The leading-order Coulomb contribution for the low-energy manifold of electronic states (6, 25) is given by the two-electron permutation operator, \( P_{2\text{e}} \), which in the cases where only electronic spins are at play, reduces to the usual Heisenberg spin exchange, \(~S_1 S_2\). For the case of a J-manifold, which in the absence of crystal fields is highly degenerate, it has the form of a permutation operator acting on a \((2J + 1) \times (2J + 1)\)-dimensional space of two neighboring Yb ions. The permutation operator interchanges states \( |n_{12}, m_{22} \rangle \) and \( |m_{12}, n_{22} \rangle \) with equal weights, thus including the processes \([|7/2, -7/2\rangle \rightarrow |7/2, 7/2\rangle \) where both moments simultaneously reverse, which cannot be achieved through conventional Heisenberg–Dirac spin exchange (Fig. 1, D and E). The crystal field lifts the degeneracy of the Yb moments, and although the effective interaction that emerges retains the birthmark of its unusual origin in exchange, it way the effective spin-1/2 XXZ model effectively evidences in our experiments by the large, \( \approx 40\text{meV} \) magnetic moment carried by spinons. The orbital exchange sets the scale for these emergent quantum dynamics, which we find by comparing the measured spinon dispersion with computed spectra (Fig. 4).

Because the orbital angular momentum dominates the total Yb moment, magnetic order in YbPt2Pb arises from orbital order, and the configuration depicted in Fig. 1, D and E, is a natural way to understand how permutation of two neighboring electrons generates two spinons in the antiferromagnetic background. This is a process that entails charge-orbital separation, because the electron count per site is unchanged by correlated hopping, but the phases of the orbital wave function on both sites are reversed. Further-neighbor orbital exchange leads to states with four spinons (Fig. 1E). Hence, long-range hopping, either by virtue of the in-chain itinerancy of the 4f electrons or via coupling to the conduction electrons in metallic YbPt2Pb, provides a natural mechanism for the spectral weight of the excitations that we observe above the two-spinon but within the four-spinon continuum boundaries.

Our results provide a specific mechanism for charge-orbital separation in YbPt2Pb, where the proliferation of spinons implies that electrons lose their orbital-phase identity. When united with the previous demonstrations of spin-charge and spin-orbital separation, this finding completes the triad of electron fractionalization phenomena in one dimension (26–28).

REFERENCES AND NOTES

6. See supplementary materials on Science Online for details.

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Water splitting–biosynthetic system with CO2 reduction efficiencies exceeding photosynthetic efficiencies

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Artificial photosynthetic systems can store solar energy and chemically reduce CO2. We developed a hybrid water splitting–biological system based on a biocompatible Earth-abundant inorganic catalyst system to split water into molecular hydrogen and oxygen (H2 and O2) at low driving voltages. When grown in contact with these catalysts, Ralstonia eutropha consumed the produced H2 to synthesize biomass and fuels or chemical products from low CO2 concentration in the presence of O2. This scalable system has a CO2 reduction energy efficiency of ~50% when producing bacterial biomass and liquid fuel alcohols, consuming 180 grams of CO2 per kilowatt-hour of electricity. Coupling this hybrid device to existing photovoltaic systems would yield a CO2 reduction energy efficiency of ~10%, exceeding that of natural photosynthetic systems.

Unlight and its renewable counterparts are abundant energy sources for a sustainable society (1, 2). Photosynthetic organisms harness solar radiation to build energy-rich organic molecules from water and CO2. Numerous energy conversion bottlenecks in natural systems limit the overall efficiency of photosynthesis (3). Most plants do not exceed 1%, and microalgae grown in bioreactors do not exceed 3%; however, efficiencies of 4% for plants and 5% to 7% for microalgae in bubble bioreactors may be achieved in the rapid (short-term) growth phase (3), Artificial photosynthetic solar-to-fuels cycles may occur at higher intrinsic efficiencies (4–7), but they typically terminate at hydrogen (8), with no process installed to complete the cycle via carbon fixation. This limitation may be overcome by interfacing H2-oxidizing autotrophic
supports CO₂ reduction into complex organic molecules at high efficiency. The Co-P alloy, which is known to promote HER under alkaline solutions (27), exhibits high HER activity in water at neutral pH with minimal ROS production. X-ray photoelectron spectroscopy of Co-P thin films supports the elemental nature of the alloy (fig. S1), and energy-dispersive X-ray spectroscopy (fig. S2) establishes a phosphorus composition of 6 weight percent, which we have found to exhibit optimal HER activity in water at neutral pH with a faradic efficiency of 99 ± 2% (fig. S3). Moreover, the activity of this Co-P alloy surpasses the activity of the Earth-abundant NiMoZn and stainless steel (SS) cathodes used previously (18) (fig. 1B). At constant voltage, a stable HER current is maintained for at least 16 days (Fig. 1C). Negligible H₂O₂ is produced during HER (fig. 1D), in contrast to that of simple metallic cathodes of Pt and SS.

