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Ultrafast Charge Transfer between Light Absorber and Co_3O_4 Water Oxidation Catalyst across Molecular Wires Embedded in Silica Membrane

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S Supporting Information

ABSTRACT: The mechanism of visible light-induced hole transfer from a molecular light absorber, in the form of a free-base porphyrin, coupled to a Co_3O_4 nanoparticle catalyst for water oxidation by a molecular wire (*p*-oligo(phenylenevinylene) featuring three aryl units) is investigated by transient absorption spectroscopy. The wires are covalently anchored on the Co_3O_4 surface and embedded in a dense, yet ultrathin (2 nm), silica layer that separates light absorber and catalyst. The porphyrin is electrostatically adsorbed on the silica surface, and aqueous colloidal solutions of the core-shell particles are used for transient optical measurements. Pulsed optical excitation of the porphyrin results in rapid injection of the photogenerated hole onto the molecular wire and concurrent formation of reduced light absorber in less than 1 picosecond (ps). Ultrafast charge separation was monitored by transient absorption of the wire radical cation, which is given by bands in the 500 to 600 nm region and at 1130 nm, while formation of reduced porphyrin was characterized by absorption at 700 nm. Forward transfer of the hole to Co_3O_4 catalyst proceeds in 255 ± 23 ps. Ultrafast transfer of positive charge from the molecular assembly to a metal oxide nanoparticle catalyst for water oxidation is unprecedented. Holes on Co_3O_4 recombined with electrons of the reduced sensitizer with biphasic kinetics on a much longer time scale of ten to several hundred nanoseconds. The unusually efficient hole transfer coupling of a molecular light absorber with an Earth-abundant metal oxide catalyst by silica-embedded *p*-oligo(phenylenevinylene) offers an approach for integrated artificial photosystems featuring product separation on the nanoscale.

1. INTRODUCTION

Nanostructured metal oxides of late transition metals, in a variety of morphologies, have recently emerged as robust, Earth-abundant catalysts for water oxidation.^{1–14} Although average turnover frequencies per exposed surface metal site of oxide catalysts for oxygen evolution are only on the order of 10^{-2} O_2 molecules per second,^{1,15–17} the very high densities of sites per geometrical area of nanostructured catalysts enables productive use of the majority of injected charges for starting fresh catalytic cycles. However, for use in artificial photosystems, efficient charge transfer coupling of the oxide to a light absorber remains a formidable challenge. This holds especially if energy loss caused by mismatched potentials of light absorber and catalyst is to be held at a minimum in order to ensure conversion of a maximum fraction of the absorbed solar photon energy to chemical energy stored in the products.

For molecular light absorbers, which offer the advantage of precise potential matching by tuning of the electronic properties through synthetic modifications, early studies by Mallouk have established rates in the millisecond range for hole transfer (positive charge) between Ru tris-bipyridyl type light absorbers ($[\text{Ru}(\text{bpy})_3]^{2+}$) and Ir oxide nanocluster catalysts.^{18,19} As a consequence of the rather slow rates, efficiency degrading back transfer of separated electrons resulted in low

photocatalytic quantum yields. Improvements have been achieved by introducing molecular relays akin to the tyrosine-histidine bridge of Nature's photosystem II, resulting in a 3-fold increase of the quantum yield.^{19–21} On the other hand, visible light-induced hole transfer from a $\text{Ru}(\text{bpy})_3$ sensitizer to a molecularly defined metal oxide structure, in the form of polyoxometalate, was found to occur within a nanosecond, suggesting that ultrafast kinetics in the case of metal oxide nanocluster catalysts might be feasible.²² While the photon flux at maximum solar intensity ($1500 \text{ photons s}^{-1} \text{ nm}^{-2}$) alone does not require such high charge transfer rates,²³ ever-present competing charge transfer processes that degrade productive use of the separated charges require forward hole transfer rates of a few nanoseconds or even picoseconds for acceptable water oxidation quantum yields to be realized.

Fast hole transfer between light absorbers and metal oxide catalysts is of particular importance for artificial photosystem designs that aim at closing the photosynthetic cycle of CO_2 reduction by H_2O on the nanoscale, while also separating products by a membrane, which is essential for the efficient photoreduction of CO_2 to liquid fuel products.²⁴ We have

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recently demonstrated ultrathin dense phase silica layers (2–3 nm) as O_2 impermeable, proton transmitting separation membranes.^{15,25} Tight control of charge transport between a light absorber on one side of the silica membrane and a Co oxide catalyst for water oxidation on the other was accomplished by embedded molecular wires composed of *p*-oligo(phenylenevinylene) featuring three aryl units.^{16,17} Energy-selective hole or electron transport across the membrane was achieved by tuning the HOMO and LUMO potentials of the embedded wire molecules, as demonstrated by visible light photoelectrochemical measurements on planar constructs.²⁶ Using aqueous colloidal solutions of spherical Co_3O_4 – SiO_2 core–shell nanoparticles with embedded wire molecules, $[Ru(bpy)_3]^{2+}$ visible light sensitizer, and sacrificial electron acceptor–revealed diffusion-controlled hole transfer to the Co_3O_4 core via embedded molecular wires.¹⁷ From this result, a lower limit of the kinetic rate constant for hole transfer from light absorber to Co_3O_4 via silica-embedded molecular wire of 10^6 s^{-1} was inferred.

An essential open question is whether ultrafast hole transfer between a molecular light absorber and a metal oxide catalyst for water oxidation can be achieved in order to outcompete efficiency degrading pathways, and whether this is feasible even in the presence of a silica separation membrane. The latter is required for realizing acceptable efficiency for CO_2 photo-reduction by H_2O to dense phase products. Here we report the direct detection and kinetic evaluation of hole transfer between a molecular light absorber and a Co_3O_4 nanocatalyst particle, coupled via molecular wires embedded in an ultrathin silica layer, by transient optical absorption spectroscopy. While inorganic heterobinuclear units such as $ZrOCo$ are our target light absorbers for integrated artificial photosystems,^{24,25} free-base porphyrin offered spectroscopic properties particularly suitable for ultrafast optical monitoring. The findings reveal unusually efficient hole transfer coupling of a porphyrin chromophore and the metal oxide catalyst via a *p*-oligo(phenylenevinylene) cast into silica, thus opening up nanoscale artificial photosystems designs with built-in membrane separation.

