Supercatalysis by Superexchange
Stephen Fletcher* and Nicholas J. Van Dijk
Department of Chemistry, Loughborough University, Ashby Road, Loughborough, Leicestershire LE11 3TU, U.K.

ABSTRACT: In modern transition state theory, the rate constant for an electron transfer reaction is expressed as the product of four factors: an exponential factor, a pre-exponential factor, an electronic transmission coefficient, and a nuclear transmission coefficient. The activation energy of the reaction manifests inside the exponential factor, and on the conventional view, catalysis occurs by decreasing this activation energy below its catalyst-free value. In the present work we report the discovery of an unusual counter-example in which catalysis occurs by increasing the electron transmission coefficient far above its catalyst-free value. The mechanism involves the formation of a superexchange bridge between an electron donor (a graphite cathode) and an electron acceptor (a pentasulfide ion). The bridge consists of a dπ orbital inside a cobalt phthalocyanine molecule. The dramatic result is the acceleration of the reduction of pentasulfide ions by more than 5 orders of magnitude compared with the catalyst-free case.

INTRODUCTION

Chemistry is the study of change at the molecular level. Of special interest to chemists are the mechanisms of chemical reactions and the speeds at which they occur. However, the fine details of molecular processes are often difficult to establish with certainty because they must be extracted from a near-infinite set of plausible alternatives. Complicating matters still further, each individual molecular trajectory involves random changes of atomic and electronic configurations that occur on vastly different time scales. Even with modern computers, this makes the complete analysis of chemical reactions impossible.

In the absence of a definitive method of solving the equations of chemical kinetics, theoreticians have developed a vast array of approximate methods. One very important subset of approximations is known collectively as Transition State Theory. At the core of transition state theory is the idea of a "bottleneck" in the configuration space through which all successful reaction trajectories must pass.

The rate at which molecules transit the bottleneck is defined as the reaction rate and the energy needed to reach the bottleneck is defined as the activation energy. The physical configuration of the system inside the bottleneck is then referred to as the transition state, and this gives the theory its name. An attractive feature of transition state theory is that it eliminates the need to compute a vast number of reaction trajectories that end in failure. Instead, it estimates the reaction rate constant from the molar Gibbs energy of activation via the heuristic equation:

\[ k_{\text{TST}}^+ = \nu \exp \left( \frac{-\Delta G^*}{RT} \right) \]  

Here \( k_{\text{TST}}^+ \) is the rate constant of the forward reaction (s\(^{-1}\)), \( \nu \) is a pre-exponential factor (s\(^{-1}\)), \( \Delta G^* \) is the molar Gibbs energy of activation (J mol\(^{-1}\)), \( R \) is the molar gas constant, (8.314 J K\(^{-1}\) mol\(^{-1}\)), and \( T \) is the absolute temperature (K) of a heat bath in equilibrium with the reacting system.

The exponential function in eq 1, widely known as the Boltzmann factor, provides a direct measure of the probability that the transition state is occupied. However, the pre-exponential factor is much more complicated and has been the subject of extensive research for more than half a century. It has been variously modeled using collision theory (Trautz, Lewis), statistical mechanics (Eyring, Evans, Polanyi, Wigner), electron transfer theory (Randles, Levich, Marcus), diffusion theory (Kramers, Grote, Hynes), and quantum theory (Voth, Chandler, Miller). Today, it is still the focus of intense theoretical interest.

An important model of \( \nu \), valid for condensed phase matter, was first described by Henry Eyring in 1935. Eyring was interested in reactions that involved bond-breaking in the transition state and sought to model them using statistical mechanics. To obtain an analytical solution, he assumed that the transition state had all the thermodynamic properties of an ordinary molecule, except in one respect: the vibrational degree of freedom of the breaking bond was deemed to be inactive, and so could be replaced by a translational degree of freedom along the same coordinate. This led to the remarkable result:

\[ \nu \approx \frac{k_B T}{h} \]  

Received: September 8, 2016
Revised: October 28, 2016
Published: October 28, 2016

DOI: 10.1021/acs.jpcc.6b09099
J. Phys. Chem. C 2016, 120, 26225–26234
where \( k_{B} \) is the Boltzmann constant (1.381 \times 10^{-23} \text{ J K}^{-1}), \( T \) is the absolute temperature (K), and \( h \) is the Planck constant (6.626 \times 10^{-34} \text{ Js}). Hence \( \nu \approx 6.212 \times 10^{12} \text{ s}^{-1} \) at 298.15 K.

As brilliant as Eyring’s idea was, his numerical estimates still failed to agree with many known values of rate constants. Eventually, after much controversy, the discrepancies were traced to the fact that reactant molecules were sometimes returning to their initial state after passing through the transition state, rather than converting spontaneously to product. To allow for this “re-crossing” of the transition state, a dimensionless constant (with value less than one) was incorporated in the rate equation. Such a constant, which we here call the “nuclear transmission coefficient” (\( \kappa_{N} \)), represents the conditional probability that a reacting molecule will adopt the configuration of the product, given that it has already adopted the configuration of the transition state.

In the case of electron transfer reactions, a second dimensionless constant known as the “electronic transmission coefficient” (\( \kappa_{E} \)) also had to be incorporated into the rate equation, to take into account the fact that the lifetime of the transition state might not be long enough for the wave function of the transferring electron to become fully established on the acceptor. Writing both transmission coefficients separately, one obtains:

\[
 k_{ET}^{+} = \kappa_{E}\kappa_{N} \exp\left(\frac{-\Delta G^{\star}}{RT}\right) \tag{3}
\]

Here \( k_{ET}^{+} \) is the forward rate constant for an electron transfer reaction (s^{-1}), \( \kappa_{E} \) is the electronic transmission coefficient (dimensionless), \( \kappa_{N} \) is the nuclear transmission coefficient (dimensionless), \( \nu \) is the pre-exponential factor (s^{-1}), \( \Delta G^{\star} \) is the molar Gibbs energy of activation (J mol^{-1}), \( R \) is the molar gas constant, (8.314 \text{ J K}^{-1} \text{ mol}^{-1}), and \( T \) is the absolute temperature (K). It is evident that the forward rate constant is a product of four factors: an exponential factor, a pre-exponential factor, and two transmission coefficients (one for electrons, the other for nuclei).

