Artificial Photosynthesis on TiO$_2$-Passivated InP Nanopillars

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Supporting Information

ABSTRACT: Here, we report photocatalytic CO$_2$ reduction with water to produce methanol using TiO$_2$-passivated InP nanopillar photocathodes under 532 nm wavelength illumination. In addition to providing a stable photocatalytic surface, the TiO$_2$-passivation layer provides substantial enhancement in the photoconversion efficiency through the introduction of O vacancies associated with the nonstoichiometric growth of TiO$_2$ by atomic layer deposition. Plane wave-density functional theory (PW-DFT) calculations confirm the role of oxygen vacancies in the TiO$_2$ surface, which serve as catalytically active sites in the CO$_2$ reduction process. PW-DFT shows that CO$_2$ binds stably to these oxygen vacancies and CO$_2$ gains an electron (−0.897 eV) spontaneously from the TiO$_2$ support. This calculation indicates that the O vacancies provide active sites for CO$_2$ adsorption, and no overpotential is required to form the CO$_2^-$ intermediate. The TiO$_2$ film increases the Faraday efficiency of methanol production by 5.7× to 4.79% under an applied potential of −0.6 V vs NHE, which is 1.3 V below the $E^0$ (CO$_2$/CO$_2^-$) = −1.9 eV standard redox potential. Copper nanoparticles deposited on the TiO$_2$ act as a cocatalyst and further improve the selectivity and yield of methanol production by up to 8-fold with a Faraday efficiency of 8.7%.

KEYWORDS: Photoelectrochemical, InP, copper, CO$_2$ reduction, TiO$_2$-passivation, methanol

With the rising level of CO$_2$ in the earth’s atmosphere, artificial photosynthesis (i.e., a process that utilizes sunlight to convert water and carbon dioxide into carbohydrates) has begun to receive increasing attention by researchers around the world. In 1978, Halmann et al. reported the first photocatalytic reduction of CO$_2$ to hydrocarbons, including formic acid, formaldehyde, and methanol. This pioneering work utilized p-type GaP under 365 nm wavelength illumination with an applied overpotential of −1.4 V (vs SCE). Many attempts have since been made to reduce CO$_2$ to hydrocarbons under UV illumination. However, few researchers have achieved photoreduction under visible illumination due to the limited selection of materials. For optimum solar utilization, the band gap of the semiconductor should lie in the range of 1.2−1.4 eV, as derived in the Schokley−Queisser limit. Also, the position of the conduction band (i.e., electron affinity) must be as close as possible to the CO$_2$ to CO$_2^-$ redox potential (−1.9 V vs NHE) in order to minimize the applied overpotential required to drive this reaction. Since the energy needed to reach the CO$_2^-$ intermediate is so high, a cocatalyst is usually added to lower the energy barrier of this intermediate species. Lastly, the surface recombination rate of the photon-induced electron hole pairs should be as low as possible. InP is a promising material for CO$_2$ reduction since its band gap of 1.34 eV is well-matched to the solar spectrum. Furthermore, the surface-recombination velocity of untreated InP is low (ca. 10$^5$ cm/s for n-type and 10$^3$ cm/s for p-type). Nanotexturing of InP can further enhance the photon-to-chemical energy conversion efficiency due to the increase in surface area and reduced reflection. CO$_2$ reduction to methanol on p-InP has been reported at relatively high applied potentials of −1.3 V (vs SCE) and with low Faraday efficiencies (around 1%). Both the poor selectivity for methanol production with respect to H$_2$ and severe photo...
corrosion have limited the application of InP in the artificial photosynthesis of hydrocarbons.

Here, we utilize TiO2-passivated nanotextured InP photocathodes to explore aqueous CO2 reduction to methanol under 532 nm illumination as a function of applied potential. The selectivity of methanol production is compared for InP samples prepared with and without Cu nanoparticles and TiO2-passivation layers. The photocatalytic surface is characterized by high resolution transmission electron microscopy (HRTEM) in order to provide a detailed picture of the nanoparticle/TiO2/InP interface. Plane wave density functional theory (PW-DFT) calculations are carried out to explore the role of surface binding of reactants and intermediate species to the TiO2 surface.