2. EXPERIMENTAL SECTION

Sample Preparation and Characterization. A surfactant-assisted solvothermal method reported previously was used for preparing ~4 nm sized Co_3O_4 nanoparticles.^{17,27} Molecular wires, of the type cesium 4-((*E*)-4-((*E*)-4-((1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)carbamoyl)styryl)styryl)benzenesulfonate (hereafter abbreviated as PV3), were synthesized according to a reported procedure¹⁶ and attached to Co_3O_4 nanoparticle surfaces using *O*-(6-chlorobenzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HCTU) peptide coupling agent, as described in an earlier paper,¹⁷ with the exception of using a tip-sonicator for efficient particle dispersion (Branson Ultrasonic model Sonifier, 3–4 W, 1 s on/1 s off). In short, PV3 (0.0081 g, 13 μmol) and HCTU (0.0017 g, 0.0042 mmol) were put in a 50 mL Schlenk flask. The flask was evacuated while being cooled to 0 °C. After 45 min, 4 mL of CH_3CN and 1 mL of 1,2-difluorobenzene were added using a syringe. The fluorescent yellow solution was allowed to warm to room temperature, after which 0.020 g of Co_3O_4 and 0.020 mL of *N,N*-diisopropylethylamine (0.115 mmol) were added to the solution. The mixture was sonicated for 30 min at 0 °C followed by stirring at room temperature for 24 h. The resulting dark solution was centrifuged at 12 500 rpm for 15 min at 10 °C, and the supernatant was decanted. Ethanol (10 mL) was added to the residue, and the suspensions were sonicated and agitated before centrifugation under the same conditions. The procedure was repeated twice.

For casting the molecular wires into silica, the Co_3O_4 –PV3 particles were dispersed in 90 mL of ethanol while continuously stirring the solution. Five milliliters of ammonia, 10 mL of water, and 0.05 mL of tetraethyl orthosilicate (TEOS) were added to the solution, which was stirred for 4 h while tip-sonicating with repetitive cycles of 1 s on/1 s off at 4 W. The temperature was maintained at 40 °C. The resulting core–shell nanoparticles, with embedded molecular wires (abbreviated Co_3O_4 –PV3– SiO_2) were collected by repeated (3 $\times$) centrifugation (12 500 rpm for 15 min at 10 °C). The precipitate was resuspended and subsequently collected and concentrated 2.5 $\times$ in a 20 mL vial. The volume was completed to 20 mL and the dispersion kept overnight to settle. Any precipitate was removed, and the resulting solution was used for spectroscopic experiments. A similar procedure was employed for core–shell samples without PV3 wires, which were used for control experiments. Samples were uniform core–shell nanoparticles consisting of a crystalline Co_3O_4 core (5 nm diameter) and an amorphous SiO_2 shell (2 nm), as shown by TEM images presented in Figure 1.

Figure 1. TEM image of Co_3O_4 – SiO_2 core–shell particles. The lattice distance is 0.25 ± 0.01 nm and corresponding to the Co_3O_4 (311) plane (PDF number 01-071-0816).

The free-base porphyrin light absorber, H_2P , was synthesized according to established methods²⁸ and is shown in Scheme 1 (H_2P = 1,1',1'',1''',1''''-((((10*r*,15*r*)-20-(2-(4-(*tert*-butyl)pyridin-1-ium-1-yl)-6-((4-(*tert*-butyl)pyridin-1-ium-1-yl)methyl)phenyl)porphyrin-5,10,15-triyl)tris(*S*-(*tert*-butyl)benzene-2,1,3-triyl))hexakis(methylene))hexakis(4-(*tert*-butyl)pyridin-1-ium). To immobilize H_2P on the silica shell of the core–shell particles, 10^{-5} M aqueous solution of H_2P^{8+} was added to aqueous suspensions of pure SiO_2 , or Co_3O_4 – SiO_2 , or Co_3O_4 –PV3– SiO_2 nanoparticles and kept at room temperature and in the dark overnight. After ultracentrifugation at 12 500 rpm at 8 °C, the colored supernatant was decanted and the process repeated. In the cases of Co_3O_4 – SiO_2 · H_2P^{8+} and Co_3O_4 –PV3– SiO_2 · H_2P^{8+} , 4 h of ultracentrifugation were necessary to obtain a clear supernatant. The Co_3O_4 –PV3– SiO_2 · H_2P^{8+} samples were redispersed in water and kept sealed until spectroscopically investigated. Particles were characterized by TEM imaging using an electron microscope model JEOL 2100-F FETEM at 200 kV. Samples were prepared by dispensing a few microliters of the dispersion on carbon-coated 200 mesh Cu grid. KBr pellets (0.5–1 wt %) were pressed (5 Ton), and FT-IR spectra were measured using a Bruker FT-IR model Vector 33 at 1 cm^{-1} resolution.