During the 1950s, the realization that the electronic transmission coefficient could be less than one led physical chemists to adopt a jargon derived from quantum theory: if the probability of electron transfer was high during the lifetime of the transition state, then \( \kappa_{E} = 1 \) and the electron transfer reaction was said to be “adiabatic.” Conversely, if the probability of electron transfer was low during the lifetime of the transition state, then \( \kappa_{E} < 1 \) and the electron transfer reaction was said to be “nonadiabatic.” This terminology remains in widespread use today. Experimentally, the lifetimes of transition states are typically in the range 10–100 fs, while second-order rate constants for “outer-sphere” electron transfer reactions are typically in the range (1 \times 10^{-3}) l mol^{-1} s^{-1} to (4 \times 10^{3}) l mol^{-1} s^{-1}.^{25}

A major breakthrough in electron transfer theory occurred in 1959, with the derivation by Veniamin Levich and Revaz Dogonadze of an equation for the rate constant of a nonadiabatic electron transfer process between two ions in solution, in the absence of bond-breaking.\(^{10}\) This takes the form

\[
 k_{ET}^{+} = \frac{2\pi}{h} |H_{DA}|^{2} \frac{N_{A}}{\sqrt{4\pi \lambda_{m} R T}} \exp\left(\frac{-\Delta G^{\star}}{RT}\right) \tag{4}
\]

where \( k_{ET}^{+} \) is the forward rate constant for electron transfer (s^{-1}), \( h \) is the reduced Planck constant (1.054 \times 10^{-34} \text{ Js}), \( H_{DA} \) is the electronic coupling matrix element between the electron donor and electron acceptor species (J), \( N_{A} \) is the Avogadro constant (6.022 \times 10^{23} \text{ mol}^{-1}), \( \lambda_{m} \) is the sum of the molar reorganization energies of the donor and acceptor species (J mol^{-1}), \( R \) is the molar gas constant (8.314 \text{ J K}^{-1} \text{ mol}^{-1}), \( T \) is the absolute temperature (K), and \( \Delta G^{\star} \) is the molar Gibbs energy of activation (J mol^{-1}). Three years later, in 1962, a similar analysis was completed for heterogeneous electron transfer reactions (i.e., those involving electron transfer between metal electrodes and species in solution) by Dogonadze and Chizmadzhev, and today this lies at the heart of modern electrode kinetics.\(^{26}\)

For a system in classical thermodynamic equilibrium, the background fluctuations that occur inside the system are of course equilibrium fluctuations. Further, by the equipartition theorem, we know that these fluctuations appear in all the quadratic degrees of freedom of a system. Accordingly, in the case of nonadiabatic electron transfer, for small departures from equilibrium, the molar Gibbs energy surface for electron transfer can be approximated as two intersecting quadratic functions (parabolas), one describing the Gibbs energy of the reactants and the other describing the Gibbs energy of the products. Based on this idea, the forward rate constant for electron transfer may be expressed as

\[
 k_{ET} = \frac{2\pi}{h} |H_{DA}|^{2} \frac{N_{A}}{\sqrt{4\pi \lambda_{m} R T}} \exp\left(\frac{-\Delta G_{m}^{0} + \lambda_{m} + FE_{\theta}}{4\lambda_{m} R T}\right) \tag{5}
\]

where \( \Delta G_{m}^{0} \) is the difference in molar Gibbs energies between the reactants and products, and \( E_{\theta} \) is the Fermi energy of the electrons in the frontier orbitals of the electrode surface. (The electrode surface is assumed metallic or quasi-metallic.)

Equation 5 is highly informative. In particular, it tells us that the rate constant for heterogeneous electron transfer \( k_{ET} \) is controlled by five experimental parameters: the molar Gibbs energy difference between the reactants and products \( \Delta G_{m}^{0} \), the molar reorganization energy \( \lambda_{m} \) the Fermi energy of the electrons \( E_{\theta} \), the absolute temperature \( T \), and the electronic coupling matrix element \( H_{DA} \). The first four of these parameters determine the location, shape, and population of the molar Gibbs energy surface on which the reaction takes place, while the fifth parameter describes a purely quantum effect. Here, let us briefly explore this fifth term in more detail.

In Dirac notation, the electronic coupling matrix element is defined as

\[
 H_{DA} = \langle \psi_{A} | H | \psi_{D} \rangle \tag{6}
\]

where \( | \psi_{A} \rangle \) is the initial state of the electron when it is fully localized on the donor species, \( | \psi_{D} \rangle \) is the final state of the electron when it is fully localized on the acceptor species, and \( H \) is the electronic Hamiltonian (J). In the limit that the electrostatic potential energies that contribute to the Hamiltonian are long-ranged over the nuclear coordinates, it is valid to make the following approximation:\(^{25}\)

\[
 H_{DA} \approx H(\psi_{A} | \psi_{D}) = H_{AD} \tag{7}
\]

Further, since

\[
 | \langle \psi_{A} | \psi_{D} \rangle |^{2} = | \langle \psi_{D} | \psi_{A} \rangle |^{2} \tag{8}
\]

one readily obtains

\[
 k_{ET} = \frac{2\pi}{h} |H_{AD}|^{2} \frac{N_{A}}{\sqrt{4\pi \lambda_{m} R T}} \exp\left(\frac{-\Delta G_{m}^{0}}{RT}\right) \tag{9}
\]
Here $H$ is the electronic Hamiltonian and $S_{DA}$ is the overlap integral. The appearance of the overlap integral inside the expression for $k_{ET}^+$ reveals the physical nature of the electronic coupling matrix element in the case of electron transfer. It is a measure of the extent of orbital overlap between the donor species and the acceptor species. At short-range (say, a van der Waals contact distance of 0.3 nm) it has been estimated that the forward rate constant $k_{ET}^+$ might reach values as high as $10^{13} \text{s}^{-1}$, whereas at long-range (say, a tunnelling distance of 3 nm) it is thought that values might fall as low as $10^9 \text{s}^{-1}$.

In the scientific literature, textbooks on catalysis generally focus on the molar Gibbs energy surfaces on which reactions occur and pay scant regard to the electronic coupling matrix element $H_{DA}$ or its proxy, the overlap integral $S_{DA}$. Indeed, most working chemists understand a catalyst to be simply “a substance that increases the rate of a reaction by diminishing the activation energy of the reaction,” and rarely consider the possibility that the electronic transmission coefficient might be having a decisive influence. In the present work, we take the road less traveled, and identify a chemical reaction that can be speeded up by a factor of $\sim 10^5$ by direct manipulation of the electronic transmission coefficient.

