VIP Very Important Paper

Nature-Inspired Design of Artificial Solar-to-Fuel Conversion Systems based on Copper Phosphate Microflowers

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Phosphates play significant roles in plant photosynthesis by mediating electron transportation and furnishing energy for CO₂ reduction. Motivated by this, we demonstrate herein an artificial solar-to-fuel conversion system, involving versatile copper phosphate microflowers as template and titanium dioxide nanoparticles as host photocatalyst. The elaborate flowerlike architectures, coupled with a unique proton-reduction cycle from interchangeability of different species of orthophosphate ions, not only offer a 2D nanosheet platform for an optimal heterostructure interface but also effectively augment charge-carrier transfer, thereby contributing to enhanced photoactivity and hydrogen generation. These nature-inspired, phosphate-derived nanocomposites advance the synthesis of a large variety of functional materials, which holds great potential for photochemical, photoelectric and catalytic applications.

Photosynthesis by plants is an exquisite example of the conversion of sunlight into molecular fuels, storing energy in the form of chemical bonds.^[1] The sophisticated process involves two stages: one is the splitting of water into hydrogen and oxygen ("light-dependent reactions"), and the other is the reduction of carbon dioxide into carbohydrates ("light-independent reactions").^[2] This natural phenomenon has motivated the design of robust chemical reactors based on semiconducting materials, aimed at the effective use of solar energy for clean and renewable resources as well as high-value-added products.^[3]

The light-dependent reactions take place in thylakoid membranes, which are primarily comprised of organic phosphates (phospholipids). These phosphates are engaged in both stages

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of photosynthesis, mediating the transport of electrons following photolysis of water and capturing protons for the cycle of adenosine triphosphate and adenosine diphosphate to furnish energy expended in carbon fixation.^[4]

In pursuit of efficient solar-to-fuel conversion systems, we present herein a biomimetic concept based on a series of inorganic copper phosphate micrometer-scale "flower" structures. The copper phosphate ensembles are generated on copper foils by a convenient, ecofriendly corrosion method. Using the microflower structures as templates, well-defined nanocomposites are then realized by in situ immobilization of nanoparticles (NPs) of titanium dioxide (TiO₂), one of the most extensively studied photocatalytic materials. Upon illumination, the liberated phosphate ions of the nanocomposites can easily be interchanged into other forms of orthophosphate ions, thus facilitating the capture of photogenerated electrons to optimize hydrogen evolution via a proton-reduction cycle, analogous to photosynthesis by plants. Unlike phosphorus-doped TiO₂ obtained from direct treatment with phosphoric acid,^[5] our simple approach not only effectively augments charge-carrier transfer but also provides an extended 2D nanosheet platform with sandwiched heterostructure interfaces optimized for directing the exposure of photoactive TiO₂ NPs to light.

Controlled corrosion with phosphoric acid facilitates the formation, in a homogeneous manner, of the 3D branched flowerlike architectures on copper foils (Figure 1). Notably, these well-defined microflowers are comprised of thin 2D nanosheets with thicknesses down to tens of nanometers. Varying the acid concentration brings about different patterns (e.g., 0.5%, 5%, and 10% in Figure 1 b, d, and f, respectively). The formation of these ensembles of nanostructures can be considered as a corrosion-mediated self-assembly involving a dissolution-redepo-



Figure 1. SEM images, at low and high magnifications, of copper phosphate microflowers obtained by corrosion with phosphoric acid at different concentrations: (a, b) 0.5%; (c, d) 5%; and (e, f) 10%.

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sition process.^[6] Briefly, copper ions are continuously disintegrated from acid etching of copper foils and coordinate with surrounding PO_4^{3-} ions to form complexes, which become nucleation sites for the crystallization of NPs. These NPs aggregate and self-assemble further into sheetlike structures, eventually clustering into intricate flowerlike structures. The dissimilarity of their shapes correlates with the growth kinetics being dependent mainly on initial acid concentrations. At the beginning of the corrosion process, higher H_3PO_4 concentrations induce a faster dissolution rate of copper atoms from the foils, resulting in a higher concentration of copper ions released.^[7] This accelerates the reaction between Cu^{2+} and PO_4^{3-} ions and further mediates redeposition of NPs, ultimately leading to smaller and more populated nanosheets.^[8]

We next investigated the crystal structures and chemical compositions of the microflowers. Figure 2a shows a typical transmission electron microscopy (TEM) image of a micrometer-scale "rose" obtained from a starting acid concentration of



Figure 2. (a, b) TEM images, (c) elemental mapping, (d) XRD spectrum, and (e) P 2p and (f) O 1s high-resolution XPS spectra of copper phosphates with the microrose structure (5% phosphoric acid).

