Integrating Zeolite-Type Chalcogenide with Titanium Dioxide Nanowires for Enhanced Photoelectrochemical Activity

Chengyu Mao,† Yanxiang Wang,‡ Wei Jiao,‡ Xitong Chen,‡ Qipu Lin,‡ Mingli Deng,§ Yun Ling,§ Yaming Zhou,§ Xianhui Bu,*∥ and Pingyun Feng*†‡⊥

†Materials Science and Engineering Program, University of California, Riverside, California 92521, United States
‡Department of Chemistry, University of California, Riverside, California 92521, United States
§Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, China
∥Department of Chemistry and Biochemistry, California State University Long Beach, 1250 Bellflower Boulevard, Long Beach, California 90840, United States

ABSTRACT: Developing photoanodes with efficient visible-light harvesting and excellent charge separation still remains a key challenge in photoelectrochemical water splitting. Here zeolite-type chalcogenide CPM-121 is integrated with TiO₂ nanowires to form a heterostructured photoanode, in which crystalline CPM-121 particles serve as a visible light absorber and TiO₂ nanowires serve as an electron conductor. Owing to the small band gap of chalcogenides, the hybrid electrode demonstrates obvious absorption in visible-light range. Electrochemical impedance spectroscopy (EIS) shows that electron transport in the hybrid electrode has been significantly facilitated due to the heterojunction formation. A >3-fold increase in photocurrent is observed on the hybrid electrode under visible-light illumination when it is used as a photoanode in a neutral electrolyte without sacrificial agents. This study opens up a new avenue to explore the potential applications of crystalline porous chalcogenide materials for solar-energy conversion in photoelectrochemistry.

1. INTRODUCTION

Heterometallic chalcogenides are among the most advanced solid-state materials and have been widely investigated in recent years.¹,² By combining synthetic and structural concepts from metal chalcogenide chemistry and nanoporous solids, a number of highly stable porous chalcogenides with structural and functional diversity have been developed.³ Compared to the well-developed crystalline porous zeolites, which are at the center of many industrial revolutions like petroleum refining and gas separation,⁴ chalcogenides possess favorable electronic band structures in semiconducting⁵,⁶ instead of insulating range, and their atomic and electronic structures can be conveniently tuned through either direct synthesis or postsynthetic modifications by varying cluster composition, type, and size, intercluster connectivity, or doping clusters with heteroatoms. Moreover, thanks to the size-tunable building blocks in chalcogenides such as supertetrahedral clusters,⁷ a pore size much larger than that in zeolites can be achieved, which makes porous chalcogenides ideal as host frameworks for guest molecules.⁹ Such integration between unique electronic properties¹⁰ and porosity makes chalcogenides promising candidates for many important applications.¹¹,¹²

The quest for efficient solar-energy conversion into chemical energy has stimulated worldwide interest in artificial photosynthesis research,¹³,¹⁴ since the first discovery of TiO₂ photocatalyst four decades ago.¹⁵ Despite their strong optical absorption, advantageous band edge positions, high stability toward photocorrosion, low toxicity, and abundance, the efficiency of metal oxide photocatalysts is limited by the large band gap and severe charge recombination.¹⁶ In comparison, heterometallic chalcogenides are known to consist of environmentally benign elements and exhibit tunable gaps in the visible-light range. As such, they are well-suited for solar-energy harvest.¹⁷−¹⁹ As photovoltaic materials, high solar-energy conversion efficiency has been achieved in solar cell devices by employing various quaternary chalcogenides such as Cu₂ZnSnS₄ (CZTS), Cu₂ZnSnSe₄ (CZTSe), and CuInₓGa₁−ₓSe₄ (CIGS).²⁰ However, for photocatalytic reactions, hole-induced oxidative photocorrosion represents a significant hindrance for the practical application of metal chalcogenide photocatalysts.²¹ Moreover, low surface area of

Received: July 12, 2017
Revised: October 2, 2017
Published: November 15, 2017
many previously reported chalcogenides also limits the available surface-active sites.