The Co-P HER and CoP OER catalysts work in synergy to form a biocompatible water-splitting system that salvages Co²⁺ cations leached from the microorganisms to electrodes that generate hydrogen or reducing equivalents directly (9–14).

We recently developed a hybrid inorganic-biological system that uses the catalysts of the artificial leaf (15, 16) in combination with the bacterium *Ralstonia eutropha* (17) to drive an artificial photosynthetic process for carbon fixation into biomass and liquid fuels (18). In this system, water is split to oxygen by a cobalt phosphate (CoPi) catalyst and hydrogen is produced by a NiMoZn alloy at applied voltages of $E_{\text{appl}} = 3.0 \text{ V}$. Because the maximum energy efficiency is limited by the value of $E_{\text{appl}}$ relative to the thermodynamic potential for water splitting, a reduction in $E_{\text{appl}}$ leads to biomass and liquid fuel efficiencies that surpass those of previous integrated bioelectrochemical systems and are commensurate with natural photosynthetic yields (18). However, reactive oxygen species (ROS) produced at the cathode were detrimental to cell growth. Because hydrogen peroxide (H₂O₂), as well as short-lived superoxide (O₂⁻) and hydroxyl radical (HO*) species, are thermodynamically favored against H₂ production at pH = 7, ROS production dominated at or below the potential to generate H₂. When $E_{\text{appl}}$ reached a sufficient overpotential to drive water splitting, H₂ production to support cell growth outweighed the toxic effects of ROS (18). In addition, leaching of Ni from the NiMoZn alloy into solution inhibited microbial growth.

To develop a biocompatible catalyst system that is not toxic to the bacterium and lowers the overpotential for water splitting, we used a ROS-resistant cobalt-phosphorus (Co-P) alloy cathode (Fig. 1A, pathway 1). This alloy drives the hydrogen evolution reaction (HER) while the self-healing CoPi anode (19, 20) drives the oxygen evolution reaction (OER). The electrode pair works in concert to maintain extraneous cobalt ions at low concentration and to deliver low $E_{\text{appl}}$ that splits water to generate H₂ for *R. eutropha*, which

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**Fig. 1.** Active water-splitting catalyst pair with minimal biological toxicity. (A) Reaction diagram and scanning electron microscopy images for Co-P alloy cathode and CoPi anode. The main water-splitting reaction is shown in black; the side reactions that yield toxicants are in red. Scale bars, 10 μm. (B) Current-voltage (I-V) characteristics of different HER catalysts (10 mV/s). (C) Stability of Co-P cathode, as demonstrated by 16-day chronoamperometry. (D) Assay of H₂O₂ accumulation for various cathodes combining with CoP anode: yellow, Pt; blue, stainless steel (SS); red, Co-P alloy. $E_{\text{appl}} = 2.2 \text{ V}$. Error bars denote SEM; n = 3. (E) Cyclic voltammetry of Co²⁺ and Ni²⁺ in the presence of phosphate (P). Metal concentrations are both 0.5 mM; 50 mVs. The current for Ni²⁺ is magnified by a factor of 50.