A schematic diagram of the sample geometry is illustrated in Figure 1a. Zn-doped p-type (100) oriented InP nanopillars (NPLs) with a dopant concentration of \(5 \times 10^{17} \text{ cm}^{-3}\) were used as the photocatalyst for CO2 reduction. The InP NPLs are around 80 nm in diameter and approximately 400 to 600 nm tall and have an average pitch of approximately 50 nm (Figure 1b). A detailed description of the InP NPLs preparation is provided in the Supporting Information. Briefly, InP bulk wafers are treated in a reactive ion O2 plasma treatment followed by a 2 min wet-etching step in HCl/H3PO4 (3:1) to remove the surface-damaged layers and contaminants. Atomic layer deposition (ALD) of TiO2 was performed at 250 °C on the p-InP wafers with TiCl4 as the titanium source and water vapor as the oxygen source. The average rate of deposition is approximately 0.44 Å per cycle, as calibrated by ellipsometry. We then evaporate copper with a nominal thickness of 0.5 nm on the top surface of the TiO2. A Zn−Au film was evaporated on the back of the p-InP to form an Ohmic contact. The Zn−Au contact was then connected to the external circuitry with a copper wire and coated with epoxy cement to insulate it from the electrolytic solution. A schematic diagram of the sample geometry is illustrated in Figure 1a. Figure 1c–e shows transmission electron microscope (TEM) images of the 0.5 nm Cu on the top of the InP NPLs. These figures indicate that, instead of forming a uniform continuous film, the evaporated 0.5 nm Cu forms crystal nanoparticles with diameters around 20 nm. In Figure 1e, a thin amorphous layer of CuO can be seen on the surface of the Cu nanoparticles, which is formed in air. The XPS spectra shown in Figure S8 of the Supporting Information confirms the existence of Cu 2p and O 1s peaks corresponding to CuO. The thickness of the deposited TiO2 is around 3 nm, as shown in Figure 1d. A three-terminal potentiostat was used with the prepared semiconductor samples as the working electrode, a Ag/AgCl electrode as the reference electrode, and a Pt electrode functioning as the counter electrode. The photocatalytic reaction rates of two sets of samples were measured in a 0.5 M KCl solution, while continuously bubbling CO2 through the solution. The products are detected using NMR spectroscopy and gas chromatography (GC). A schematic diagram of the photoelectrochemical measurement setup is shown in Figure S6 of the Supporting Information.

While photocatalytic CO2 reduction on InP and other III−V compound semiconductors has been demonstrated previously,3,5 these materials corrode rapidly under photoelectrochemical conditions and are significantly degraded after just 30 min of illumination.9,10 Several research groups have shown that by depositing thin films of TiO2 on these unstable semiconductors, they can be protected from corrosion.8−12 In order to make InP photochemically stable, we passivated the surface using a 3 nm thin film of TiO2 deposited by ALD, as illustrated schematically in Figure 1a. Under 532 nm illumination, the photocurrent of InP nanopillars with TiO2-passivation is stable for at least 12 h, as shown in Figure S1 in the Supporting Information.

Figure 2a shows the photocurrent−voltage curves measured in a 0.5 M KCl solution under 532 nm illumination for bare InP nanopillars and InP nanopillars passivated with TiO2. With TiO2-passivation, the photocurrent is substantially increased for all applied potentials. The bare InP nanopillar sample (blue curve) has an onset of photocurrent at a potential of approximately 0.03 V (vs NHE), as indicated in Figure 2b. For TiO2-passivated InP (red curve), we observe a clear shift in the onset potential by about 0.1 V in these photo-J−V characteristics. We attribute this, in part, to a p-n-junction formed between the TiO2, which is n-type due to oxygen vacancies, and the p-type InP.3,13 This p-n-junction creates a built-in potential that assists in the separation of photo-generated electron−hole pairs and results in a shift of the onset potential of this reaction. Figure 2c shows the methanol peaks observed in the NMR spectra of bare InP nanopillars and TiO2-passivated InP nanopillars after 12 h reactions at an applied potential of −0.6 V vs NHE under 532 nm illumination, as shown in the energy band diagram of this photocatalytic system (Figure S7 of the Supporting Information). If we consider the one electron reduction of CO2 to CO2− as the first step on this reaction, this is 1.3 V below the \(E^\circ(\text{CO}_2/\text{CO}_2^-)\) = −1.9 eV standard redox potential. Figure 2d shows the Faraday efficiencies of methanol (i.e., the selectivity of methanol) for these two types of samples. This figure indicates that the TiO2-passivation layer not only enhances the overall photon-conversion efficiency but also increases the selectivity of methanol from H2 and other hydrocarbons from 0.85% to 4.8%. We attribute the increased methanol selectivity to oxygen vacancies that are inherent to these thin TiO2 films, which provide the catalytically active sites for CO2 reduction.14−16 Peaks corresponding to Ti3+ states (i.e., O-vacancies) are observed in the XPS spectra taken from TiO2 deposited on InP, as shown in Figure S5 of the Supporting Information.
In order to verify the role of these oxygen vacancies in the photocatalytic reduction of CO₂, all plane wave density functional theory (PW-DFT) calculations were performed with the Quantum Espresso package using the most recently available ultrasoft pseudopotentials with scalar relativistic corrections, and spin-unrestricted calculations were done employing the Perdew-Burke-Ernzerhof (PBE) functional. Clean, stoichiometric anatase and defective anatase with an oxygen vacancy were both investigated in this study. Details of the calculation are given in the Supporting Information. The DFT+U approach was adopted in order to recover these highly localized states with a self-consistently computed U term of 3.6 eV applied to Ti atoms, well within Finazzi et al.’s suggested range of 3–4 eV for anatase. Although one study found the oxygen vacancy to be present deep in slabs of varying size, others were unable to determine the most stable vacancy structure. Our DFT+U calculations identified the oxygen vacancy to be at the surface, specifically, the 2-fold coordinated bridging oxygen (see Figure 3), as energetically favorable compared to other sites. Adsorption energies were calculated by subtracting the two components (molecule and surface) from the adsorbed system:

\[ E_{\text{ads}} = E[\text{surf + molecule}] - E[\text{surf}] - E[\text{molecule}] \]

where the molecule was H₂O, CO₂, or CO₂⁻ and the surface, stoichiometric anatase or defective anatase with a surface oxygen vacancy. A thorough, manual search was performed to determine the global minimum of adsorbed molecules to the anatase support. Adsorption energies were favorable between neutral CO₂ adsorbed to stoichiometric (−0.48 eV) and defective anatase (−0.94 eV), as illustrated in Figure 3. The global minima found reproduced the geometries of Sorescu et al.’s PW-DFT study of the adsorption of CO₂ on anatase. The difference in adsorption energies to Sorescu et al.’s results may be attributed to our smaller cell and computational parameter (see Supporting Information for details). In our study, we investigated alternative roles of the anatase support such as stabilization of CO₂⁻ intermediate. However, the adsorption of CO₂⁻ to stoichiometric and defective anatase resulted in repulsive, unstable systems, requiring thermodynamically unfavorable energies of 4.39 and 2.57 eV, respectively, to form. The chemical bonding analysis obtained using the Bader charge localization scheme is shown in Figure S3 in the Supporting Information. In Figure 2b, the linear CO₂ molecule becomes bent upon adsorption to the defective

Figure 2. (a) Photocatalytic current-potential curves where the dashed line indicates the potential applied during the methanol test. (b) Log plot of photocatalytic current-potential curves. (c) Methanol peak in NMR spectra and (d) Faraday efficiencies of methanol production for InP nanopillars with and without 3 nm TiO₂ under 532 nm illumination in a CO₂ saturated 0.5 M KCl solution.

Figure 3. PW-DFT calculated structure for anatase TiO₂ with O vacancies (a) before CO₂ adsorption and (b) after CO₂ adsorption and relaxation.
anatase support, its C effectively filling the bridging oxygen vacancy. Moreover, CO$_2$ gains an electron ($-0.897e$) spontaneously from the TiO$_2$ support. This calculation indicates that the O vacancies provide active sites for CO$_2$ absorption, and no overpotential is required to form the CO$_2^-$ intermediate. In fact, 4 of the 8 minima found by Sorescu et al. formed the CO$_2^-$ intermediate. These CO$_2^-$ intermediates then react with H$_2$O to form methanol. Therefore, this thin TiO$_2$ film can not only protect InP from photocorrosion, but also increase the methanol yields without applying high overpotentials.

In order to further improve the selectivity of methanol with respect to H$_2$ evolution in aqueous solution, we deposited copper nanoparticles on the TiO$_2$-passivated InP nanopillars. Cu and its oxide are known catalysts for CO$_2$ reduction by lowering the energy barriers of intermediate states in the reaction and have been intensively studied in the electrochemical reduction of CO$_2$. Figure 4a shows the photo-$I$--$V$ characteristics of InP nanopillars with copper nanoparticles (green curve) and TiO$_2$-passivated InP nanopillars with copper (purple line). From this Figure, we find that the addition of Cu nanoparticles to the bare InP NPLs (green curve) does not change the photo-$I$--$V$ characteristics. However, it does increase the Faraday efficiency of methanol from 0.85% to 2.8%, indicating that copper is an active catalyst for CO$_2$ reduction to methanol. By depositing Cu nanoparticles on the TiO$_2$-passivated InP nanopillars, we successfully increase the selectivity to 8.7%, as shown in Figure 4b. This improvement in the selectivity likely results from the interface of the copper nanoparticles and the TiO$_2$-passivation layer. For Cu as a metal catalyst (and likely CuO), there have been several previous works reporting that it has a moderate hydrogen overvoltage and weak CO$_2$ adsorption characteristics, and that it can facilitate the reaction of CO with H$_2$ to generate hydrocarbons, aldehydes, and alcohols as major products. We believe it is the oxygen vacancies in the TiO$_2$ and Cu together that promote the selectivity of methanol over H$_2$ production; however, a detailed reaction mechanism is still under investigation.