Transient Absorption Spectroscopy. The ultrafast laser pump beam was produced by a Coherent Libra Ti:sapphire regenerative amplifier coupled to a Coherent OPerA Solo optical parametric amplifier. The 430 nm output (700 nJ pulse⁻¹, 0.3 mm diameter) of ≤ 150 fs duration at 1 kHz repetition rate was directed toward the

Scheme 1. Light Absorber H₂P = 1,1',1'',1''',1''''-(((10*r*,15*r*)-20-(2-(4-(*tert*-Butyl)pyridin-1-ium-1-yl)-6-((4-(*tert*-butyl)pyridin-1-ium-1-yl)methyl)phenyl)porphyrin-5,10,15-triyl)tris(5-(*tert*-butyl)benzene-2,1,3-triyl))hexakis(methylene))hexakis(4-(*tert*-butyl)pyridin-1-ium) and Molecular Wire PV3 = Cesium 4-((*E*)-4-((*E*)-4-((1,3-Dihydroxy-2-(hydroxymethyl)-propan-2-yl)carbamoyl)styryl)styryl)benzenesulfonate

sample. A portion of the Ti:sapphire fundamental output beam was used to generate white light probe pulses by directing it through a variable delay line to a sapphire disk. White light transmitted through the aqueous colloid sample, held in a quartz cuvette, was recorded by a grating spectrometer coupled to a Si CMOS detector array for analysis in the 400–800 nm range. For the case of transient absorption spectroscopy measurements on the nanosecond to millisecond time scale, the same pump laser and detection system were used, but the probe beam was generated with a Leukos Systems supercontinuum laser with a pulse width of <1 ns and broad band emission. The differential absorption was collected as a function of pump–probe delay through accumulated random sampling of electronically triggered delay times.

UV–vis Spectrum of Co₃O₄ Nanoparticle Suspension Oxidized by Ce(IV) in Aqueous Solution. In order to obtain an optical spectrum of Co₃O₄ nanoparticles during hole injection under steady-state conditions, the absorption spectrum of a 0.17 mg mL^{−1} sonicated suspension of Co₃O₄ particles (3 mL) diluted with 10 μL of water was collected (sample 1). Analogously, the spectrum of 3 mL of water with 10 μL of 100 mM Ce(IV) aqueous solution added was taken (sample 2). Then 10 μL of 100 mM Ce(IV) aqueous solution was added to a 3 mL suspension of Co₃O₄ particles (0.17 mg mL^{−1}), the solution was stirred, and the absorption spectrum was measured (sample 3). The spectrum of the oxidized form of Co₃O₄ was then calculated by subtracting spectra 1 and 2 from sample 3.

Chemicals. All reagents and solvents used for the synthesis of molecular wires, porphyrin light absorbers, Co₃O₄ nanoparticles, and silica shells described were obtained commercially (reagent grade) and used as-received unless noted otherwise.

3. RESULTS

3.1. Spectroscopic Characterization of Core–Shell Particles with Adsorbed Sensitizer. Figure 2 trace 1 shows the UV–vis spectrum of a colloidal aqueous solution

Figure 2. UV–vis absorption spectra of aqueous suspensions of Co₃O₄–SiO₂ core–shell particles with embedded PV3 wires and adsorbed H₂P light absorber ((1) red trace). Co₃O₄–SiO₂ core–shell particles with embedded PV3 wires without adsorbed H₂P ((2) blue trace). Aqueous suspension of H₂P adsorbed on SiO₂ nanoparticles ((3) green trace). Traces were shifted vertically for clarity because they showed differences in scattering behavior. Solutions of plain wires have been reported in a previous paper.¹⁶ The inset shows the difference of trace 1 – trace 2 on an expanded scale.

of Co₃O₄–SiO₂ core–shell particles with PV3 wire molecules embedded inside the silica shell and free-base porphyrin H₂P electrostatically adsorbed on the SiO₂ surface (Co₃O₄–PV3–SiO₂·H₂P). The spectrum of the same particles without adsorbed H₂P is shown in trace 2 for comparison (Co₃O₄–PV3–SiO₂). The spectrum of H₂P adsorbed in SiO₂ nanoparticles is presented in trace 3. Optical absorption by the charge transfer transitions of the Co₃O₄ core particle causes the tail that rises from the near-infrared toward the UV region and the weak broad maximum between 700 and 800 nm.¹⁷ The difference spectrum for the 450–800 nm range is shown on an expanded scale in the inset of Figure 2. The strong broad absorption between 300 and 400 nm is due to the PV3 π – π^* transition.^{16,29} From the intensity of this band and the known extinction coefficient,¹⁶ a loading of 210 PV3 molecules per core–shell particle is derived (4 PV3 nm^{−2}). The intense Soret band of H₂P adsorbed on SiO₂ nanoparticles at 432 nm and Q-bands at 522, 555, 597, and 653 nm are in agreement with literature.³⁰ From the intensity, a loading of 0.7 porphyrin molecules per particle is derived. In addition, a weak band is observed at 480 nm that only appears when both H₂P and PV3 are present. It is most likely due to charge transfer interaction between ground-state porphyrin and PV3, with electron density partially shifted from the wire molecule to the porphyrin. The integrity of molecular wires embedded in silica shells was confirmed by infrared spectroscopy. As shown in Figure S1, the fingerprint FT-IR spectrum of embedded PV3 molecules agrees well with the spectrum of the free wire molecule.

3.2. Ultrafast Optical Spectroscopy of Visible Light-Induced Charge Transfer. Time-resolved optical measurements were initiated by excitation of the Soret band of H₂P visible light sensitizer within Co₃O₄–PV3–SiO₂·H₂P assemblies with a 150 fs pulse at 430 nm. Because the Co₃O₄ absorbs at the same wavelength, a modest fraction of the laser pulse results in transient charge-transfer absorption of Co₃O₄. In agreement with recent literature,³¹ spectral traces with broad maxima at 600 and 850 nm are observed following excitation of aqueous colloids of bare Co₃O₄–SiO₂ particles (Figure 3A). Adsorbing H₂P on Co₃O₄–SiO₂ particles (no embedded wires) led in addition to transient spectra of H₂P and Co₃O₄ upon 430 nm excitation. This is seen in Figure 3B where the broad maxima at 600 and 850 nm are superimposed by peaks at 527,

