) and presence (○) of 25 mM $NaNO_3$. [MV^{2+}] = 10 mM. Particles are 12 nm in diameter.

approach of e^-_{aq} to the particle and not the rate of finding MV^{2+} on the particle. In this mechanism the rationale for the dependence of the rate on [MV^{2+}] is less clear; ideally, the rate should be independent of MV^{2+} concentration. This dependence is attributed to the effect of the adsorbed acceptor on the charge density at the interface. Increasing the density of adsorbed MV^{2+}, upon increasing its total concentration, partially masks the negative surface charge of the particle. Because the rate of the reaction is determined by the rate approach of e^-_{aq} to the particle, it is expected to increase when the negative surface charge is masked. To verify this hypothesis, the effect of an inert salt, $NaClO_4$, on the reaction rate, at constant concentration of SiO_2 and MV^{2+}, was measured. The rate significantly increases upon increasing [$NaClO_4$] in the range 0−25 mM. In the absence of silica the rate was found to decrease upon increasing the ionic strength of the solution. Therefore, it is concluded that the rate-determining step in the reaction of e^-_{aq} with MV^{2+} in the presence of SiO_2 particles proceeds under a negative electrostatic field, i.e., with the adsorbed ion. Similar arguments were used to rationalize the effect of ionic strength on the reaction between e^-_{aq} and several acceptors at negatively charged micellar interfaces.[22,23]

Competitive Electron Scavenging. To distinguish between e^-_{aq} that originate from ionization of silica and those from the ionization of water, the aqueous-phase reaction between e^-_{aq} and surface-adsorbed MV^{2+} needs to be effectively removed. Several scavengers that remain in the bulk aqueous phase were introduced into the suspensions. The scavengers chosen were NO_3^-, NO_2^-, and N_2O, and their respective rate constants for reaction with e^-_{aq} are 9.7×10^9, 4.1×10^9, and 9.1×10^9 M^{-1} cm^{-1}, respectively.[11] Whereas nitrite is an efficient scavenger of both H atoms and e^-_{aq}, the rate of the reaction of H with MV^{2+} is too slow to observe on the time scales studied here. Nitrate and N_2O on the other hand scavenge only e^-_{aq} in the system studied. The negatively charged ions, nitrate and nitrite, are expected to remain exclusively in the aqueous phase. Results obtained for N_2O were quantitatively the same as those for the anionic e^-_{aq} scavengers, indicating that N_2O does not appreciably adsorb to the surface of silica particles in aqueous solutions.
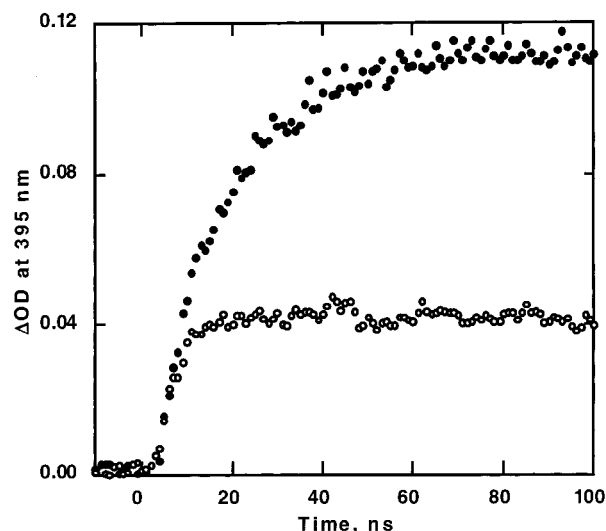
Figure 3 shows the transient absorption profile of MV^+ following irradiation of deaerated suspensions containing 36.8 wt % SiO_2 and 10 mM MV^{2+} with and without added bulk scavenger, 25 mM $NaNO_2$ in this case. Biphasic formation of MV^+ can be seen in the absence of nitrite, but accurate discrimination between the two is difficult. In the presence of nitrite, however, only the prompt formation of MV^+ can be seen with the slower formation having been eliminated. The prompt formation of the MV^+ signal in the presence of $NaNO_2$ appears at a fraction of the yield obtained in the solution containing no additional scavenger. As shown above, the rate of reaction between hydrated electrons and MV^{2+} has been reduced by at least an order of magnitude because of adsorption onto the particle surface (Figure 2). Thus, the observed yield of MV^+ in solutions containing added bulk scavengers is not the result of reaction 1. Rather, this prompt formation is attributed to a reaction with electrons that are generated in the silica particles.