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**Fig. 2.** Energy efficiencies $\eta_{\text{bioc}}$ and kinetics of the hybrid CO₂ reduction device. (A) $\eta_{\text{bioc}}$ values for the production of biomass and chemicals at different values of $E_{\text{appl}}$ and various configurations (table S1). Solid bars are 5- to 6-day averages; hatched bars are 24-hour maxima. Error bars denote SEM; n ≥ 3. (B and C) Optical density at 600 nm (OD₆₀₀; indicator of biomass accumulation) and amounts of electric charges that were passed, plotted versus the duration of experiments with 100% CO₂ (B) and air (C) in the headspace at 1 atm pressure. $E_{\text{appl}} = 2.0 \text{ V}$. Error bars denote SEM; n = 4 for (B) and n = 3 for (C). (D) A microbial growth model predicts linear correlation between electric charges and biomass accumulation, when the H₂ generation rate by water splitting (1/2FV) is smaller than the maximum rate of H₂ consumption by active biomass (fmax X₀) (23) (fig. S12). Dashed line indicates Michaelis constant of hydrogenase for H₂. (E) Real-time monitor of biomass accumulation under “day”/”night” cycle test.
Fig. 3. Efficient synthesis of selectively produced chemicals from CO₂ and water. (A to F) PHB [(A) and (B)], isopropanol (C₂H₅OH) [(C) and (D)], and C₄ and C₅ alcohols [(E) and (F)] were selectively produced from the hybrid device. In (A), (C), and (E), the ODP₃0₀ values, concentrations of selective chemicals, and charges passed through the electrodes are plotted versus the duration of experiments. Shown in (B), (D), and (F) are averaged ηₐelec values for different products, measured at 24-hour intervals. Also shown are overall ηₐelec values combining biomass and chemical formation. The ηₐelec values for biomass, defined as intracellular organics excluding PHB, have been corrected to exclude the PHB interference in (B) (23) (see fig. S13 for values before correction). Error bars denote SEM; n = 3.

electrodes (Fig. 1A, pathway 2). In the cyclic voltamogram of CO₂ in the phosphate buffer (pH 7) (Fig. 1E), a pre-wave to the catalytic water-splitting current corresponds to the oxidation of CO₂⁺ to CO₃⁻, which drives deposition of the catalyst. The Co₃P₀₂₃ catalyst is also known to exhibit a deposition rate that is linearly proportional to CO₂⁺ concentration (22). The self-healing property of Co₃P₀₂₃ is derived from this interplay of the potential at which OER occurs versus the potential at which the catalyst deposits (20). In concert, the Co-P and Co₃P₀₂₃ catalysts preserve extremely low concentrations of Co₂⁺ in solution through activity derived from the self-healing process. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of a Co₃P₀₂₃Co₃P₀₂₃ catalyst system (Eₐpp = 2.2 V) (20) reveals submicromolar levels of Co₂⁺ in solution after 24 hours. This concentration of Co₂⁺ (0.32 ± 0.06 μM) is well below the concentration of Co₂⁺ (half-maximal inhibitory concentration IC₅₀ = 25 μM) that is toxic to R. eutropha (fig. S4).

When diffusion between the two electrodes is arrested by a porous glass frit, Co₂⁺ concentrations rise to ~50 μM. We note that for the NiMoZn cathode, Ni₃⁺ concentrations are not regulated by self-healing, as Ni₃⁺ cannot form from Ni₃⁺, and the deposition to NiO occurs at >1.5 V versus normal hydrogen electrode (NHE) (Fig. 1E; see fig. S5 for comparison with potentials of relevant redox processes).

Interfacing the biocompatible Co₃P₀₂₃Co₃P₀₂₃ water-splitting catalysts with R. eutropha results in a system capable of CO₂ fixation. The Co₃P₀₂₃ catalyst was deposited on a high-surface area carbon cloth as the electrode support (Fig. 1A and fig. S6), resulting in high currents (fig. S7) and a faradic efficiency of 96 ± 4% (fig. S8). CO₂ reduction proceeded under a constant voltage within a batch reactor (fig. S9), which was half-filled with a solution containing only inorganic salts (mostly phosphate) and trace metal supplements (23).

The Co₃P₀₂₃Co₃P₀₂₃|R. eutropha hybrid system can store more than half its input energy as products of CO₂ fixation at low Eₐpp (Fig. 2A and table S1). Entries 1, 2, 3, and 5 show that ηₐelec increases with decreasing Eₐpp under 100% CO₂ until Eₐpp < 2.0 V. Below Eₐpp = 2.0 V (entry 8), a higher salt concentration (108 mM phosphate buffer) is required to facilitate mass transport and attendant current (fig. S10). However, high salt concentrations are undesirable for R. eutropha metabolism. Thus, a concentration of 36 mM phosphate and Eₐpp = 2.0 V resulted in optimal ηₐelec for biomass production was 54 ± 4% (entry 5, n = 4) over a duration of 6 days. Our CO₂ reduction efficiency from H₂ is comparable to the highest demonstrated by R. eutropha during H₂ fermentation (25). This biomass yield is equivalent to assimilating ~4.1 mol (180 g) of CO₂ captured at the cost of 1 kWh of electricity. The amount of captured CO₂ is 30% of the amount caught by amine-based carbon capture and storage (~2000 g at the cost of 1 kWh) (26), whose processed product cannot be used as fuel. Enlarging the batch reactor volume by a factor of 10 did not perturb the efficiency (entries 4 and 6), indicating that the system is scalable and the reactor volume does not pose immediate limits. Note that ηₐelec under air (400 ppm CO₂) is 20 ± 3% (entry 7, n = 3), which is lower than for pure CO₂ by a factor of only 2.7, although the partial pressure of CO₂ is reduced by a factor of 2500. This indicates that CO₂ is not a limiting reagent (see below). The ~20% of ηₐelec for biomass is equivalent to as-