Figure 3. Ultrafast transient absorption spectra upon excitation at 430 nm with a 150 fs laser pulse (0.7 μ J) of: (A) Co_3O_4 - SiO_2 colloidal aqueous solution. From dark purple to light yellow: 0.756; 2.49; 11.4; 65; 412; 1300; 2730 ps. (B) Co_3O_4 - SiO_2 - H_2P . From dark purple to light yellow: 0.473; 7.8; 22; 82.4; 217; 701 ps. Peaks at 527, 581, and the shoulder at 622 nm are characteristic for the S_1 excited state. For each trace, the absorption of $\text{H}_2\text{P}(\text{S}_1)$ is superimposed by transient Co_3O_4 absorption shown in A, giving rise to very broad absorptions centered around 600 and 850 nm. (C) Co_3O_4 - SiO_2 core-shell particles with embedded PV3 wires and adsorbed H_2P . From dark purple to light yellow: 0.482; 0.718; 1.04; 6.03; 29.0; 59.6; 89.0; 149; 320; 734; 1310; 2320 ps. Blue continuous line is the static difference spectrum of Co_3O_4 - SiO_2 -PV3 with and without adsorbed H_2P . (D) Near-IR region of the same spectral traces. From dark purple to light yellow: 1.23; 3.15; 7.39; 33.1; 60; 136; 266; 313; 557; 640; 769; 968; 1310; 1400; 1980; 2370 ps.

581, and a shoulder at 622 nm, which are characteristic of the $\text{H}_2\text{P}(\text{S}_1)$ excited state as reported in the literature.³² For further verification, transient absorption traces of H_2P adsorbed on SiO_2 particles, shown in Figure S2, were compared with transient absorption traces of Co_3O_4 - SiO_2 - H_2P of Figure 3B. The comparison confirms the absence of the broad transient absorption originating from direct 430 nm excitation of Co_3O_4 (Figure 3A) (note that the transient bleach of ground-state H_2P Q bands (at 522, 555, 597, and 653 nm) is more pronounced for this sample than for the Co_3O_4 - SiO_2 - H_2P samples (shown in Figure 3B) because a substantially larger fraction of H_2P is excited by 430 nm light (differences in photon loss by scattering and absorption by Co_3O_4). Hence, for ultrafast transient spectra of core-shell particles with molecular wires embedded in the silica and adsorbed H_2P (Co_3O_4 -PV3- SiO_2 - H_2P), discussed next, contributions of Co_3O_4 and H_2P excited-state absorptions, in addition to spectral changes induced by electronic interaction between the components, have to be considered.

In addition to the broad transient spectral response associated with Co_3O_4 , excitation of the H_2P Soret band of colloidal Co_3O_4 -PV3- SiO_2 - H_2P particles in aqueous solution resulted in a subpicosecond rise of peaks at 509, 539, 579, 633, 695, and 1130 nm, as shown in Figure 3C and 3D. The broad 695 nm absorption is characteristic for one-electron-reduced H_2P (abbreviated $\text{H}_2\text{P}^{\text{red}}$).³³ The bands at 509, 539, 579, 633, and 1130 nm coincide with absorption peaks of the one-

electron-oxidized PV3 wire molecules (abbreviated PV3^+).³⁴ In addition, the intensity at 633 nm contains a contribution from absorption by $\text{H}_2\text{P}^{\text{red}}$.³³ Previously measured transient radical cation spectra of PV3 wire molecules anchored on SiO_2 nanoparticles sensitized by $[\text{Ru}(\text{bpy})_3]^{3+}$ in aqueous solution show similar spectral structure.¹⁶ Small differences between the radical cation spectrum generated by hole transfer from $[\text{Ru}(\text{bpy})_3]^{3+}$ and the spectra of Figure 3C are due to spectral overlap with the H_2P ground-state bleach, with the pattern of decreasing features exactly matching the $\text{H}_2\text{P}(\text{S}_0)$ Q-band peaks in the 500–650 nm region.

The presence of transient spectral signatures from $\text{H}_2\text{P}^{\text{red}}$ and PV3^+ indicates injection of photogenerated holes from the sensitizer to the wire. Comparison of transient absorption spectra of Co_3O_4 -PV3- SiO_2 - H_2P samples (Figure 3C and 3D) with those of (wire-free) Co_3O_4 - SiO_2 - H_2P systems, which show electronically excited H_2P (Figure 3B), indicates that no electronically excited singlet H_2P is present in the Co_3O_4 -PV3- SiO_2 - H_2P system at 1 ps and beyond. Hence, charge separation is complete within 1 ps.

As can be seen in Figure 3C, a pronounced absorbance bleach was detected at 485 nm from Co_3O_4 -PV3- SiO_2 - H_2P . To aid identification of this bleach feature, reference measurements were performed on an analogous system with the Co_3O_4 nanoparticle core replaced by a SiO_2 core (SiO_2 -PV3- SiO_2 - H_2P). No such absorbance loss below 500 nm was observed upon excitation of the SiO_2 -PV3- SiO_2 - H_2P system (Figure

4A), demonstrating that the negative 485 nm signal is only observed in the presence of the Co oxide core. Furthermore,

Figure 4. (A) $\text{SiO}_2\text{-PV3-SiO}_2\text{-H}_2\text{P}$ ultrafast optical spectra upon 430 nm (150 fs) excitation. $\text{H}_2\text{P}^{\text{red}}$ bands are at 498 and 695 nm, and PV3^+ peaks at 509 (shoulder), 539, 579, 633 nm. No transient bleach is observed at 485 nm. From dark purple to light yellow: 1.07; 2.55; 4.01; 6.50; 17.3; 38.2; 91.0; 319; 1560; 2110 ps. (B) Static difference UV-vis spectrum of Co_3O_4 oxidized with Ce(IV) from Co_3O_4 . A bleach at 485 nm is observed.

