

Efficiency of Hot Carrier Trapping by Outer-Sphere Redox Probes at Quantum Dot Interfaces

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The action spectra of the colloidal TiO₂-photosensitized oxidations of bifunctional aromatics in 1 mM phosphate colloidal media provide firm evidence that electron transfer from outer-sphere donors can compete with excited hole relaxation at nanoparticle interfaces. The possibility and extent of the competition are largely determined by the dependence of Marcus nuclear factors on the donors' *reversible* redox potentials $E^{\circ}_{D/D^{+}}$ relative to the valence band edge. Good electron donors are degraded by OH radicals produced in the oxidation of water by thermal holes, whereas direct electron transfer into excited holes (the pathway favored by less oxidizable substrates) leads to enhanced quantum efficiencies at short wavelengths. The ultimate decline of the quantum efficiency for the oxidation of phthalate (the most endoergic donor of the set) by $\lambda \leq 320$ nm photons indicates that the relaxation of highly excited carriers takes place in discrete steps commensurate with electron transfer reorganization energies. The latter observation is consistent with the opening of low order multiphonon channels for the disposal of kinetic energy quanta larger than the depth of surface $\bar{\nu}_{O-H} \sim 3700$ cm⁻¹ vibrational sinks.

Introduction

Interfacial electron transfer is one of the most important classes of chemical reactions.^{1–3} Redox processes between molecular species and photoseparated charges at semiconductor interfaces mimic photosynthetic events and are the basis of solar energy conversion and storage schemes.^{1a} Charges generated by polychromatic solar radiation may carry excess energy if rapidly delivered to the interface.^{4–9} In fact, single band gap devices would attain 66% power conversion efficiency, i.e., twice the maximum efficiency of an ideal thermal conversion unit, if excess photon energy could be harnessed as chemical potential.¹⁰ Here, we address the issue of under which conditions and to what extent can such excess energy be utilized rather than dissipated. At stake is the question of whether interfacial electron transfer can actually compete with hot carrier deactivation.^{1,2,4,5,11,12} Small domains (such as 3-D quantum dots) in which hot carriers can rapidly reach the interface seem essential to the task.^{5,12} It has been argued that kinetic energy discretization in quantum dots may also slow the multiphonon transitions involved in hot carrier deactivation into the crystal lattice.^{5,6} Little is known, however, about how to chemically control the fate of excess energy in these systems. We now report the action spectra of photooxidation quantum yields for aromatic donors with redox potentials ranging from mid band gap to well into valence band energies of colloidal TiO₂, which bear on these topics. Present results provide novel information on redox processes and hot carrier relaxation at quantum dot interfaces dealing with several standing issues regarding the mechanism of photocatalysis. Five facts clearly emerge. (1) The occurrence of hot carrier effects does not seem to require prior donor binding to the surface. (2) Photocatalytic oxidations are not always mediated by OH-radicals but can proceed by direct electron transfer. (3) Their actual mechanisms can be predicted from *reversible* redox potentials $E^{\circ}_{D/D^{+}} = E^{\circ}_D$ for the production of radical cations: $D \rightleftharpoons D^{+} + e$. (4) The required E°_D

data—those that do not generally coincide with electrochemical values measured for the irreversible reactions in water: $D + H_2O \Rightarrow DOH + H^{+} + e$ —can be estimated from ionization potentials. (5) The deactivation of highly excited carriers in TiO₂ nanoparticles is compatible with the multiphonon relaxation of quantized holes into lattice vibrational sinks.

Experimental Section

Visually clear, nonscattering nanocrystalline TiO₂ sols absorbing at $\lambda \leq 380$ nm ($E_g = 3.2$ eV) were prepared by exhaustive ultracentrifugation of previously sonicated 2 g/L TiO₂ (Fredriks Research Products, 76% anatase–24% rutile) slurries in 1 mM PO₄H₂Na (pH \sim 4.5).^{12,13} Atomic force microscopy (PSI) of sol samples dried on mica holders reveals the presence of fine particles ($\langle r \rangle \leq 3$ nm) interspersed with a few larger ($r \sim 10$ nm) aggregates. Air saturated sols (3 cm³, absorbance $A \sim 0.3$, [O₂] = 0.3 mM) containing variable concentrations of phthalate (P), salicylate (S), or resorcinol (R) were irradiated with monochromatic (10 nm bandwidth) UV light at several wavelengths. We found no spectral evidence of surface chelation under present conditions,¹⁴ confirming the role of phosphate as a competitive inhibitor of adsorption.^{12,15} Hence, we consider that (1) radiation is exclusively absorbed by TiO₂ nanocrystals and (2) substrates behave as outer-sphere redox donors.^{2,11,16} Photooxidation quantum ϕ_{-D} yields were determined from decay rates R_{-D} determined by HPLC and from absorbed photon fluxes I_a measured using the phenylglyoxylic acid actinometer, $\phi_{-D} = R_{-D}/I_a$. In all cases, ϕ_{-D} is independent of I_a below $\approx 10^{15}$ photons cm⁻² s⁻¹.^{12,13,17}