5%. Loosely stacked nanosheets with dimensions of several hundred nanometers are visible, consistent with the structures shown in Figure 1 d. A high-resolution TEM image (Figure 2 b) shows lattice fringes with an interplanar spacing of 0.21 nm, attributable to copper phosphate.^[9] Elemental analysis (Supporting Information, Figure S1) indicates the presence of Cu, P, and O, without other impurities. The elements are uniformly distributed on the structure, as demonstrated by elemental mapping images (Figure 2c). An X-ray diffraction (XRD) pattern recorded from the sample (Figure 2d) revealed diffraction peaks that match well with copper phosphate (JCPDS card: 21-0298). High-resolution X-ray photoelectron spectroscopy (XPS) spectra (Figure 2 e and 2 f) reveal a P2p_{3/2} peak at 133.7 eV, indicating a pentavalent oxidation state (P⁵⁺), and O1s peaks at 531.2 and 532.6 eV, which can be assigned to P-O bonds and OH groups, respectively. Collectively, these findings support the successful synthesis of flowerlike structures composed of crystalline copper phosphates.

Subsequently, TiO_2 was introduced onto the copper phosphate nanostructures to obtain synergistic biphasic heterojunc-

tions, aiming to deliver an effective photocatalytic system for solar energy conversion. The as-synthesized copper phosphate flowers show intact morphologies and chemical constitutions even after a TiO₂ annealing process at 450 °C (Supporting Information, Figure S2). The attribute of good structural integrity, coupled with the feature of offering large 2D nanosheets, warrants the use of these microflowers as robust templates for in situ growth of a secondary material to form hierarchical nanocomposites with bi-/multiphasic properties. The TiO₂ NPs, obtained by hydrothermal treatment of titanium tetraisopropoxide, present a mean size distribution of 70 nm and a pure anatase phase (Supporting Information, Figure S3). Typically, the microstructures are retained well after amalgamation of TiO₂ (Figure 3 a), with their "petals" remarkably roughened. In



Figure 3. (a) Low- and (b) high-magnification SEM images, and (c) Ti 2p and (d) O 1s high-resolution XPS spectra of a typical TiO_2 /copper phosphate nanocomposite (TCP-2).

a high-magnification image of the area indicated by the red box in Figure 3 b, closely packed and uniformly distributed TiO₂ NPs are found to envelop the copper phosphate nanosheets, giving rise to a "sandwichlike" structure. EDX spectroscopy confirms that, apart from Cu, O, and P, an additional peak attributable to Ti appears in the nanocomposites (Supporting Information, Figure S4). In the XPS spectra (Figure 3c), binding energies at 458.9 and 464.7 eV can be attributed to Ti 2p_{3/2} and $Ti 2p_{1/2}$, corresponding to Ti^{4+} with a tetragonal structure. Notably, a peak at 128.6 eV was not observed (Supporting Information, Figure S6), suggesting the absence of Ti-P bonds. Furthermore, the O1s region of the nanocomposites can be fitted into three peaks (Figure 3 d): Ti-O (530.0 eV), P-O (530.5 eV), and OH groups (532.1 eV). In contrast to copper phosphates, the binding energies of O1s in the nanocomposites shift slightly, by ca. 0.6 eV, which is possibly due to interactions between TiO₂ and the copper phosphates. Copper cations are believed to bridge oxygen from TiO₂ with oxygen from phosphates, leading to enhanced interface bonding between the two constituents.^[10]



The nanocomposites embedded with copper phosphates are capable to effectively harness sunlight for photocatalytic hydrogen generation from water splitting. For clarity, they are named as TCP-1, TCP-2, and TCP-3 according to the different acid concentrations used to prepare the templates (0.5%, 5%, and 10%, respectively). Bare TiO₂ NPs produce hydrogen at a low rate of 80 μ mol g⁻¹h⁻¹, because they are restricted by their inefficient light absorption only in the UV range of solar spectrum, and rapid the recombination of photogenerated electrons and holes (e⁻/h⁺).^[11] The hydrogen generation rates of the nanocomposites were 180 μ mol g⁻¹h⁻¹ for TCP-1, 330 μ mol g⁻¹h⁻¹ for TCP-2 (increased by 4.1 times), and 120 μ mol g⁻¹h⁻¹ for TCP-3 (Figure 4a), with an apparent quan-