the 485 nm bleach is absent for $\text{Co}_3\text{O}_4\text{-SiO}_2\text{-H}_2\text{P}$ core-shell particles that lack embedded PV3 (Figure 3B), indicating that the negative signal requires electronic linkage between light absorber and Co_3O_4 . Therefore, we attribute the bleach at 485 nm to charge transfer from the wire molecule to Co_3O_4 . Because a hole is injected onto PV3 upon H_2P reduction, the bleach is assigned to arrival of a hole from PV3^+ onto the Co oxide core, yielding $\text{Co}_3\text{O}_4(\text{h}^+)$. The resulting charge-separated state is $\text{Co}_3\text{O}_4(\text{h}^+)\text{-PV3-H}_2\text{P}^{\text{red}}$. As shown in Figure 4B, the assignment of this transient bleach feature to $\text{Co}_3\text{O}_4(\text{h}^+)$ is further supported by the observation of a bleach at wavelengths shorter than 550 nm when exposing aqueous colloidal solution of Co_3O_4 nanoparticles to Ce^{4+} , which is well-known to induce water oxidation by hole injection into Co_3O_4 particles. It is important to note that the bleach below 500 nm caused by direct absorption of the 430 nm photolysis pulse by Co_3O_4 and the dip at 480 nm in the first time slice of Figure 3C originating from excitation of the $\text{H}_2\text{P-PV3}$ ground-state absorption both get smaller on the ps time scale, opposite to the kinetic behavior of the 485 nm bleach attributed to hole transfer to Co_3O_4 .

None of the transient absorptions associated with $\text{H}_2\text{P}^{\text{red}}$ or $\text{Co}_3\text{O}_4(\text{h}^+)$ of the $\text{Co}_3\text{O}_4\text{-PV3-SiO}_2\text{-H}_2\text{P}$ system were observed for $\text{Co}_3\text{O}_4\text{-SiO}_2\text{-H}_2\text{P}$ particles that did not have wire molecules embedded in the silica shell. Instead, excited

singlet $\text{H}_2\text{P}(\text{S}_1)$ bands are detected as mentioned above (Figure 3B). The observed decay time of the $\text{H}_2\text{S}(\text{S}_1)$ state is 580 ± 50 ps, which represents the internal relaxation time of the sensitizer and competes with charge transfer to the wire in the case of the fully assembled $\text{Co}_3\text{O}_4\text{-PV3-SiO}_2\text{-H}_2\text{P}$ system.

For elucidating the kinetics of the charge transfer processes in $\text{Co}_3\text{O}_4\text{-PV3-SiO}_2\text{-H}_2\text{P}$ assemblies, the 1130 nm absorption of PV3^+ and the 695 nm band of $\text{H}_2\text{P}^{\text{red}}$ were selected to represent the transient behavior because they exhibit the least overlap with other spectral features. We note that in the visible region the 509 nm band follows the same kinetics within uncertainty as the 1130 nm band. However, for clarity, only the 1130 nm band is shown and discussed further. Figure 5A and

Figure 5. Kinetic behavior of molecular wire and porphyrin bands. (A) 695 nm absorption of $\text{H}_2\text{P}^{\text{red}}$. (B) 1130 nm band of PV3^+ . (C) Fit of decay of the PV3^+ and $\text{H}_2\text{P}^{\text{red}}$ species. Solid traces are least-squares fits according to eqs 1–3. The inset shows the kinetic behavior of the 485 nm bleach attributed to $\text{Co}_3\text{O}_4(\text{h}^+)$. Baseline treatment: The peak area at 695 nm was calculated by fitting a Gaussian-shaped band with cubic baseline that follows the Co_3O_4 transient absorption shape near 695 nm. These were used for the kinetic calculations and plots shown in panel C. In panels A and B, background subtracted spectra are presented. The 695 nm peak was smoothed by seven-point binomial smoothing, while for the 1130 band raw data are shown.

5B shows the absorbance changes of the baseline-corrected 695 and 1130 nm bands on the tens of picoseconds time scale. The 1130 nm band completely vanishes within less than 300 ps. The decay of the 695 nm absorption levels off in the same time interval but shows residual intensity extending to nanoseconds. More extensive sets of data points for both bands, together with the temporal behavior of the bleach at 485 nm, are presented in the kinetic plots of Figure 5C. Recovery of this 485 nm bleach, shown in Figure 6A, follows biphasic kinetics, with most occurring on the time scale of 10 ns with a slower phase extending to about 1 μs , as displayed in Figure 6B. While colloidal solutions of spherical $\text{Co}_3\text{O}_4\text{-PV3-SiO}_2$ core-shell

Figure 6. (A) Nanosecond to microsecond transient absorption spectra of Co_3O_4 - SiO_2 core-shell particles with embedded PV3 wires and adsorbed H_2P light absorber. From dark to light red: 1.04; 2.55; 4.95; 10.6; 24.6; 113; 2060 ns. The inset shows spectra of Co_3O_4 - SiO_2 core-shell particles with adsorbed H_2P light absorber but without embedded wires, demonstrating that the broad absorption with a maximum at 580 nm originates from excitation of the Co_3O_4 core, but the bleach at 485 nm is only observed when PV3 wires are in the silica shell. (B) Kinetics of differential absorption traces of core-shell particles with embedded PV3 wires (full symbols) and without (empty symbols) from nanosecond to microsecond at 485 (▼) and 580 nm (●), and with SiO_2 core (□). The red continuous line is a biexponential fit to 485 nm (▼) data.

nanoparticles were found to provide optimal sensitivity for transient spectroscopic studies, water molecules are unable to access the Co oxide surface; hence, catalytic activity cannot be monitored with these samples. However, we have previously shown that water oxidation catalysis occurs upon hole injection into Co_3O_4 via PV3 wires for Co_3O_4 -PV3 particles prior to casting of silica.¹⁵ The Co_3O_4 -silica core-shell construct for actual water oxidation has nanotube geometry where the inside surface of the Co_3O_4 nanotube is open and accessible to water.^{15,24,25}