MV^+ yields as a function of added [$NaNO_3$] at constant concentration of MV^{2+} (10 mM) and silica particles of 12 nm diameter (36.8 wt % SiO_2), measured 100 ns after the pulse, are shown in Figure 4. The radiolytic yield of MV^+ decreases as the nitrate increases until it levels off at approximately 10 mM $NaNO_3$. At this level all of the solvated electrons in the bulk of the aqueous phase have been scavenged by the added nitrate anions. The residual yield of MV^+ under such conditions corresponds to an interfacial reaction between surface-adsorbed MV^{2+} and those electrons originating in the ionization of silica.

Similarly, the effect of [MV^{2+}] on the production of MV^+ was measured in the colloidal solutions in the presence of 10 mM nitrate or nitrite. For solutions of both the 7 nm silica particles at 27.5 wt % SiO_2 and the 12 nm particles at 36.8 wt % SiO_2, in the presence of the added e^-_{aq} scavengers, the radiolytic yield of MV^+ (at 100 ns) increases upon increasing the concentration of adsorbed MV^{2+}. At the highest allowable MV^{2+} concentration prior to gelation, no plateau was observed in the production of the radical cation. Thus, as the concentration of MV^{2+} at the particle surface increases, the yield of MV^+ increases as well. The reason for this dependence is not clear and is discussed below.

As already discussed above, the percentage of surface sites covered by MV^{2+} is <30%, and thus, any effect on surface-charge density is believed to be small. Nonetheless, the
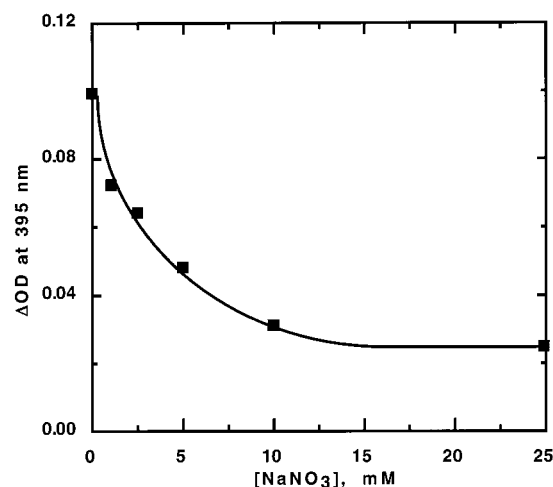
Figure 4. Dependence of the absorbance of MV^+ at 100 ns on concentration of added $NaNO_3$ in deaerated 36.8 wt % SiO_2 aqueous suspensions. $[MV^{2+}] = 10$ mM. Particles are 12 nm in diameter.

interfacial scavenging of electrons might be affected by the small changes in surface potential introduced through the adsorption of MV^{2+}. The effect of a doubly charged positive ion, Mg^{2+}, which modifies the surface potential but does not react with e^-_{aq}, was determined in order to test this question.[24] The yield of solvated electrons in the presence of $Mg(ClO_4)_2$ at concentrations up to 25 mM was measured directly at 600 nm and at two different $[SiO_2]$ concentrations. No observable changes to the production of hydrated electrons could be detected upon addition of Mg^{2+}. Even the increase in $[e^-_{aq}]$ as a function of weight percent SiO_2 in the presence of Mg^{2+} is identical to that reported previously for Mg^{2+}-free solutions. Thus, the effectiveness of surface-adsorbed MV^{2+} toward capturing escaping electrons results only from its ability to trap electrons due to its relatively positive reduction potential. Merely altering the surface potential of the particles is not a determining factor, and a trap for the electrons at the surface seems necessary. In another set of experiments, the effect of the width of the electrical double layer at the particle interface was measured. Increasing the ionic strength of the solution by addition of $NaClO_4$, and thus reducing the thickness of the double layer,[21] had no effect on the yield of either e^-_{aq} or MV^+ in two corresponding sets of experiments. Clearly, the surface potential seems to have little influence on the escape probability of electrons from the particle.