Figure 4. (a) Hydrogen evolution performance of bare TiO_2 and $TiO_2/copper$ phosphate nanocomposites, with the stability test of TCP-2 for three cycles. (b) Linear sweep voltammetry curves of different samples coated on FTO glass. (c) UV-vis, and (d) PL spectra of bare TiO_2 and $TiO_2/copper$ phosphate nanocomposites. The inset of (c) shows photos of the powder samples. (e) Schematic illustration of the $TiO_2/copper$ phosphate system during the photocatalytic water splitting process (HPO₄^{2–} ions are shown, representing different forms of orthophosphate ions).

tum efficiency of 1%. The photocatalytic processes of these nanocomposites are stable, as indicated by the continuous and steady production of hydrogen from the best-performing sample, TCP-2, over many cycles. The augmented hydrogen generation rate is attributed to the multiple roles played by the distinctly structured copper phosphates. The phosphate-based microflowers provide abundant 2D planar nanosheet platforms for firm anchoring of TiO₂ NPs due to strong interface bonding, rendering the whole system with a high specific surface area up to $152.3 \text{ m}^2 \text{g}^{-1}$ (Supporting Information, Figure S7). This is beneficial for contact between water molecules

and TiO₂ surfaces, facilitating water-splitting reactions. In comparison, a physically blended mixture of copper phosphates (5%) and TiO₂ NPs gave a much lower hydrogen rate of 90 μ mol g⁻¹ h⁻¹ (Supporting Information, Figure S8). Beyond the structure aspect, the physiochemical features of TiO₂/ copper phosphate nanocomposites are also improved, befitting the photocatalytic performances. Firstly, the absorption edges of the nanocomposites (UV-vis spectra in Figure 4b) show an obvious red-shift up to 395 nm (TCP-2), as compared to 370 nm for bare TiO₂ NPs, suggesting enhanced light-harvesting capacity. Evidently, the color of the samples changed from white (TiO₂ NPs) to greenish in the case of the nanocomposites. Secondly, a small amount of PO₄³⁻ ions can be directly dissipated into the suspension upon light illumination, despite the low solubility product constant of copper phosphate (1.40×10^{-37}) . The negatively charged domains introduce a negative surface electrostatic field (NSEF),^[12] which, in essence, consumes photogenerated holes and prolongs the lifetime of photogenerated charges.^[13] PL spectra provide indirect evidence of the separation capacity of photoinduced carriers. Broad PL emission peaks centred at ca. 366 nm (λ_{ex} = 300 nm) resulted from the surface-defect-related recombination are observed in all samples (Figure 4 d). Bare TiO₂ NPs display the highest PL intensity, implying a rapid e^{-}/h^{+} recombination. The PL intensities of the nanocomposites are reduced, in which TCP-2 shows the lowest intensity, which indicates that the separation of e⁻/h⁺ pairs is greatly promoted.^[14] The intimate contact between the heterojunctions of TiO₂ and copper phosphates is critical for rapid charge-carrier transport. Thirdly, a portion of PO₄³⁻ ions readily deform into other types of orthophosphate ions, such as HPO₄²⁻ or H₂PO₄⁻, when reacting with water upon light illumination. These orthophosphate ions are apparently more active than water, whereby the protons (H⁺) are much more prone to seizing electrons to produce hydrogen.^[4b] Meanwhile, HPO_4^{2-} or $H_2PO_4^{-}$ will regenerate PO_4^{3-} ions as they lose one or two protons to form a proton-reduction cycle. Analysis of linear sweep voltammetry (LSV) curves determined that the nanocomposites possess a much lower onset potential versus a reversible hydrogen electrode (RHE), and a higher current density of 0.41 mA cm⁻², validating enhanced proton conductivity over bare TiO₂ NPs.^[15] The mechanism of the TiO₂/copper phosphate system for photocatalytic reactions is illustrated in Figure 4e. In brief, NSEF induced by PO4³⁻ ion domains consumes photo-generated holes, thus favoring the separation of e^{-}/h^{+} pairs. Meanwhile, a sustainable proton-reduction cycle is generated involving the interchangeability of different types of orthophosphate ions, which benefits the capture of photo-generated electrons so as to maximize hydrogen production, assimilating the plant photosynthesis.

In summary, a nature-inspired design of solar-to-fuel conversion systems is presented, involving copper phosphate micro-flowers as templates and in situ deposited TiO_2 NPs as host photocatalyst. The hydrogen evolution performance is markedly enhanced, by a factor of 4.1 compared to bare TiO_2 , owing to their large specific surface area, extended light absorption, and effective mitigation of electron-hole recombination. Signif-



icantly, a proton-reduction cycle of phosphate ions contributes to a faster combination with photogenerated electrons for improved hydrogen generation. The uniqueness and versatility of these biomimetic phosphate-derived nanocomposites advances the synthesis of diverse functional materials, potentially useful for photochemical, photoelectric, and catalytic systems.

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