3.3. Kinetic Analysis. Based on these data, the simplest kinetic model we can conceive of for the excited-state processes upon excitation of the H_2P light absorber is presented in Scheme 2. Hole transfer from the H_2P sensitizer excited at 430 nm to embedded PV3 wires produces PV3^+ and $\text{H}_2\text{P}^{\text{red}}$ within hundreds of femtoseconds. Competition between back hole transfer from PV3^+ to $\text{H}_2\text{P}^{\text{red}}$ to regenerate ground state and forward hole transfer from PV3^+ to Co_3O_4 determines the rate of decay of the wire radical cation and the reduced H_2P on the time scale of tens to hundreds of picoseconds. These processes are temporally separated from the much slower recombination of the hole on Co oxide ($\text{Co}_3\text{O}_4(\text{h}^+)$) and $\text{H}_2\text{P}^{\text{red}}$ to regenerate

Scheme 2. Energy Diagram of Electronic States Involved in the Observed Charge Transfer Processes of the Co_3O_4 -PV3- SiO_2 - H_2P System, and Rate Constants Used for Fitting of the Kinetic Data

the Co_3O_4 -PV3- SiO_2 - H_2P ground state. The latter process takes place because no sacrificial acceptor is present for removing transferred electrons or holes. The equations for the kinetic model are (in absorbance units)

$$A_{(\text{Co}_3\text{O}_4-\text{PV3}^+-\text{H}_2\text{P}^{\text{red}})}(t) = A_{0(\text{Co}_3\text{O}_4-\text{PV3}^+-\text{H}_2\text{P}^{\text{red}})}e^{-(k_1+k_2)t} \quad (1)$$

for the decay of the initial charge-separated wire-porphyrin state, and

$$A_{(\text{Co}_3\text{O}_4(\text{h}^+)-\text{PV3}-\text{H}_2\text{P}^{\text{red}})}(t) = A_{0(\text{Co}_3\text{O}_4-\text{PV3}^+-\text{H}_2\text{P}^{\text{red}})}\left(\frac{k_2}{k_1+k_2}\right)(1-e^{-(k_1+k_2)t}) \quad (2)$$

for the rise of the transferred hole in the Co_3O_4 particle. k_1 is the rate constant for back electron transfer, k_2 is the rate constant for hole transfer from PV3^+ to Co_3O_4 , and A_0 is the initial absorbance of the $\text{Co}_3\text{O}_4(\text{h}^+)$ -PV3- $\text{H}_2\text{P}^{\text{red}}$ species. The decay of the PV3^+ band at 1130 nm follows the kinetics of eq 1 while the temporal behavior of the 485 nm bleach is described by eq 2. The kinetics of the 695 nm absorbance of $\text{H}_2\text{P}^{\text{red}}$ is described by

$$A_{(\text{H}_2\text{P}^{\text{red}})}(t) = A_{0(\text{Co}_3\text{O}_4-\text{PV3}^+-\text{H}_2\text{P}^{\text{red}})}\left(\frac{1}{k_1e^{-(k_1+k_2)t} + k_2}\right) \quad (3)$$

Least squares fits of the kinetics of the 1130 and 695 nm bands give $k_1 + k_2$ values $(2.0 \pm 0.16) \times 10^{10} \text{ s}^{-1}$ ($1/e$ decay time of $50 \pm 4 \text{ ps}$) for the 1130 nm band, and $(2.1 \pm 0.2) \times 10^{10} \text{ s}^{-1}$ ($1/e$ decay time of $48 \pm 5 \text{ ps}$) at 695 nm. The values for $k_1 + k_2$ of the two bands agree within uncertainties. As can be seen from the inset of Figure 5C, the kinetic behavior of the 485 nm bleach assigned to $\text{Co}_3\text{O}_4(\text{h}^+)$ follows that of the 1130 and 695 nm species, but the uncertainty of the absorbance changes is substantially larger than for the PV3^+ and $\text{H}_2\text{P}^{\text{red}}$ bands, primarily due to the more extensive spectral overlap with neighboring bands. Therefore, the 485 nm feature was not included in the kinetic fits. According to eq 3, $k_2/(k_1 + k_2)$ is equal to the ratio of the asymptotic absorbance of $\text{H}_2\text{P}^{\text{red}}$ (approximated by the fit value of the asymptotic absorbance of the 695 nm band taking data points over the initial 300 ps) and the starting absorbance of $\text{H}_2\text{P}^{\text{red}}$, which is $0.0036/0.0181 = 0.20$. Hence, $k_1 = (1.6 \pm 0.2) \times 10^{10} \text{ s}^{-1}$ ($62 \pm 6 \text{ ps}$), $k_2 = (3.9 \pm 0.4) \times 10^9 \text{ s}^{-1}$ ($255 \pm 23 \text{ ps}$). While the value of k_2 obtained from curve fitting is close to the uncertainty of the fit value of k_1

+ k_2 , the asymptotic amplitude of H_2P and the concurrent observation of the 485 nm bleach clearly show hole transfer to Co_3O_4 .

As can be seen from Figure 6B, the recovery of the 485 nm bleach is multiphasic with most of the back transfer of holes occurring in the initial 10 ns followed by slower processes extending to one μs . The absorbance vs log t plot shows a biexponential fit with time constants and amplitude $k_{3a} = (1.24 \pm 0.06) \times 10^8 \text{ s}^{-1}$ ($8.1 \pm 0.4 \text{ ns}$), $A_1 = 4.9 \times 10^{-4}$, and $k_{3b} = (1.4 \pm 0.4) \times 10^6 \text{ s}^{-1}$ ($700 \pm 200 \text{ ns}$), $A_2 = 9.4 \times 10^{-5}$.