Integrating merits of different types of materials by forming hybrid structures could provide a feasible pathway to circumvent some limitations of single-component photocatalysts. For instance, chalcogenides can be anchored onto a wide band gap photocatalyst to form a heterojunction. Electrons generated under visible-light irradiation in the conduction band (CB) of chalcogenides can be effectively transferred into the conduction band of the other photocatalyst, which allows for a more efficient solar-light absorption and photogenerated electron–hole separation. TiO$_2$ nanowire photoanode sensitized with CdS quantum dots (QDs) or shells is a classic example of heterostructured photoelectrode for photoelectrochemical (PEC) water splitting. More recently, reduced graphene oxide (RGO) sheets, which can offer excellent electron mobility and high optical transparency, are widely used as an electron acceptor to promote charge separation. In our own work, by integrating RGO sheets and OCF-40-ZnGaSnS chalcogenide (OCF stands for organically directed chalcogenide frameworks) T4 super-tetrahedral clusters (T4 means there are 4 metal sites along the edge of the tetrahedron), we were able to fabricate a hybrid material using a two-step approach. The resulting hybrid photoanode shows a significantly enhanced photocurrent compared to either TiO$_2$ photoanode or CPM-121 photoanode directly deposited on FTO, demonstrating the synergetic effect of both components.

2. EXPERIMENTAL SECTION

Materials Synthesis. To integrate zeolite-type chalcogenide CPM-121-ZnGeGaS with TiO$_2$, TiO$_2$ nanowires were first grown on a substrate using a hydrothermal method. A clean FTO substrate with conductive side facing down was immersed into the autoclave filled with a solution of hydrochloric acid and Ti(IV) isopropoxide. The autoclave was put in a preheated 200 °C oven for 90 min. Afterward, FTO substrate covered with TiO$_2$ nanowires was recovered from the autoclave, dried overnight first, and annealed in air at 400 °C for 1 h.

CPM-121-ZnGeGaS was then fabricated on FTO-TiO$_2$. A slurry containing GeO$_2$, Zn(NO$_3$)$_2$·6H$_2$O, Ga(NO$_3$)$_3$·xH$_2$O, sulfur, and 3 mL of N-(2-aminoethyl) morpholine (AEM) was first stirred overnight until no aggregates existed. The as-obtained slurry was dropped onto the TiO$_2$ side of FTO-TiO$_2$ by using a glass rod. FTO-TiO$_2$ was then moved into an empty autoclave. The vessel was then sealed and heated at 190 °C for 1 week. After cooling to room temperature, the FTO was recovered and the yellow crystals were grown on the TiO$_2$ surface.

Characterization. The X-ray diffraction (XRD) patterns were measured using a Bruker D8 Advance powder diffractometer with Cu Kα emission. Scanning electron microscopy (SEM) images and
energy-dispersive X-ray spectroscopy (EDX) were obtained using a Nova Nano-SEM450 equipped with Oxford Instruments Aztec energy-dispersive spectroscopy detector. Optical properties were investigated by a SHIMADZU UV-3150 UV–vis scanning spectrophotometer equipped with an integration sphere.

**Photoelectrochemical Characterization.** Photoelectrochemical study was performed in a three-electrode configuration with samples as a working electrode, Pt as a counter electrode, and Ag/AgCl as a reference electrode. A 150 W xenon lamp coupled with a 420 nm cutoff filter was used as the visible-light source, and 0.5 M Na2SO4 aqueous solution at pH = 6.3 was employed as the electrolyte. A Solartron 1287 electrochemistry interface coupled with a Solartron 1260 impedance/gain-phase analyzer was used to collect the data. The gaseous product on the cathode was collected by electrolyte-displacement method and analyzed by a gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD). Stability test was also performed in 0.5 M Na2SO4 solution at 1.23 V vs reversible hydrogen electrode (RHE) with a 455 nm cutoff filter.