We also isolated a ROS-resistant variant of R. eutropha from one SS(CO₃P₀₂₃ water-splitting reactor after 11 consecutive days of operation (Eₐpp = 2.3 V) with a H₂O₂ generation rate of ~0.6 μM/min. Genome sequencing found several mutations between the strain (BC4) and the wild type (H16) (table S2). In the presence of parquat as a ROS inducer (27), the IC₅₀ of parquat for BC4 is almost one order of magnitude higher than that of the wild type (fig. S11). There is no obvious benefit of the BC4 strain with regard to ηₐelec (table S1), further confirming the absence of ROS in our system (see above). Nonetheless, BC4 should find great utility for achieving high ηₐelec in systems where ROS is problematic.

We found that biomass accumulation scales linearly with the amount of charge passed under pure CO₂ (Fig. 2B) or ambient CO₂ levels (Fig. 2C). The linear growth is accounted for by a model that combines governing equations for H₂ generation from water splitting and biomass accumulation from carbon fixation (23). The model predicts a linear correlation between biomass and charge passed after an induction period of low population density of bacteria and high H₂ concentration (Fig. 2D and fig. S12), which is consistent with the data shown in Fig. 2, B and C, where the induction period is too short to be observed. Gas chromatography measurements revealed a H₂ concentration in the reactor headspace of 0.19 ± 0.04% (n = 3) in 100% CO₂ and 0.10 ± 0.05% (n = 3) in air, corresponding to 1.5 ± 0.3 μM and 0.8 ± 0.4 μM, respectively, in water. These concentrations of H₂ are well below the Michaelis constant of ~6 μM for membrane-bound hydrogenases in R. eutropha (28), which suggests that H₂ is facilely consumed by R. eutropha. Moreover, similar linear growth conditions for both pure and ambient CO₂ atmospheres provide evidence that H₂ oxidation rather than CO₂ reduction is rate-limiting for biosynthesis. Lastly, R. eutropha halted growth during “night” cycles and continued CO₂ reduction 12 hours later upon resumption of the water-splitting reaction (Fig. 2E), confirming the intrinsic dependence of R. eutropha on H₂ generation. These data also reveal that the CO₃P₀₂₃Co₃P₀₂₃|R. eutropha hybrid system is compatible with the intermittent nature of a solar energy source. Direct CO₂ reduction from air highlights the relatively high affinity of R. eutropha for CO₂ at low pressures and high O₂ concentrations, in contrast to results reported for synthetic catalysts (29), individual enzymes (30, 31), and strictly anaerobic organisms such as acetogens and methanogens (11–14) (table S3).

Metabolic engineering of R. eutropha enables the renewable production of an array of fuels and chemical products (17). When R. eutropha confronts nutrient constraints coupled with carbon excess, the biosynthesis of poly(3-hydroxybutyrate) (PHB) is triggered in the wild-type H16 strain as an internal carbon storage pathway (17). As such, digestion is necessary for PHB collection (23). Under a constant rate of water splitting, PHB synthesis was not manifest until nitrogen became...
limiting (~2 days), as indicated by the cessation of biomass accumulation (Fig. 3A) as well as the \( \eta_{\text{elec}} \) measured every 24 hours (Fig. 3B) and fig. S1A). With a titer of ~700 mg/l, the 6-day average for PHB synthesis was \( \eta_{\text{elec}} = 36 \pm 3\% \) (Fig. 2A, entry 9) with a 24-hour maximum of \( \eta_{\text{elec}} = 42 \pm 2\% \) (n = 3) (Fig. 3B). In engineered strains (32, 33), this PHB pathway could be modified to excrete the fusel alcohols isopropanol (C\(_3\)), isobutanol (C\(_4\)), and 3-methyl-1-butanol (C\(_5\)), which possess energy densities of 24, 28, and 31 MJ/liter, respectively. The accumulation of these liquid fuels followed trends similar to those observed for PHB synthesis. As shown in Fig. 3, C and E, biomass production reached a plateau of biomass accumulation (Fig. 3A) as well as the \( \eta_{\text{elec}} \) measured every 24 hours (Fig. 3B and fig. S13). The achieved titers are higher than previous reported values, and \( \eta_{\text{elec}} \) values have increased by a factor of at least 20 to 50 (10, 18).