4. DISCUSSION

According to the Weller equation, the energetics for charge separation between excited H_2P sensitizer and embedded PV3 wire molecule is

$$\begin{aligned} \Delta G_{\text{el}}(\text{kcal} \cdot \text{mol}^{-1}) = & 23.06 \times [\varepsilon^0(\text{PV3}^+/\text{PV3}) \\ & - \varepsilon^0(\text{H}_2\text{P}/\text{H}_2\text{P}^{\text{red}})] \\ & - w_{\text{el}}(\text{PV3}^+/\text{H}_2\text{P}^{\text{red}}) + w_{\text{el}}(\text{PV3}/\text{H}_2\text{P}) \\ & - \Delta G_{00} \end{aligned} \quad (4)$$

where $\varepsilon^0(\text{PV3}^+/\text{PV3}) = 1.01 \text{ V}$ (SCE in butyronitrile),³⁵ $\varepsilon^0(\text{H}_2\text{P}/\text{H}_2\text{P}^{\text{red}}) = -1.19 \text{ V}$ (SCE in pyridine),³⁶ and $\Delta G_{00} = 43.8 \text{ kcal mol}^{-1}$ (energy of $\text{H}_2\text{P}(\text{S}_1)$).³⁷ The Gibbs free energy part (i.e., not taking into account the w_{el} term) is $+6.9 \text{ kcal mol}^{-1}$. The large positive charge of H_2P (+8) and the small dielectric constant of SiO_2 (3.9) inflate the electrostatic part of the free energy ($w_{\text{el}}(\text{PV3}^+/\text{H}_2\text{P}^{\text{red}}) - w_{\text{el}}(\text{PV3}/\text{H}_2\text{P})$), for which $6.7 \text{ kcal mol}^{-1}$ is calculated at a separation of 0.2 nm, and smaller for larger separations. Taking the maximum value of $6.7 \text{ kcal mol}^{-1}$ (0.2 nm), we estimate that the energy of the charge-separated $\text{PV3}^+ \cdot \text{H}_2\text{P}^{\text{red}}$ state is $22.4 \text{ kcal mol}^{-1}$ smaller than the absorbed photon energy at 430 nm, as shown in Scheme 2. Hence, the observed subpicosecond formation of oxidized molecular wire and reduced porphyrin implies that hole transfer occurs from vibrationally excited S_1 and possibly the S_2 state according to the picosecond lifetime of these unrelaxed levels,^{38,39} designated as H_2P^* in Scheme 2. Such a rapid primary charge separation ensures that hole transfer to the wire dominates over slower reaction and recombination pathways. The forward transfer of the hole on the wire moiety of $\text{Co}_3\text{O}_4\text{--PV3}^+\text{--SiO}_2\text{--H}_2\text{P}^{\text{red}}$ to Co_3O_4 to yield $\text{Co}_3\text{O}_4(\text{h}^+)\text{--PV3--SiO}_2\text{--H}_2\text{P}^{\text{red}}$ is energy neutral or exoergic by a few kcal mol^{-1} depending on the separation of porphyrin and wire (Scheme 2). This path compares with 44 kcal mol^{-1} exoergic for back charge transfer of $\text{Co}_3\text{O}_4\text{--PV3}^+\text{--SiO}_2\text{--H}_2\text{P}^{\text{red}}$ to yield the $\text{Co}_3\text{O}_4\text{--PV3--SiO}_2\text{--H}_2\text{P}$ ground state (using 0.75 V for the redox potential of the Co_3O_4 valence band maximum⁴⁰) (Scheme 2). The large driving force difference between the two competing processes reflects the 4-fold difference in the rate constants, resulting in a quantum yield of 0.2 for hole transfer from the H_2P light absorber to the Co_3O_4 catalyst. Another potential contribution to the reorganization energy is the rigidity of the SiO_2 shell encapsulating PV3.

The electronic coupling between Co_3O_4 and PV3 through the tripodal linker, along with the aforementioned redox gradient in the $\text{Co}_3\text{O}_4\text{--PV3--SiO}_2\text{--H}_2\text{P}$ assembly provides the basis for ultrafast hole transfer to the catalyst. It is important to note that a gradient of relative permittivity further governs the transfer across the $\text{Co}_3\text{O}_4/\text{PV3}$ interface, from SiO_2 ($\varepsilon_r = 3.9$) to Co_3O_4 ($\varepsilon_r = 12.9$). In effect, PV3 allows hole-selective injection of charge from the sensitizer to the Co_3O_4 core, and

low relative permittivity of SiO_2 is key in minimizing environmental contributions to the total reorganization energy for charge transfer. However, we also note that another potential contribution to the reorganization energy is the rigidity of the SiO_2 shell encapsulating the PV3 molecule. We conclude that charge shift from light absorber to Co_3O_4 is favored over the back charge transfer with kinetics in the normal and inverted regions of the Marcus parabola, respectively.⁴¹ It is interesting to note that instances of geminate recombination as reported by Hammarstroem in hole transfer reactions across interfaces play per se no significant role in compromising the efficient formation of $\text{Co}_3\text{O}_4(\text{h}^+)\text{--PV3--H}_2\text{P}^{\text{red}}$.⁴² As a result, charges, namely a hole on Co_3O_4 and an electron on H_2P , are separated in the $\text{Co}_3\text{O}_4\text{--PV3--H}_2\text{P}$ system by the insulating SiO_2 matrix. Keeping H_2P at a long distance from Co_3O_4 slows down competing reactions.