### 3. RESULTS AND DISCUSSION

Rutile TiO2 nanowires were grown on FTO by a hydrothermal method.37 Both powder X-ray diffraction (PXRD) and SEM characterizations (Figure 1A and Figure S1A) confirmed the formation of TiO2 nanowires. Energy-dispersive X-ray spectroscopy (EDX) collected at the same spot as the SEM images reveals that the nanowires are composed of Ti and O (Figure S1B). With its high chemical stability, TiO2 nanowires could serve as the backbone during the following solvothermal reactions, and crystallized chalcogenide clusters can be grown on its surface. The crystallization of Ge/Sn chalcogenide zeotypes induced by a small amount of divalent metal ions was systematically investigated in our previous study. Built of superoctahedral T2 clusters, the as-obtained CPM-121 crystals could be simplified into a noninterpenetrated superdiamond, and its adamantane cage is depicted in Figure 1B. The detailed procedure for CPM-121 formation on the TiO2 backbone by the reaction of Zn(NO3)2·6H2O, Ga(NO3)3·9H2O, GeO2, and S with the assistance of N-(2-aminoethyl) morpholine (AEM) template is described in the Experimental Section and Supporting Information. As shown in the SEM image of Figure S2, TiO2 nanowires kept their original morphology after its recovery from the autoclave while octahedral-shaped crystals in a few micrometers were obtained on TiO2 surfaces. From a larger-scale SEM image in Figure 1C, uniformly distributed octahedral crystals with a narrow size distribution were observed on the TiO2 substrate. Diffraction peaks ascribed to CPM-121 were also spotted in the PXRD pattern of the as-obtained sample (Figure 1A) in addition to those signals coming from TiO2 substrate. The signatures from Zn, Ge, Ga, and S in EDX spectra (Figure 1D) further verified the formation of CPM-121. Moreover, the elemental mapping (Figure S3) revealed that those signals only came from the locations where the octahedral crystals were formed. More specifically, S and Ge elements were homogeneously distributed on the octahedral-shaped crystals while Ti signals were coming from the nanowires. Given the small amount of Zn and Ga in the chalcogenide cluster, their signals were not strong in the elemental mapping. Powder samples prepared in the autoclave were also examined by powder X-ray diffraction. Their crystallinity and purity were further verified by comparing the X-ray diffraction pattern obtained from the powders and that simulated from single-crystal data (Figure S4).

The optical properties of the heterostructural electrodes as well as FTO-TiO2 were investigated by UV–vis absorbance spectra.38 As shown in Figure S5A, crystalline CPM-121 powder showed strong absorption in the entire range of wavelengths, making it an ideal light absorber for efficient solar-energy harvest. The band gap was determined to be 1.94 eV from its corresponding Tauc plot (Figure S5B). On the other hand, Figure 2A showed that TiO2 nanowires grown on FTO current collector only demonstrated a strong absorbance below 420 nm, consistent with its intrinsic large band gap of 2.97 eV. When the TiO2 photoelectrode was integrated with the chalcogenide crystals, an obvious absorption in the visible-light region was observed. Furthermore, the light absorption in the UV region was also enhanced. The results confirmed the effectiveness of the heterostructure for light harvest and suggested that the hybrid electrode may absorb more photons to generate electrons and holes and thus enhance the photoelectrochemical activity. Tauc plot of the heterostructured photoelectrode in Figure 2B revealed two distinct band gaps at 2.99 and 1.84 eV, corresponding to the band gap of rutile TiO2 and CPM-121, respectively. An X-ray photoelectron spectroscopy valence band (XPS-VB) spectrum was also collected for CPM-121 (Figure S6), and the valence band maximum was determined to be at 0.56 eV. Conduction band minimum of rutile and CPM-121 could then be estimated using their measured band gap, which were at −1.12 and −1.28 eV, respectively.39 As a result, a type-II gap could be formed between rutile and CPM-121 to facilitate charge transport. The slight deviation of the band gap from each individual component may be the result of strong interfacial interaction between the two components.