At first sight, it appears that the electronic coupling matrix element $H_{DA}$ might be a constant for a given D–A pair and thus impossible to change. On closer examination, however, it becomes clear that the magnitude of $H_{DA}$ can actually be modified by the insertion of an intermediate state from the nearby environment, known as a bridge state. Provided the orbital symmetry is suitable, electrons can then tunnel from D to A through the bridge molecule B, which supplies an empty (or half-empty) orbital for the purpose. Indeed, the D–B–A motif has evolved widely in nature and has also been artificially constructed for use in molecular electronics.

Today, it is well established that electron transfer through short bridges may occur by two limiting mechanisms. If the energy of the intermediate state is less than $-14k_B T$ above the energy of the donor state ($\sim 350$ mV at $25^\circ \text{C}$), the dwell time of the electron in the intermediate state may become so long that the electron becomes bound. In this limit (known as hopping) the oxidation number of the bridge molecule temporarily decreases by one unit and the lower oxidation state becomes detectable spectroscopically. By contrast, if the energy of the intermediate state is more than $-14k_B T$ above of the energy of the donor state, then the dwell time of the electron in the intermediate state is so short that the electron remains unbound. In this limit (known as superexchange) the oxidation number of the bridge molecule remains unchanged.

In the case of a single bridge on a single bridge species, the electronic coupling matrix element $H_{DA}$ for a superexchange process takes the form:

$$H_{DA} = \frac{H_{DB}H_{BA}}{\Delta \epsilon_{\text{GAP}}}$$

where $H_{DB}$ and $H_{BA}$ are the electronic coupling matrix elements for the donor–bridge and bridge–acceptor subsystems and $\Delta \epsilon_{\text{GAP}}$ is the energy gap between the bridge state and the paired donor-and-acceptor states (here assumed degenerate). Degenecy, meaning "equal energy", is achieved when the energies of the donor and acceptor states are temporarily equalized by electrostatic fluctuations in the surrounding medium (which is typically an electrolyte solution). The importance of degeneracy is that it guarantees the conservation of energy during the electron transfer process.

The overall effect of introducing the bridge state is to increase the rate constant of the forward reaction. The basic concept is illustrated in Figure 1. The presence of the term $\Delta \epsilon_{\text{GAP}}$ in the denominator of eq 10 indicates that the greatest effect on the superexchange-boosted rate constant arises from the pair of orbitals that has the smallest value of $\Delta \epsilon_{\text{GAP}}$. Normally, this pair of orbitals consists of the highest occupied molecular orbital of the donor species and the lowest unoccupied molecular orbital of the bridge species. The functional form of eq 10 also indicates that if $\Delta \epsilon_{\text{GAP}}$ can be lowered (e.g., by a change in the chemical identity of the bridge species) then the rate constant of the overall reaction can be raised. However, before demonstrating this effect experimentally, we add one word of caution. In general, lowering $\Delta \epsilon_{\text{GAP}}$ to very small values might also trigger the formation of long-lived bridge states, and these can increase the probability of unwanted side reactions involving hopping. Accordingly, it makes sense to restrict the lowering of $\Delta \epsilon_{\text{GAP}}$ to values that do not permit hopping, or else to use bridge molecules that are inert against side reactions (such as transition metal macrocycles).

The system that we use to demonstrate "superexchange catalysis" is the electrochemical reduction of the pentasulfide ion $S_5^{2-}$ on carbon electrodes. In our laboratories, we have found that this reaction occurs by two different, parallel, mechanisms. One of these mechanisms is a CE reaction, while the other is an EC reaction. The CE reaction takes place at low cathodic overpotentials and is rate-limited by the slow dissociation of the $S_5^{2-}$ ion. This reaction is best observed on...
very high surface area electrode materials, such as microporous activated carbon, and is unaffected by surface catalysts. The EC reaction, by contrast, generally takes place at high cathodic overpotentials and is rate-limited by eq 9. This reaction is best observed on nonporous graphite electrodes and is strongly affected by surface catalysts.

### EXPERIMENTAL SECTION

**Working Electrodes.** Working electrodes having a multi-layer structure (see Figure 2) were prepared using a DEK 65 screen printer. The outer layer was either a nonporous graphite composite (thermally cured Conducting Graphite Ink G-449 from Ercon Inc., 7 Kendrick Road, Wareham, MA 02571, USA) or a porous activated carbon composite (Sutcliffe Speakman 207c, 10–15 μm particle size, London, United Kingdom). In the latter case, the homemade binder was poly(vinylidene) fluoride from Kynar, Arkema Group Inc., King of Prussia, PA. The latter was dried at 110 °C in a vacuum oven (2 mbar) for 24 h before dispersing in propylene carbonate at 60 °C. Depending on cell design, the nonporous graphite composite electrodes were printed as 1.0 cm² squares or as 3 mm diameter disks. Based on nitrogen BET measurements, the surface area of the rough activated carbon electrodes was >1 m² for each screen-printed geometrical area of 1 cm². The polymer substrate was flexible laser printing film (Lloyd Paton Ltd., Manchester, U.K.), and the silver current collector was thermally cured silver ink E-1660-136 from Ercon Inc.

In a typical experiment, a finely ground test catalyst (ca. 100 mg) was mixed with a few drops of isophorone (CAUTION: POSSIBLE CARCINOGEN) to form a viscous slurry. This was then stirred into 6.4 g of the carbon ink, which contained 40% by weight of graphite (estimated). We chose this latter product because of its ability to mask the electrochemistry of the underlying silver current collector. The crude mixture of ingredients was then homogenized using an agate planetary ball mill (Fritsch Pulverisette 7), with rotation speeds in the range 200–400 rpm for 2–4 min. After milling, the homogenized ink was printed by extrusion through a stainless steel screen having a mesh count of 80 strands per centimeter. After curing at 120 °C for 1 h, a layer of insulator (R-488B, Ercon) was stenciled on top, in order to define a 3 mm diameter disk electrode. The entire assembly was finally cured at 120 °C for another hour. The use of screen printing allowed us to manufacture large numbers of electrodes in a reproducible, low-cost, and disposable format.