Results and Discussion

Experimental ϕ_{-D} data vs excess photon energy E^* ($E^* = h\nu - E_g$) are shown in Figure 1(A–C). Quantum yields obey linear ϕ_{-D}^{-1} vs $[D]^{-1}$ dependences (not shown), as expected for hole capture rates directly proportional to $[D]$ (step 3

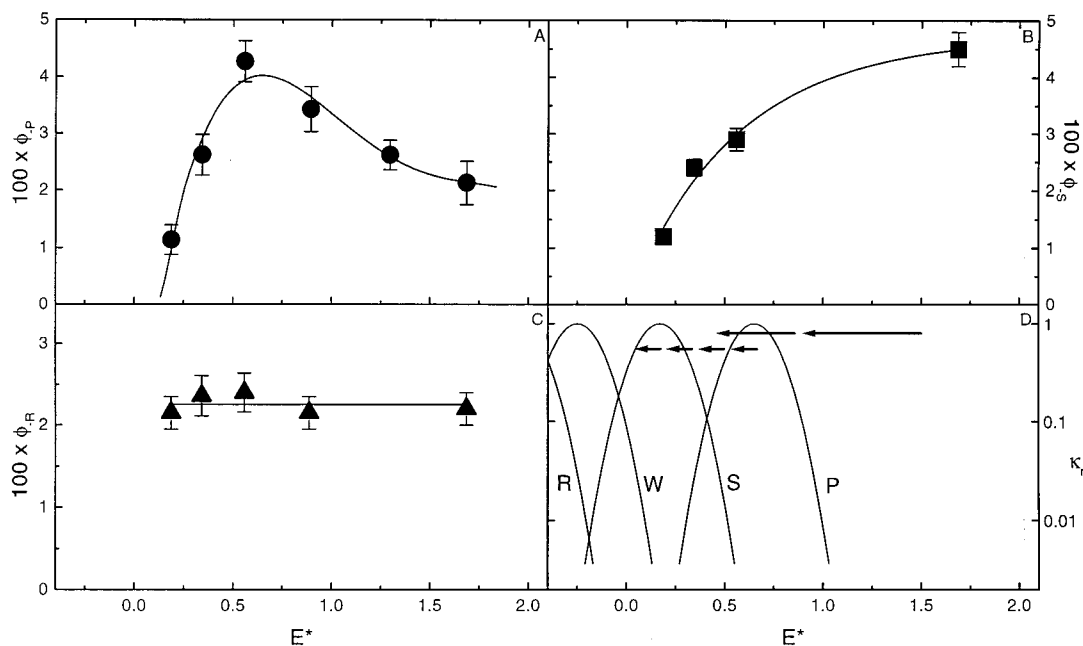


Figure 1. A–C: Quantum yields ϕ vs excess photon energy E^* for phthalate ([P] = 33 mM, pH = 4.25), salicylate ([S] = 67 mM, pH = 4.50), and resorcinol ([R] = 68 mM, pH = 5.88), respectively. D: The nuclear factors κ_n for the interfacial oxidations of resorcinol (R), water (W), salicylate (S), and phthalate (P) vs E^* . Calculations based on eq 6 with $E_{vb} = 2.95$ V, $\lambda_R = 0.5$ eV, $E^\circ_R = 2.11$ V, $E^\circ_W = 2.53$ V, $E^\circ_S = 3.11$ V, $E^\circ_P = 3.45$ V. The arrows convey the stepwise relaxation of hot carriers. The arrow lengths portray the size of the deactivation steps. A faster deactivation channel opens up at ca. 0.8 eV (see text).

below).¹² Since the effective masses of the hole and electron in the energy bands of anatase crystals are in the ratio $m_h/m_e \approx 0.08$,¹⁸ conservation of momentum implies that E^* is largely channeled into the hole.⁶ Hence, our results can be analyzed with reference to the following scheme:¹²



Whereas photon absorption (step 1), the dissipation of excess kinetic energy into crystal vibrations (step 2) or carrier recombination (step 4), may occur anywhere within TiO₂ nanoparticles, electron transfer reactions (steps 3 and 5) can take place only at their interfaces. Step 2 presumably proceeds stepwise on account of the anticipated energy quantization in nanoparticles.^{5,6} On the other hand, Marcus theory predicts that rate constants for reaction 3 depend on photon energy according to^{2,11,16}

$$k_{3,D} = \nu_n \kappa_{el} \kappa_{n,D} = A_{3,D} \exp\{-(h\nu - E_g + E_{vb} - E^\circ_D - \lambda_R)^2 / 4\lambda_R k_B T\} \quad (6)$$

$A_{3,D}$, the product of the nuclear frequency ν_n times the electronic coupling term κ_{el} , is assumed to be independent of E^* . Here, $E_g = 3.2$ eV and $E_{vb} = 3.25 - 0.06$ pH (vs NHE) are the TiO₂ band gap energy and valence band edge potential, respectively.^{3,19} The nuclear factor $\kappa_{n,D}$ is given by the exponential factor in the right-hand side of eq 6 where λ_R is the reorganization energy for interfacial electron transfer, which is assumed to have a common value ≈ 0.5 eV independent of the substrate.²⁰ The optimal exoergicity is defined as $\Delta G_{op} =$