The visible-light-driven photoelectrochemical activity of the hybrid electrode was studied here. The transient photocurrents of the FTO-TiO2-CPM-121, FTO-TiO2, and CPM-121 crystals deposited directly on the FTO by electrophoresis were

**Figure 2.** (A) UV–vis spectra and (B) Tauc plots of FTO-TiO2-CPM-121 and FTO-TiO2.

DOI: 10.1021/acs.langmuir.7b02403

Langmuir 2017, 33, 13634–13639
recorded in Figure 3A during repeated on/off illumination cycles at 1.0 V vs RHE. The RHE potential was converted from the saturated Ag/AgCl reference electrode using $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.57$ V. All samples exhibited prompt and reproducible responses toward light illumination, with photocurrents decreasing to almost zero upon irradiation interruption and fully recovering upon light switching on. The spike observed upon irradiation was due to the rapid effect upon power excitation, and then it quickly returned to the steady state. The photocurrent of FTO-TiO$_2$-CPM-121 reached 55 $\mu$A/cm$^2$ upon visible-light illumination, whereas FTO-TiO$_2$ is only 16 $\mu$A/cm$^2$. The >3-fold enhancement in photocurrent confirmed the synergistic effect of the heterostructure, where CPM-121 acts as an efficient visible-light absorber while TiO$_2$ substrate contributed to the electron transfer and suppressed charge recombination. The gaseous product generated on the counter electrode (Pt) was collected by electrolyte displacement and analyzed by gas chromatography, and the results are presented in Figure S10. Signals from air were used as a reference. Only a prominent H$_2$ peak was identified from the gaseous product on the cathode side and confirmed as the product of the photoelectrochemical reaction. Action spectra of photocurrents of FTO-TiO$_2$-CPM-121 and FTO-TiO$_2$ were also obtained by measuring the photocurrents under each 20 nm wavelength interval from 300 to 600 nm. The spectra in Figure S8 further demonstrated that the hybrid electrode has a superior activity in both UV and visible-light range due to the synergistic effect between the small gap CPM-121 and TiO$_2$ nanowires, which was consistent with their optical properties and the photocurrent measurements discussed above. Although CPM-121 powder demonstrated strong light adsorption in the entire light range, it only exhibits a limited photocurrent of 1.4 $\mu$A/cm$^2$ upon visible-light illumination. The poor photoelectrochemical performance should be ascribed to the difficult electron transport between the directly deposited crystals and the current collector, which could lead to severe photoexcited electron–hole pairs recombination. Note that the photocurrent achieved by the FTO-TiO$_2$-CPM-121 here was even >2 times higher than that by Pt-loaded CPM-120 photoanode with sacrificial agent. This superior performance by FTO-TiO$_2$-CPM-121 hybrid electrode may result from more efficient charge separation owing to the heterojunction formation, as well as the enhanced light harvesting. This result was further confirmed by the linear sweep voltammetry (LSV) in Figure 3B, where FTO-TiO$_2$ only achieved a photocurrent of 30.5 $\mu$A/cm$^2$ at 1.23 V vs RHE. In contrast, FTO-TiO$_2$-CPM-121 also exhibited a substantially higher photocurrent over the entire potential range. At the same 1.23 V applied voltage, FTO-TiO$_2$-CPM-121 showed a nearly 2-fold enhancement in photocurrent density, up to 59.6 $\mu$A/cm$^2$. On the other hand, CPM-121 only exhibited an inferior photoelectrochemical performance and a much smaller photocurrent of 12.2 $\mu$A/cm$^2$ at 1.23 V vs RHE.