**Counter Electrodes.** Counter electrodes consisted of 4 cm² platinum gauze mesh (Sigma-Aldrich Company Ltd., Dorset, England, 99.9%, 52 mesh) spot-welded to platinum wire. They were flame-annealed before use. Reference half-cells. Reference half-cells were saturated calomel electrodes (KCI) unless stated otherwise. Liquid junctions were formed inside porous glass disks. **Equipment and instrumentation.** Voltammetric experiments were carried out using an Autolab PGSTAT 20 or a µ-Autolab 70282 (type II) potentiostat (Metrohm-Autolab, Eco-Chemie, Utrecht, The Netherlands). The operating software was General Purpose Electrochemical System (GPEs), version 4.9 (Eco-Chemie Utrecht, The Netherlands). No IR compensation or noise filters were applied. Temperature control was achieved by means of an F2S-ME thermostatic oil bath with external circulation (Julabo Labotechnik GmbH, Seelbach, Germany). The operating software was EasyTemp, version 3.20 (Julabo Labotechnik GmbH, Seelbach, Germany).

**Computer software.** MarvinSketch, version 5.3 (2010), was used for drawing 2D chemical structures and MarvinSpace, version 5.3 (2010), was used for modeling chemical structures in 3D. Jasc Paint Shop Pro, version 7, was used for image formatting. Analysis of data was carried out using Microsoft Office Excel (2010). Graphs were plotted using OriginLab, version 6.1 (2001). **Reagents.** All chemicals were purchased from Fisher-Scientific (Loughborough, UK) and were reagent grade. Cobalt phthalocyanine was 97% by weight. All water was obtained from a Millipore Milli-Q gradient A10 water system (18.2 MΩ internal standard). Nitrogen gas for deoxygenation was supplied in a BOC cylinder (The Linde Group, UK). Polysulfide solutions were made fresh daily.

**Polysulfide Solutions.** Polysulfide solutions were prepared by dissolving solid sulfur in aqueous sodium sulfide solutions. The solution chemistry is complex, but well understood.68-52 The initial dissolution of Na2S in water produces an equimolar mixture of hydrosulfide ions HS⁻ and hydroxide ions OH⁻:

$$\text{Na}_2\text{S} + \text{H}_2\text{O} \rightarrow 2\text{Na}^+ + \text{HS}^- + \text{OH}^-$$

The addition of zerovalent sulfur (octasulfur) S₈⁰ then produces polysulfide species Sₙ⁻ of various chain lengths n:

$$\text{HS}^- + \text{OH}^- + (n - 1)\text{S}_8^{0} \rightarrow \text{S}_n^{2-} + \text{H}_2\text{O}$$

Spectroscopic measurements indicate that the maximum chain length of polysulfide species that can form spontaneously at room temperature is n = 5. Longer chains are unstable, precipitating colloidal sulfur.68-54

The electrochemical reduction of polysulfide species involves two major steps: a chemical (dissociation) step and an electrochemical (reduction) step, summarized by the overall reaction:55-63

$$\text{S}_{n+m}^{2+} + 2e^- \rightarrow \text{S}_n^{2-} + \text{S}_m^{2-}$$

Objectively, either the chemical step occurs first or the electrochemical step occurs first. If the chemical step occurs first (i.e., a CE mechanism), then

$$\text{S}_{n+m}^{2+} \rightarrow \text{S}_n^{*} + \text{S}_m^{*}$$

and this is followed by the electrochemical reduction of the singly charged free radicals Sₙ⁺ and Sₘ⁺:

$$\text{S}_n^{*} + e^- \rightarrow \text{S}_n^{2-}$$

$$\text{S}_m^{*} + e^- \rightarrow \text{S}_m^{2-}$$

Alternatively, if the electrochemical step occurs first (i.e., an EC mechanism), then...
and this is followed by the chemical dissociation of the triply charged species

\[ S_{n+m}^{3-} \rightleftharpoons S_n^{2-} + S_m^* \]

followed by radical termination

\[ S_m^* + e^- \rightleftharpoons S_m^{2-} \]

By printing a wide range of carbon electrode sizes and types, we found that the CE and EC mechanisms could be resolved by changing the surface area of the working electrode. On high-surface-area activated carbon electrodes, the CE mechanism dominates the voltammetric response, particularly at high temperatures (T > 50 °C), and a steady state current is observed over a wide potential range. By contrast, on low-surface-area graphite composite electrodes, at low temperatures (T < 25 °C), the EC mechanism dominates the voltammetric response, and the current increases exponentially at high cathodic overpotentials. This is just as we would expect for an interfacial electron transfer process.64

**RESULTS**

The speciation diagram of polysulfide species (derived from refs 53 and 54) is shown in Figure 3. Two solution compositions are highlighted, Na2S2.7 and Na2S4.6. Both contain 40% S42−. However, the former contains negligible S52−, whereas the latter contains 60% S52−.

Figure 3. Speciation diagram of polysulfide solutions highlighting the test compositions Na2S2.7 and Na2S4.6. Both contain 40% S42−. However, the former contains negligible S52−, whereas the latter contains 60% S52−.

Figure 4. Cyclic voltammograms showing the CE reaction at low cathodic overpotentials in two different polysulfide solutions. Data acquired on high-surface-area activated carbon electrodes at 2 mV s⁻¹, third cycle shown.

Figure 5. Temperature dependence of the S52− reduction reaction in Na2S4.6 solution, in the CE regime. Data acquired on high-surface-area activated carbon electrodes at 2 mV s⁻¹, third cycle shown.

Figure 6. Cyclic voltammograms of 1.29 mol L⁻¹ Na2S4.1 solution on low-surface-area graphite composite electrodes, showing the transition from the CE to the EC mechanism at high cathodic overpotentials, and the remarkable effect of adding cobalt phthalocyanine to the electrode composition. The percentages indicate the approximate w/w catalyst-to-carbon ratios.

The ultimate goal of the present work was to find the best possible catalyst for the electrochemical reduction of pentasulfide ions S52−. The figure of merit that we selected was the decrease in cathodic overpotential compared with the “no catalyst” case. For each catalyst tested, the overpotential of the reduction reaction of the pentasulfide ion was measured by slow-scan cyclic voltammetry (10 mV s⁻¹). Typically, ten cyclic voltammograms were recorded and data from the third cycle were analyzed. The last seven cycles were used as cross-checks to ensure the stability of the catalytic effect. Every catalyst
measurement was then replicated eight times, each time on a fresh electrode, in order to estimate the size of any statistical errors. (Coefficients of variation were typically below 4%). The catalyst loading was ~5% w/w catalyst/carbon, representing a compromise between ease of measurement and commercial cost. The solution was 1.0 mol L\(^{-1}\) Na\(_2\)S\(_{2}\)S\(_{6}\) (aq) containing 1.0 mol L\(^{-1}\) NaBr as supporting electrolyte.