The previous work of Lee et al. showed that these nanotextured InP photocathodes exhibit about a 40% enhancement in the photoconversion efficiency compared to planar surfaces in photocatalytic water splitting. In the work presented here, we also observed an enhancement by a factor of 2 in total conversion efficiency when comparing InP nanopillars to planar InP. The Faraday efficiencies of methanol production, however, are around 1% for both planar and nanopillar InP, and thus, the selectivity of methanol with respect to H$_2$ is almost the same, as listed in Table S1 in the Supporting Information. By depositing Cu nanoparticles on TiO$_2$-passivated InP nanopillars, the Faraday efficiency increases to 8.7%. The H$_2$ yields produced by these samples were measured by GC after 12 h of illumination with 532 nm wavelength light under an applied potential of $-0.6$ V vs NHE, as shown in Figure 5. Table 1 lists the H$_2$ yields from these GC measurements, methanol yields from NMR spectroscopy, and the total integrated charge running through the device. For 3 nm TiO$_2$-passivated InP nanopillars, the Faraday efficiency is 83.6% in total and 76.9% for H$_2$ evolution. This indicates that, in aqueous solution, simultaneous H$_2$ evolution is an inevitable competing reaction with a lower energy barrier than CO$_2$ reduction. In order to suppress the H$_2$ competing reaction, a nonaqueous solution should be used in future studies.

In summary, photocatalytic CO$_2$ reduction with water to produce methanol is observed using TiO$_2$-passivated InP

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**Figure 4.** (a) Photocatalytic current--potential curves and (b) Faraday efficiencies of methanol production for samples of bare InP, InP/Cu, and InP/TiO$_2$/Cu under 532 nm illumination in a CO$_2$ saturated 0.5 M KCl solution for a 12 h reaction.

**Figure 5.** Gas chromatograph (GC) data taken after 12 h reaction on InP/TiO$_2$/Cu sample under 532 nm illumination in a CO$_2$ saturated 0.5 M KCl solution.

**Table 1.** Faraday Efficiencies of Hydrogen and Methanol of 12 h Reaction on InP/TiO$_2$/Cu Sample under 532 nm Illumination in a CO$_2$ Saturated 0.5 M KCl Solution

<table>
<thead>
<tr>
<th>3 nm TiO$_2$ and Cu</th>
<th>H$_2$</th>
<th>CH$_3$OH</th>
<th>H$_2$ and CH$_3$OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faraday efficiency</td>
<td>76.9%</td>
<td>8.7%</td>
<td>85.6%</td>
</tr>
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nanopillar photocathodes under 532 nm wavelength illumination. In addition to providing a stable photocatalytic surface, the TiO$_2$-passivation provides substantial enhancement in the photocatalytic efficiency through the introduction of O vacancies associated with the non-stoichiometric growth of TiO$_2$ by atomic layer deposition. The role of these oxygen vacancies as catalytically active sites in the photocatalytic reduction of CO$_2$ is established by PW-DFT calculations, which indicate that CO$_2$ binds stably to these oxygen vacancies and gains an electron ($-0.897 \text{e}^-$) spontaneously from the TiO$_2$ support. Therefore, no externally applied overpotential is required to form the CO$_2^-$ intermediate, which can subsequently react with H$_2$O to form methanol. Copper nanoparticles deposited on the TiO$_2$ act as a cocatalyst, which further improves the selectivity and yield of methanol production by up to 8-fold giving a Faraday efficiency of 8.7%.

**ASSOCIATED CONTENT**

1. Supporting Information
   The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b02511.

Details of plane wave density functional theory calculations, InP nanopillar fabrication, energy band diagram of the TiO$_2$-passivated InP structure and schematic diagram of photoelectrochemical measurement setup are included. Ti 2p level, Cu 2p, and O 1s core level XPS spectra. Faraday efficiencies and time dependence of methanol at 12 h reaction on InP/TiO$_2$Cu sample illuminated with 532 nm light at an applied overpotential of $-0.6 \text{ V vs NHE}$.

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J.Q. and G.Z. equally contributed to this paper.

**Notes**
The authors declare no competing financial interest.

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**REFERENCES**