Notable is the unusual function of PV3 in the $\text{Co}_3\text{O}_4\text{--PV3--SiO}_2\text{--H}_2\text{P}$ system. Wasielewski and collaborators have documented very low attenuation factors in oligo-PVs of variable length, when linked, in one specific case, to a porphyrin for coherent electron tunneling.³⁵ In that work, oligo-PV wire molecules act solely as rigid, molecular bridges without actively storing, even transiently, electrons either for forward or backward transfer. However, $\text{Co}_3\text{O}_4\text{--PV3--SiO}_2\text{--H}_2\text{P}$ features a hole-accepting Co_3O_4 rather than a hole-donating reservoir, in contrast to the reported cases.³⁵ This leaves hole hopping as the *modus operandi*. The silica-embedded PV3 wire functions as an independent electroactive component and not as a charge-mediating bridge between electron acceptors and donors. As a matter of fact, hole hopping with significant changes in the energies between $\text{Co}_3\text{O}_4(\text{h}^+)\text{--PV3--SiO}_2\text{--H}_2\text{P}^{\text{red}}$ and $\text{Co}_3\text{O}_4\text{--PV3}^+\text{--SiO}_2\text{--H}_2\text{P}^{\text{red}}$ leads to electronic decoupling of $\text{Co}_3\text{O}_4(\text{h}^+)$ from $\text{H}_2\text{P}^{\text{red}}$ and, in turn, separation of the charges. Importantly, a strong coupling/direct linkage of H_2P to the catalyst would lead to very low product quantum yields as even observed in sacrificial systems due to competing reactions.

A remarkable finding is the very high hole transfer rate of $1.9 \times 10^9 \text{ s}^{-1}$, from the wire molecule to Co_3O_4 . This rate is many orders of magnitude faster than the ones reported to date for charge transfer from molecular light absorbers to metal oxide nanoparticle catalysts for water oxidation. As alluded to in Introduction, Mallouk conducted the first transient optical study of visible light-induced hole transfer from a molecular light absorber, $[\text{Ru}(\text{bpy})_3]^{2+}$, to an oxide nanoparticle catalyst, IrO_2 .^{17,18} In this assembly, the Ru dye was anchored by malonate groups on the metal oxide catalyst and, at the same time, was attached by phosphonate groups to a TiO_2 film. The hole transfer time from the oxidized sensitizer to the metal oxide cluster of 2.2 ms was subsequently improved 3-fold by introducing a redox relay (benzimidazole–phenol) between the IrO_2 catalyst and the light absorber.¹⁹ This relay acted as a fast hole acceptor, thereby increasing the rate by which the oxidized sensitizer was reduced by electrons that were extracted on a slower time scale from the metal oxide catalyst. Further improvement is anticipated by covalently linking the benzimidazole–phenol relay to the light absorber (porphyrin in this case) once the assembly is coupled to the IrO_2 catalyst.²⁰

Much faster hole transfer on the time scale of nanoseconds has been reported for a molecular sensitizer coupled to a molecularly defined metal oxide cluster for water oxidation in the form of Ru polyoxotungstate by the groups of Hill and Bonchio.^{43,44} Specifically, very fast hole transfer for the initial

oxidation step was reported for a Ru polyoxotungstate $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$ catalyst coupled to a metal polypyridine sensitizer $[\text{Ru}(\text{bpy})_2(\text{dpbpy})]^{2+}$ (dpbpy = 4,4'-diphosphonic acid-2,2'-bipyridyl). The very large electrostatic interaction of dye and POM molecule due to the high negative charge of the latter and the positive charge of the former may be an important factor for the high rate of hole transfer.⁴³ In the general area of dye-sensitized semiconductor electrodes, ultrafast hole injection from an excited coumarin light absorber to p-type NiO electrode is well established.^{42,45} Hammarstroem found 200 fs transit time for hole transfer from anchored (by carboxyl group) excited coumarin C343 to NiO, which in turn enabled efficient electron transfer from the excited dye to a coadsorbed artificial hydrogenase.⁴⁶

For incorporating a molecular light absorber–metal oxide assembly into a complete artificial photosystem, transfer of electrons concurrently produced upon photoexcitation to an acceptor and subsequently to catalytic sites for CO_2 reduction needs to occur on a time scale that is fast compared to reverse hole transfer. For excited molecular (organic or organometallic) light absorbers, subpicosecond electron transfer to the conduction band of semiconductor or molecular catalysts has been demonstrated, outpacing the 60 ps hole recombination time observed here by approximately 2 orders of magnitude.^{47–49} For the specific Co oxide core–silica shell nanoscale design pursued here, heterobimetallic ZrOCo light absorbers covalently anchored on the silica shell surface and coupled to an Ir oxide nanoparticle catalyst for water oxidation were shown to drive CO_2 reduction by H_2O to CO and O_2 with a respectable quantum yield of 17%.⁵⁰ Studies are in progress to determine whether such favorable charge transfer kinetics similarly apply to ZrOCo –wire– Co_3O_4 systems.

5. CONCLUSIONS

Ultrafast transient absorption spectroscopy of photoinduced hole transfer from a molecular light absorber to Co oxide catalyst across silica-embedded *p*-oligo(phenylenevinylene) allowed the direct observation of charge arrival on the wire molecule, which takes place in less than 1 ps. Subsequent forward transfer of the positive charge to the Co oxide particle occurred within 250 ps, exceeding known hole transfer rates from anchored molecular light absorbers to metal oxide catalyst particles for water oxidation by several orders of magnitude. The finding reveals unusually efficient hole transfer coupling, made possible by the *p*-oligo(phenylenevinylene) linkage between a visible light absorber and a metal oxide catalyst. A key task ahead is to gain a detailed understanding of the factors that render anchored organic moieties with this structure to be efficient hole transfer conduits to metal oxide catalysts.

Ultrafast hole transfer from molecular light absorbers to metal oxide catalysts for water oxidation is essential for achieving high quantum efficiency of photodriven water oxidation. The fast transfer is achieved here by separation of light absorber and oxygen-evolving catalyst by a 2 nm thick silica layer, which can also function as a proton-conducting, O_2 -impermeable membrane. This assembly opens up capabilities for developing artificial photosystems that incorporate separation of water oxidation catalysis from the incompatible environment of light absorber and reduction catalyst by an ultrathin membrane while maintaining efficient electronic coupling between the components. Such systems are currently being explored in our laboratory.²⁴

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b01070.

Figures S1 and S2, showing FT-IR spectra of silica-embedded wire molecules and ultrafast absorption spectra of control samples (PDF)

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Notes

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