The catalysts reported here are all transition metal macrocycles. (A macrocycle is a molecule that contains a cyclic framework of repeating subunits linked by bridging moieties and possibly containing a central metal ion.) Many macrocycles in nature have evolved as electron transfer catalysts, so they were a logical starting point for our screening program. Two types of macrocycle were tested, namely, porphines and phthalocyanines (see Figure 7).

![Figure 7. Structural formulas of metal porphines (left) and metal phthalocyanines (right).](image)

Porphines are planar aromatic macrocycles, consisting of four pyrrole subunits joined by methine linkages (\(\equiv\text{CH}\)–) and having an extensively delocalized \(\pi\)-system. The parent compound is called 21\(\text{H},23\text{H}\)-porphine, and substituted porphines are sometimes called porphyrins. Porphines form complexes with many metal ions; one of the best-known is heme, the oxygen transport pigment in red blood cells.

Phthalocyanines are also planar aromatic macrocycles, consisting of four isoindole subunits joined by imine linkages (\(\equiv\text{N}\)–) and having an extensively delocalized \(\pi\)-system. The parent compound is called 29\(\text{H},31\text{H}\)-phthalocyanine. As with porphines, the two hydrogen atoms of the central cavity can be replaced by metal ions, generating a range of possible products.

Cathodic overpotentials for the electrochemical reduction of the pentasulphide ion \(\text{S}_2\)\(^{2−}\) in the presence of various transition metal macrocycles are compiled in Table 1. The choice of macrocycles was dictated largely by commercial availability. From the table it is evident that cobalt(II) phthalocyanine was the best catalyst tested, decreasing the reduction overpotential of \(\text{S}_2\)\(^{2−}\) by 690 mV compared with graphite alone. This remarkable decrease in driving force corresponds to an increase in rate constant of more than 5 orders of magnitude, assuming a 120 mV Tafel slope for the one-electron reduction reaction. Such a massive effect poses the question of the catalytic mechanism.

### DISCUSSION

The catalytic mechanism we propose is that electron transfer occurs by a process of superexchange from the HOMO of the graphite surface to the LUMO of the pentasulphide ion via the half-empty \(d_z^2\) orbital of the cobalt(II) phthalocyanine molecule. The orientation of the adsorbed cobalt(II) phthalocyanine molecule that permits this is shown in Figure 8.

Table 1. Reduction of Pentasulphide Ions, \(\text{S}_2\)\(^{2−}\)

| Catalyst                          | Median cathodic overpotential/mV @ 2.25 mA cm\(^{-2}\) (±10 mV) |
|-----------------------------------|---------------------------------------------------------------|
| cobalt(II) phthalocyanine         | −194                                                          |
| manganese(II) phthalocyanine      | −237                                                          |
| Bis(salicylaldehyde) cobalt(II)   | −246                                                          |
| 2,3,7,8,12,13,17,18-octaethyl-21\(\text{H},23\text{H}\)-porphine cobalt(II) | −249                                                          |
| manganese(III) phthalocyanine     | −337                                                          |
| iron(II) phthalocyanine          | −357                                                          |
| N,N’-Bis(salicylidene)-1,2-phenylenediamino cobalt(II) | −393                                                          |
| vitamin B12 (cyanocobalamin)     | −400                                                          |
| 5,10,15,20-tetraphenyl-21\(\text{H},23\text{H}\)-porphine cobalt(II) | −530                                                          |
| N,N’-Bis(salicylidene) ethylenediamino cobalt(II) | −559                                                          |
| silver(II) phthalocyanine        | −579                                                          |
| titanyl phthalocyanine           | −634                                                          |
| lead(II) phthalocyanine          | −671                                                          |
| titanium(IV) phthalocyanine      | −686                                                          |
| dichloride                       | −703                                                          |
| copper(II) phthalocyanine        | −714                                                          |
| nickel(II) phthalocyanine        | −715                                                          |
| Bis(salicylidinimato-3-propyl) methylamino cobalt(II) | −789                                                          |
| 5,10,15,20-tetraphenyl-21\(\text{H},23\text{H}\)-porphine iron(II) | −885                                                          |
| zinc(II) phthalocyanine          | −887                                                          |
| 5,10,15,20-tetraphenyl-21\(\text{H},23\text{H}\)-porphine zinc(II) | −887                                                          |
| tin(II) phthalocyanine           | −888                                                          |
| 5,10,15,20-Tetraphenyl-21\(\text{H},23\text{H}\)-porphine copper(II) | −889                                                          |
| vanadyl 2,3-naphthalocyanine     | −889                                                          |
| 5,10,15,20-tetraphenyl-21\(\text{H},23\text{H}\)-porphine nickel(II) | −889                                                          |
| graphite (no catalyst)           | −884                                                          |

*Median cathodic overpotentials for the electrochemical reduction of pentasulphide ions \(\text{S}_2\)\(^{2−}\) on nonporous graphite electrodes in the presence of various solid catalysts. The electrolyte solution was 1.0 mol L\(^{-1}\) Na\(_2\)S\(_{2}\)S\(_{6}\) (aq) containing 1.0 mol L\(^{-1}\) NaBr, and the scan rate was 10 mV s\(^{-1}\).*

8. Evidently the \(d_z^2\) orbital of the Co\(^{2+}\) ion lies at right angles to the plane of the phthalocyanine molecule, which is flat on the electrode surface. This is precisely the orientation that has been observed on bulk graphite, as revealed by scanning tunneling microscopy.\(^{65−67}\) Interestingly, the flat orientation of the cobalt(II) phthalocyanine molecule also allows the Co\(^{2+}\) ion to screen the electrostatic repulsion between the negatively charged graphite surface and the arriving pentasulphide ion.