To gain further insight into the charge-transport behaviors of all samples, electrochemical impedance spectroscopy (EIS) measurements were performed on the electrodes studied above. A Mott–Schottky plot was generated based on the capacitance derived from the impedance at different applied potentials of FTO-TiO$_2$-CPM-121 (Figure S9) as well. The positive slope in the linear part of the Mott–Schottky plot described the behavior of an n-type semiconductor, which was working as a photoanode in the photoelectrochemical cell. The semicircle in the as-obtained Nyquist plots was associated with the charge-transfer process, and a smaller arc corresponds to smaller impedance and a better charge separation. As shown in Figure 4A, FTO-TiO$_2$-CPM-121 photoanode exhibited a much smaller radius than FTO-TiO$_2$, further proving the advantageous charge separation upon heterojunction formation in the as-fabricated photoanode. The equivalent circuit shown in Figure S11 was employed to further analyze the Nyquist plot, where $R_s$ stands for a series resistance, $R_w$ stands for charge-transfer resistance, $CPE$ stands for a constant phase element for imperfect capacitance, and $W_n$ is Nernst diffusion impedance. While $R_s$ did not change much between FTO-TiO$_2$ and FTO-TiO$_2$-CPM-121(from 46.9$\Omega$ to 40.3$\Omega$), $R_w$ decreased significantly from 11 891$\Omega$ to 1 889$\Omega$, proving the beneficial charge transfer in the hybrid material. Meanwhile, CPM-121 powder deposited on FTO current collector had a significantly larger semicircle (Figure 4B), suggesting the poor electron transport within the electrode and consistent with our observations in photoelectrochemical tests. The photocurrent of FTO-TiO$_2$-CPM-121 in the presence and the absence of H$_2$O$_2$ under AM.

**Figure 3.** (A) Transient photocurrents and (B) linear sweep voltammetry of FTO-TiO$_2$-CPM-121, FTO-TiO$_2$, and CPM-121 deposited on the FTO electrode.

**Figure 4.** (A) Nyquist plot of FTO-TiO$_2$-CPM-121, FTO-TiO$_2$, and (B) CPM-121 deposited on the FTO electrode.
1.5 illumination was measured to estimate the hole-injection yield. Because the injection yield becomes 100% when H₂O₂ is in the electrolyte, the charge-injection yield into water can be estimated by dividing two photocurrents. As shown in Figure S12, the hole-injection yield rises steeply for FTO-TiO₂-CPM-121 and remains close to 100% at high potentials. Stability test was also performed on FTO-TiO₂-CPM-121, and the result is displayed in Figure S13. The as-fabricated photoanode exhibited a steady activity, with 90% photocurrent remaining after 30 min of visible-light illumination.

4. CONCLUSIONS

In summary, we have rationally designed a heterostructured photoanode consisting of heterometallic zeolite-type chalcogenide CPM-121 and TiO₂ nanowires for efficient solar-energy conversion. The crystalline porous chalcogenides act as a visible-light absorber to generate electrons and holes upon irradiation, while the TiO₂ nanowire serves as the scaffold for chalcogenide formation and facilitates the electron transfer during the photoelectrochemical reactions. The interface formed between two components significantly promotes charge separation and reduces the electrochemical impedance. As a result, a profoundly enhanced photoelectrochemical activity in the neutral electrolyte is realized under visible-light illumination on the hybrid electrode. Given the richness of compositional and topological variations in crystalline porous chalcogenide materials and their tunable optical and electronic properties, this study opens up a new avenue to explore their potential applications for solar-energy conversion in photoelectrochemistry.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b02403.

Experimental details, XRD patterns, SEM, EDX, UV−vis spectra, Mott−Schottky plot, and GC profile (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: xianhui.bu@csulb.edu.
*E-mail: pingyun.feng@ucr.edu.

ORCID

Yun Ling: 0000-0002-6956-4504
Yaming Zhou: 0000-0003-2720-9536
Xianhui Bu: 0000-0002-2994-4051
Pingyun Feng: 0000-0003-3684-577X

Present Address
†C.M.: Energy and Transportation Science Division, Oak Ridge National Laboratory, One Bethel Valley Road, P.O. Box 2008, Oak Ridge, TN 37831, United States.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation (DMR-1506661, P.F.). W.J. thanks the financial support of Fudan University and the NSFC (51402314, W.J.)