Normalized MV^+ yields for two different silica particle sizes resulting from the capture of electrons escaping the silica particles at the solid−liquid interface are shown in Figure 5 as a function of weight percent SiO_2. Superimposed on the top portion of the figure are the limiting curves previously determined for the hydrated electron and hole production in the radiolysis of aqueous colloidal silica suspensions.[3,4] The fraction of energy absorbed by the silica particles (indicated by the double-arrowhead line) is also recast as a function of weight percent SiO_2 near the bottom of the figure (solid line). The data points strongly correlate with the fraction of energy absorbed by the silica particles. Thus, all of the electrons that are generated in the particle, as defined by the experiments of Figure 4, can be captured by the adsorbed MV^{2+}. However, because the yield of MV^+ as a function of $[MV^{2+}]$ does not attain a saturation level, it cannot be ascertained whether the presence of the molecules at the surface affects the capture yield. The MV^{2+} adsorbate may enhance charge separation within the particles, compete with bulk scavengers for solvated electrons near the interface, or perhaps undergo a fast reaction with
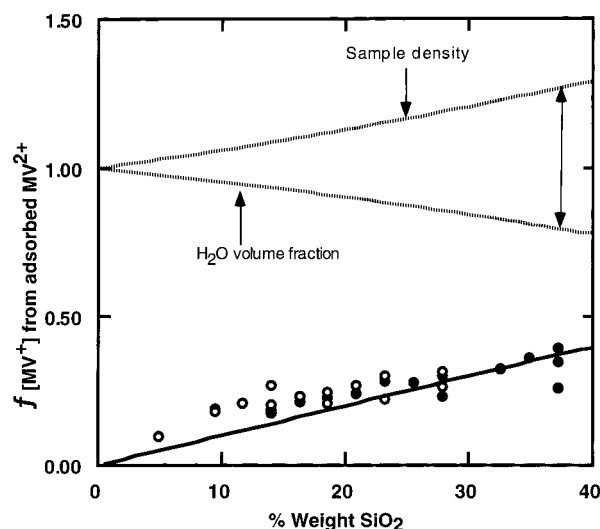

Figure 5. Fraction of MV^+ (from total e^-_{aq}) that results from capture of electrons escaping SiO_2 particles at the interface as a function of weight percent SiO_2. Concentration of MV^{2+} is 10 mM and of the competing e^-_{aq} scavenger is 25 mM. Silica particles are 7 nm (○) or 12 nm (●) in diameter. The solid line is the fraction of energy absorbed by SiO_2.

hydrogen atoms produced via radiolytic homolysis of surface O−H bonds.[25,26]

Finally, the characteristics of the fast component in the radiation-induced production of MV^+ in the suspensions have been detailed above. At longer times than described here, a slower growth process can be observed, which eventually results in approximately a 2-fold increase in the overall MV^+ absorbance. It has often been suggested that the dissipation of absorbed radiation energy in metal oxide materials leads to the formation of hydrogen atoms from surface hydroxyl groups.[25,26] The H adduct on the N atom of MV^{2+} (MVH^{2+}) is equivalent to the acid form of MV^+ and exhibits the same absorption spectrum. Therefore, the slow growth of the transient absorption observed at 395 nm in aqueous colloidal silica solutions containing MV^{2+} is tentatively ascribed to reaction between MV^{2+} and atomic hydrogen.

Conclusions

We have demonstrated for aqueous systems of nanosize silica particles that electron migration to the solid−liquid interface is the ultimate pathway of chemical change following ultrabandgap excitation. Essentially all of the ionizing radiation energy absorbed by the silica particles is converted into electron−hole pairs, and the electrons can be efficiently captured by surface-adsorbed methyl viologen. The mobile electrons initially formed within the silica nanoparticles by the absorbed energy must undergo substantial energy degradation in order to permit their capture by the surface-adsorbed MV^{2+}. Since all of the energy that is deposited in the solids can be captured at the interfacial region before it is channeled into the aqueous phase, one concludes that the escaping electrons are relatively low in energy. Although the electrons can efficiently migrate into the aqueous phase,[4] we show here that surface-adsorbed acceptors can intercept the radiolytically generated reducing equivalents at the solid−liquid interface. Since the electrons contribute to the generation of molecular hydrogen from the aqueous phase, the presence of acceptors is likely to affect that yield. H_2 evolution in the storage of radionuclides is a problem of significant importance. Therefore, the production of molecular hydrogen in aqueous colloidal silica suspensions is the subject of additional studies in our laboratory.

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