Viewed as two-dimensional projections, porphines and phthalocyanines appear to be very similar. Yet the electrochemical reduction of 5,10,15,20-tetraphenyl-21\(\text{H},23\text{H}\)-porphine cobalt(II) (−530 mV) is more than 2 orders of magnitude slower than cobalt(II) phthalocyanine (−194 mV). Why is this? The answer lies in the distance dependence of the electron tunneling process. In 5,10,15,20-tetraphenyl-21\(\text{H},23\text{H}\)-porphine cobalt(II) the four phenyl groups protrude out of the plane of the porphine ring, which means that the cobalt \(d_z^2\) orbital cannot make close contact with the graphite surface (Figure 9). By contrast, in cobalt(II) phthalocyanine, there are no protruding substituents and so the cobalt \(d_z^2\) orbital can readily make contact with the graphite surface. Supporting
evidence for this explanation is provided by the voltammetry of 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine cobalt(II). Even though the latter molecule has eight substituents, none of them extend very far from the plane of the porphine ring (Figure 10). Accordingly, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine cobalt(II) has almost the same catalytic power as cobalt phthalocyanine (Figure 11). Stereochemical evidence of this kind provides powerful evidence that superexchange is the key factor in determining the reaction rate in this system. As is well-known, the electronic transmission coefficient for superexchange varies hypersensitively with donor−acceptor distance, according to the semiempirical formula

$$\kappa E \approx \kappa_0 \exp(-\beta d)$$

Here $$\kappa_0$$ is the electronic transmission coefficient, $$\kappa_0$$ is a constant, $$d$$ is the donor−acceptor distance (nm), and $$\beta$$ (beta) is the decay constant (nm$$^{-1}$$). Typically, $$\beta$$ is of the order 10 nm$$^{-1}$$.
In summary, the overall reduction of the pentasulfide ion on graphite electrodes proceeds by the reaction

$$S_2^{2-} + 2e^- = S_2^{2-} + S_2^{2-}$$

Two parallel mechanisms are observed, CE and EC. The CE reaction rate is insensitive to surface catalysis, whereas the EC reaction rate is very sensitive. Indeed, the EC reaction rate can be increased by a factor $\times 10^3$ simply by adding a few percent of cobalt phthalocyanine to the graphite electrode. The reason for this exceptional response is the introduction of a half-filled $d_z^2$ orbital orthogonal to the electrode surface, which provides a superexchange bridge for the electron transfer process.

Given the observation of the superexchange mechanism in the pentasulfide system, it is reasonable to suppose that the same phenomenon might be found in other systems for which cobalt phthalocyanine is a catalyst. Examples include oxygen reduction,$^{27,23}$ hydrogen peroxide activation,$^{74}$ and carbon dioxide reduction.$^{25}$ A reappraisal of these cases might yield interesting insights.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: stephen.fletcher@Lboro.ac.uk*

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was sponsored by the EPSRC (UK) Grant Number: EP/M009394/1, “Electrochemical Vehicle Advanced Technology” (ELEVATE). N.J.V.D. also thanks Regenesys Technologies Ltd. for a scholarship.

**REFERENCES**

(1) Laidler, K. J.; King, M. C. Development of Transition-State Theory. *J. Phys. Chem.* 1983, 87 (15), 2657–2664.

(2) Hänggi, P.; Talkner, P.; Borkovec, M. Reaction-Rate Theory: Fifty Years after Kramers. *Rev. Mod. Phys.* 1990, 62 (2), 251–341.

(3) Truhlar, D. G.; Garrett, B. C.; Klippenstein, S. J. Current Status of Transition-State Theory. *J. Phys. Chem.* 1996, 100 (31), 12771–12800.

(4) Trautz, M. The Law of Reaction Rates and Gases in Equilibrium. Confirmation of the Additivity of Cv-3 /2R, and a New Determination of the Integration Constant and the Molecular Diameter. *Z. Anorg. Allg. Chem.* 1916, 96 (1), 1–28.

(5) Lewis, W. C. M. Studies in catalysis. Part IX. The Calculation in Absolute Measure of Velocity Constants and Equilibrium Constants in Gaseous Systems. *J. Chem. Soc., Trans.* 1918, 113, 471–492.

(6) Eyring, H. The Activated Complex in Chemical Reactions. *J. Chem. Phys.* 1935, 3 (2), 107–115.

(7) Evans, M. G.; Polanyi, M. Some Applications of the Transition State Method to the Calculation of Reaction Velocities, especially in Solution. *Trans. Faraday Soc.* 1935, 31, 875–894.

(8) Wigner, E. The Transition State Method. *Trans. Faraday Soc.* 1938, 34, 29–41.

(9) Randles, J. E. B. Kinetics of Rapid Electrode Reactions. Part 2.—Rate Constants and Activation Energies of Electrode Reactions. *Trans. Faraday Soc.* 1952, 48, 828–832.

(10) Levich, V. G.; Dogonadze, R. R. The Theory of Non-Radiative Electron Transfer between Ions in Solution. *Dokl. Akad. Nauk SSSR* 1959, 124 (1), 123–126.

(11) Marcus, R. A. Chemical and Electrochemical Electron-Transfer Theory. *Annu. Rev. Phys. Chem.* 1964, 15 (1), 155–196.

(12) Kramers, H. A. Brownian Motion in a Field of Force and the Diffusion Model of Chemical Reactions. *Physica* 1940, 7 (4), 284–304.

(13) Grote, R.; Hynes, J. T. The Stable States Picture of Chemical Reactions. II. Rate Constants for Condensed and Gas Phase Reaction Models. *J. Chem. Phys.* 1980, 73 (6), 2715–2732.

(14) Hynes, J. T. Chemical Reaction Dynamics in Solution. *Annu. Rev. Phys. Chem.* 1985, 36 (1), 573–597.

(15) Talkner, P.; Hänggi, P., Eds. *New Trends in Kramers’ Reaction Rate Theory*; Springer Science & Business Media: Dordrecht, Netherlands, 1995.

(16) Voth, G. A.; Chandler, D.; Miller, W. H. Rigorous Formulation of Quantum Transition State Theory and its Dynamical Corrections. *J. Chem. Phys.* 1989, 91 (12), 7749–7760.

(17) Berne, B. J.; Borkovec, M.; Straub, J. E. Classical and Modern Methods in Reaction Rate Theory. *J. Phys. Chem.* 1988, 92 (13), 3711–3725.

(18) Hänggi, P.; Talkner, P.; Borkovec, M. Reaction-Rate Theory: Fifty Years after Kramers. *Rev. Mod. Phys.* 1990, 62 (2), 251–341.

(19) Pollak, E. Variational Transition State Theory for Reactions in Condensed Phases. *J. Chem. Phys.* 1991, 95 (1), 533–539.