\( R. eutropha \) has demonstrated tolerance toward isopropanol (Fig. S14), allowing for enriched product concentrations under extended operation.

Our combined catalyst design mitigates biotoxicity at a systems level, allowing water-splitting catalysis to be interfaced with engineered organisms to realize high CO\(_2\) reduction efficiencies that exceed natural photosynthetic systems. Because \( E_{\text{appl}} \) required for water splitting is low (1.8 to 2.0 V), high \( \eta_{\text{elec}} \) Values are achieved that translate directly to high solar-to-chemical efficiencies (\( \eta_{\text{SCE}} \)) when coupled to a typical solar-to-electricity device (\( \eta_{\text{SCE}} = \eta_{\text{isol}} \times \eta_{\text{elec}} \)). For a photovoltaic device of \( \eta_{\text{isol}} = 18\% \), the Co-P(CoP)\(_n\) hybrid system can achieve \( \eta_{\text{SCE}} = 9.7\% \) for biomass, 7.6% for bioplastic, and 7.1% for fusel alcohols. This approach allows for the development of artificial photosynthesis with efficiencies well beyond that of natural photosynthesis, thus providing a platform for the distributed solar production of chemicals.

ECOTOXICOLOGY

Environmentally relevant concentrations of microplastic particles influence larval fish ecology

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The widespread occurrence and accumulation of plastic waste in the environment have become a growing global concern over the past decade. Although some marine organisms have been shown to ingest plastic, few studies have investigated the ecological effects of plastic presence in marine ecosystems. Here we show that exposure to environmentally relevant concentrations of microplastic polystyrene particles (90 micrometers) inhibits hatching, decreases growth rates, and alters feeding preferences and innate behaviors of European perch (Perca fluviatilis) larvae. Furthermore, individuals exposed to microplastics do not respond to olfactory threat cues, which greatly increases predator-induced mortality rates. Our results demonstrate that microplastic particles operate both chemically and physically on larval fish performance and development.

Global plastic production is estimated to be about 300 million metric tons (Mtt) annually and is increasing by 20 Mtt per year (1). As a direct consequence of the massive use of plastics in modern society, plastic waste is accumulating, especially in and around urbanized areas, where it often ends up in waterways and is ultimately transported into the ocean (2, 3). Because plastic polymers show minimal biological degradation, they remain in the environment for hundreds to thousands of years, where they break down into smaller pieces owing to ultraviolet radiation, physical forces, and hydrolysis (4). Hence, plastic particles continue to accumulate as small fragments (hereafter termed microplastics, and defined as <5 mm in size) throughout the world’s oceans (4, 5). Plastic debris can affect marine biota both physically (e.g., by blocking the alimentary tract when ingested) (6) and chemically (e.g., by leaching toxic pollutants that are part of the plastics or that have been absorbed by the plastic) (7).

To date, passive ingestion of plastic microdebris by filter feeders is known to occur, but the ecological significance of ingestion is poorly understood (3, 8, 9). There is increasing concern that
Water splitting–biosynthetic system with CO₂ reduction efficiencies exceeding photosynthesis

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Artificial photosynthesis steps up

Photosynthesis fixes CO₂ from the air by using sunlight. Industrial mimics of photosynthesis seek to convert CO₂ directly into biomass, fuels, or other useful products. Improving on a previous artificial photosynthesis design, Liu et al. combined the hydrogen-oxidizing bacterium Raistonia eutropha with a cobalt-phosphorus water-splitting catalyst. This biocompatible self-healing electrode circumvented the toxicity challenges of previous designs and allowed it to operate aerobically. When combined with solar photovoltaic cells, solar-to-chemical conversion rates should become nearly an order of magnitude more efficient than natural photosynthesis.

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