$E^*_{op} + E_{vb} = E^\circ_D + \lambda_R$. In the present context, E°_D corresponds to the reversible oxidation of D into radical cations at the surface. They are expected to be more positive than the standard electrochemical E° values measured in hydrophilic media, which involve the irreversible solvolysis of radical cations.²² Redox potentials for the reversible ($D \rightleftharpoons D^{\cdot+} + e$) couples were estimated from ionization potentials IP_D (in eV): $E^\circ_D = 0.78$ IP_D - 4.26, as suggested by Eberson.²¹ Calculated $\kappa_{n,D}$ values vs E^* for electron transfer from R, S, P, and water (W) into excited holes are shown in Figure 1D. It is apparent that (1) the nuclear factors for resorcinol and water oxidations are in the inverted region and comply with $\kappa_{n,R} < \kappa_{n,W}$ at $E^* \geq 0$; (2) only salicylate and phthalate oxidations can be favorably affected by excess photon energy because both span an energy interval in which $\partial\kappa_n/\partial E^* > 0$. On this basis, resorcinol is to be degraded by the OH radicals formed in water oxidation rather than directly in step 3.^{23,24} Notice that since radical cations are rapidly solvated ($D^{\cdot+} + H_2O \rightleftharpoons DOH + H^+$) the same products would be formed in either pathway.²⁵ Moreover, considering that the condition $k_2 \gg k_{3,D}$ is appropriate in the inverted region, water will be predominantly oxidized by thermalized holes, i.e., $\phi_{-R} \leq \phi_{-W}$ cannot be but weakly dependent on wavelength, as observed. A similar argument obviously applies to any donor that satisfies the condition $E^\circ_D < E^\circ_W$. A different scenario may prevail, however, in semiconductors whose E_{vb} potentials are less positive than TiO₂. It should be emphasized that these verifiable predictions follow from absolute E°_D values, rather than from the mere proportionality between E°_D and IP.

On the other hand, the fact that ϕ_{-S} does not decrease with E^* indicates that even highly excited holes eventually relax rather than annihilate. Indeed, ϕ_{-S} would necessarily decrease at sufficiently short wavelengths if an additional channel (e.g., fast dissipative recombination) were accessible above some E^* threshold value. The essence of this argument makes it applicable to any substrate. Therefore, the experimental maximum found for phthalate quantum yields at $E^* \approx 0.6$ eV must be a consequence of the fact that in this case electron transfer actually

probes a higher energy region. In effect it implies that highly excited holes relax in a single step to energies below the region in which electron transfer is fastest for phthalate. The implicit corollary is that E^* must be quantized, for otherwise the optimal exoergic region would have been visited and a maximum ϕ_{-p} had been absent.

Size quantization effects in photocatalysis have been analyzed in terms of simplified models dealing with effective-mass particles confined to boxes.^{5,6,26} The coarser energy spacing in small particles results in blue-shifted band gap thresholds, slower hot carrier cooling, and, possibly, in the conversion of indirect to direct semiconductors.^{5,26–28} Indeed, $r \sim 1.5$ nm particles would sustain hole energy spacings at least compatible with those required by our phthalate results.²⁶ However, there remains the issue of why energy levels close to E^*_{op} can be populated directly but not via deactivation from the levels reached by higher energy photons. In principle, the relaxation of the more widely spaced carrier quanta at higher energies should result in exponentially decreasing relaxation rates.²⁹ For example, the nonradiative loss of $E^* \leq 0.5$ eV = 4000 cm⁻¹ by hot carriers in anatase requires the simultaneous excitation of up to four 826 cm⁻¹ B_{2g} lattice phonons³⁰ or five 780 cm⁻¹ E_u surface phonons.³¹ In contrast, the 3700 cm⁻¹ O–H stretching vibrational quantum available in hydrated interfaces is nearly a resonant sink for the dissipation of $E^* = 0.48$ eV.³² On this basis, we tentatively ascribe the occurrence of a maximum in Figure 1A to the fact that more direct deactivation channels become accessible above $E^* \sim 4000$ cm⁻¹ on quantum dot/water interfaces. The availability of a much deeper vibrational sink reduces the order of the required multiphonon relaxation processes, significantly enhancing their probability.³¹

Summing up, the action spectra of the photosensitized oxidations of selected substrates provide clear evidence of hot carrier effects on nanoparticles and rule out a universal mechanism of photocatalysis.^{23,24,33,34} The actual mechanism for specific donors depends in a predictable manner on their reversible redox potentials for the generation of radical cations relative to the semiconductor valence band position. The quantized energy carried by excited holes in TiO₂ nanoparticles is dissipated into the lattice in a manner consistent with the theory of multiphonon relaxation processes.

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References and Notes

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