(20) Pollak, E. Theory of Activated Rate Processes. In *Dynamics of Molecules and Chemical Reactions*; Wyatt, R.E., Zhang, J. Z. H., Eds.; Marcel Dekker: New York, 1996; pp 617–669.

(21) Truhlar, D. G.; Garrett, B. C.; Klippenstein, S. J. Current Status of Transition-State Theory. *J. Phys. Chem.* 1996, 100 (31), 12771–12800.

(22) Pollak, E.; Talkner, P. Reaction Rate Theory: What it Was, Where is it Today, and Where is it Going? *Chaos* 2005, 15 (2), 026116.

(23) Langer, J. S. Statistical Theory of the Decay of Metastable States. *Ann. Phys. (Amsterdam, Neth.)* 1969, 54 (2), 258–275.

(24) Berezkovskii, A. M.; Pollak, E.; Zitserman, V. Y. Activated Rate Processes: Generalization of the Kramers-Grote-Hynes and Langer Theories. *J. Chem. Phys.* 1992, 97 (4), 2422–2437.

(25) Fletcher, S. The Theory of Electron Transfer. *J. Solid State Electrochem.* 2010, 14 (5), 705–739.

(26) Dogonadze, R. R.; Chizmadzhev, Y. A. Kinetics of Some Electrochemical Oxidation-Reduction Reactions on Metals. *Dokl. Akad. Nauk SSSR* 1962, 145 (4), 848–851.

(27) Gray, H. B.; Winkler, J. R. Electron Transfer in Proteins. *Annu. Rev. Biochem.* 1996, 65, 537–561.

(28) George, P.; Griffith, J. S. The Enzymes. In *Electron Transfer and Enzyme Catalysis*; Boyer, P. D., Lardy, H., Myrbäck, K., Eds.; Academic Press, 1959; Chapter 8, pp 347–389.

(29) Halpern, J.; Orgel, L. E. The Theory of Electron Transfer Between Metal Ions in Bridged Systems. *Discuss. Faraday Soc.* 1960, 29, 32–41.
(30) McConnel, H. M. Intramolecular Charge Transfer in Aromatic Free Radicals. J. Chem. Phys. 1961, 35 (2), 508−515.
(31) Taube, H. Electron Transfer between Metal Complexes—a Retrospective View (Nobel lecture). Angew. Chem., Int. Ed. Engl. 1984, 23 (5), 329−339.
(32) Moser, C. C.; Keske, J. M.; Warncke, K.; Farid, R. S.; Dutton, P. L. Nature of Biological Electron Transfer. Nature 1992, 355 (6366), 796−802.
(33) Hopfield, J. J. Electron Transfer between Biological Molecules by Thermally Activated Tunneling. Proc. Natl. Acad. Sci. U. S. A. 1974, 71 (9), 3640−3644.
(34) Jortner, J. Dynamics of Electron Transfer in Bacterial Photosynthesis. Biochim. Biophys. Acta, Rev. Bioenerg. 1980, 594 (4), 193−230.
(35) Marcus, R. A.; Sutin, N. Electron Transfers in Chemistry and Biology. Biochim. Biophys. Acta, Rev. Bioenerg. 1985, 811 (3), 265−322.
(36) Sigel, H., Sigel, A., Eds. Metal Ions in Biological Systems: Electron Transfer Reactions in Metalloproteins; CRC Press, 1991; Vol. 27.
(37) Gray, H. B.; Winkler, J. R. Electron Transfer in Proteins. Annu. Rev. Biochem. 1996, 65, 357−561.
(38) Regan, J. J.; Ramirez, B. E.; Winkler, J. R.; Gray, H. B.; Malmström, B. G. Pathways for Electron Tunneling in Cytochrome c Oxidase. J. Bioenerg. Biomembr. 1998, 30 (1), 35−39.
(39) Page, C. C.; Moser, C. C.; Chen, X.; Dutton, P. L. Natural Engineering Principles of Electron Tunneling in Biological Oxidation−Reduction. Nature 1999, 402 (6757), 47−52.
(40) Regan, J. J.; Onuchic, J. N. Electron-Transfer Tubes. In Advances in Chemical Physics: Electron Transfer - from Isolated Molecules to Biomolecules. Part 2; Prigogine, I., Rice, S. A., Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, 1999; Vol. 107, pp 497−553.
(41) Segal, D.; Nitzan, A.; Davis, W. B.; Wasielewski, M. R.; Ratner, M. A. Electron Transfer Rates in Bridged Molecular Systems 2. A Steady-State Analysis of Coherent Tunneling and Thermal Transitions. J. Phys. Chem. B 2000, 104 (16), 3817−3829.
(42) Jortner, J.; Bixon, M.; Voityuk, A. A.; Rösch, N. (2002). Superexchange Mediated Charge Hopping in DNA. J. Phys. Chem. A 2002, 106 (33), 7599−7606.
(43) Saito, K.; Kimura, T.; Maki, K.; Sumi, H. Sequential or Superexchange Mechanism in Bridged Electron Transfer Distinguished by Dynamics at a Bridging Molecule. Phys. Chem. Chem. Phys. 2009, 11 (26), 5290−5301.
(44) Lewis, F. D.; Zhu, H.; Daublain, P.; Fiebig, T.; Raytchev, M.; Wang, Q.; Shafirovich, V. Crossover from Superexchange to Hopping as the Mechanism for Photoinduced Charge Transfer in DNA Hairpin Conjugates. J. Am. Chem. Soc. 2006, 128 (3), 791−800.
(45) Renaud, N.; Berlin, Y. A.; Lewis, F. D.; Ratner, M. A. Between Superexchange and Hopping: An Intermediate Charge-Transfer Mechanism in Poly (A)-Poly (T) DNA Hairpins. J. Am. Chem. Soc. 2013, 135 (10), 3953−3963.
(46) Paulson, B. P.; Miller, J. R.; Gan, W. X.; Closs, G. Superexchange and Sequential Mechanisms in Charge Transfer with a Mediating State between the Donor and Acceptor. J. Am. Chem. Soc. 2005, 127 (13), 4680−4686.
(47) Heizler, H. M.; Marks, T. J.; Ratner, M. A. Molecular Donor-Bridge-Acceptor Strategies for High-Capacitance Organic Dielectric Materials. J. Am. Chem. Soc. 2015, 137 (22), 7189−7196.
(48) Ellis, A. J.; Sigel, A., Sigel, H., Eds. Metal Ions in Biological Systems: Equilibrium Constants and Thermodynamics of Ionization of Aqueous Hydrogen Sulphide. Hydrometallurgy 1977, 2 (3), 293−299.
(49) Cobble, J. W.; Stephens, H. P. Thermodynamic Properties of the Aqueous Sulfide and Bisulfide ions and the Second Ionization Constant of Hydrogen Sulphide over Extended Temperatures. Inorg. Chem. 1971, 10 (3), 619−625.
(50) Stephens, I. E.; Ducati, C.; Fray, D. J. Correlating Microstructure and Activity for Polysulfide Reduction and Oxidation at WS2 Electrocataysls. J. Electrochem. Soc. 2013, 160 (6), A757−A768.
(51) Legrix, A. Phase Behaviour in Polysulfide Solutions. Ph.D. Thesis, Bristol University, UK, 2000.
(52) Gigan, W.; Cunningham, E.; Plummer, S. Photophysical and Photochemical Energy Conversion: Electrocataytic Sulphur Electrodes. J. Appl. Electrochem. 1977, 7 (2), 181−182.
(53) Lessner, P. M.; McLarnon, F. R.; Winnick, J.; Cairns, E. J. Aqueous Polysulfide Flow-Through Electrodes: Effects of Electrocatayltic and Electrolyte Composition on Performance. J. Appl. Electrochem. 1992, 22 (10), 927−934.
(54) Lessner, P.; Winnick, J.; McLarnon, F. R.; Cairns, E. J. Kinetics of Aqueous Polysulfide Solutions I. Theory of Coupled Electrochemical and Chemical Reactions, Response to a Potential Step. J. Electrochem. Soc. 1986, 133 (12), 2510−2516.
(55) Lessner, P.; Winnick, J.; McLarnon, F. R.; Cairns, E. J. Kinetics of Aqueous Polysulfide Solutions II. Electrochemical Measurement of the Rates of Coupled Electrochemical and Chemical Reactions by the Potential Step Method. J. Electrochem. Soc. 1986, 133 (12), 2517−2522.
(56) Lessner, P.; McLarnon, F. R.; Winnick, J.; Cairns, E. J. Kinetics of Aqueous Polysulfide Solutions Part III. Investigation of Homogeneous and Electrode Kinetics by the Rotating Disk Method. J. Electrochem. Soc. 1987, 134 (11), 2669−2677.
(57) Hodes, G.; Manassen, J.; Cahn, D. Electrocatalytic Electrodes for the Polysulfide Redox System. J. Electrochem. Soc. 1980, 127 (3), 544−549.
(58) Licht, S. An Energetic Medium for Electrochemical Storage Utilizing the High Aqueous Solubility of Potassium Polysulfide. J. Electrochem. Soc. 1987, 134 (9), 2137−2141.
(59) Licht, S. Comment on “Kinetics of Aqueous Polysulfide Solutions”[J. Electrochem. Soc., 133, 2517] II. Electrochemical Measurement of the Rates of Coupled Electrochemical and Chemical Reactions by the Potential Step Method. J. Electrochem. Soc. 1988, 135 (1), 258−259.
(60) Remick, R. J.; Camara, E. H. Electrochemistry of the Sulfide/Poly- sulfide Coupl; Final report, November 1, 1982−June 30, 1983 (Lawrence Berkeley Laboratory Report, No. LBL-16850); Institute of Gas Technology, Chicago, IL, 1983.
(61) Fletche, S. Tafel Slopes from First Principles. J. Solid State Electrochem. 2009, 13 (4), 537−549.
(62) Hopps, K. W.; Lu, X.; Wang, X. D.; Mazur, U. Metal d-Orbital Occupation-Dependent Images in the Scanning Tunneling Microscopy of Metal Phthalocyanines. J. Phys. Chem. B 1996, 100 (27), 11207−11210.
(63) Lu, X.; Hopps, K. W. Scanning Tunneling Microscopy of Metal Phthalocyanines: d6 and d8 Cases. J. Phys. Chem. B 1997, 101 (27), 5391−5396.
(64) Lu, X.; Hopps, K. W.; Wang, X. D.; Mazur, U. Scanning Tunneling Microscopy of Metal Phthalocyanines: d7 and d9 Cases. J. Am. Chem. Soc. 1996, 118 (30), 7197−7202.
(65) Kirk, M. L.; Shultz, D. A.; Stasiew, D. E.; Lewis, G. F.; Wang, G.; Brannen, C. L.; Sommer, R. D.; Boyle, P. D. Superexchange Contributions to Distance Dependence of Electron Transfer/Transport: Exchange and Electronic Coupling in Oligo (para-phenylene)- and Oligo (2, 5-thiophene)-Bridged Donor-Bridge-Acceptor Biradical Complexes. J. Am. Chem. Soc. 2013, 135 (45), 17144−17154.
(66) Rosa, A.; Baersens, E. J. Metal-Macrocycle Interaction in Phthalocyanines: Density Functional Calculations of Ground and excited States. Inorg. Chem. 1994, 33 (3), 584−585.
(67) Reynolds, P. A.; Figgs, B. N. Metal Phthalocyanine Ground States: Covalence and ab initio Calculation of Spin and Charge Densities. Inorg. Chem. 1991, 30 (10), 2294−2300.
(68) Scrocco, M.; Ercolani, C.; Paolleti, A. M. Electron Energy Loss and X-Ray Photoelectron Spectra. Part 2. Phthalocyanine and its Ni,
Cu and Co Derivatives in their Alpha-Form. *J. Electron Spectrosc. Relat. Phenom.* 1993, 63 (2), 155−166.

(72) Jasinski, R. A New Fuel Cell Cathode Catalyst. *Nature* 1964, 201 (4925), 1212−1213.

(73) Jasinski, R. Fuel Cell Electrodes Having a Metal Phthalocyanine Catalyst. Canadian Patent No. 797,924, 1965.

(74) Li, N.; Liu, W.; Pei, K.; Yao, Y.; Chen, W. Ordered-Mesoporous-Carbon-Bonded Cobalt Phthalocyanine: a Bioinspired Catalytic System for Controllable Hydrogen Peroxide Activation. *ACS Appl. Mater. Interfaces* 2014, 6 (8), 5869−5876.

(75) Lieber, C. M.; Lewis, N. S. Catalytic Reduction of Carbon Dioxide at Carbon Electrodes Modified with Cobalt Phthalocyanine. *J. Am. Chem. Soc.* 1984, 106 (17), 5033−5034.