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What Is the Role of Pyridinium in Pyridine-Catalyzed CO_2 Reduction on p-GaP Photocathodes?

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Supporting Information

ABSTRACT: Experimental evidence suggests that pyridinium plays an important role in photocatalytic CO_2 reduction on p-GaP photoelectrodes. Pyridinium reduction to pyridinyl has been previously proposed as an essential mechanistic step for this reaction. However, theoretical calculations suggest that this step is not feasible in solution. Here, cluster models and accurate periodic boundary condition calculations are used to determine whether such a reduction step could occur by transfer of photoexcited electrons from the p-GaP photocathode and whether this transfer could be catalyzed by pyridinium adsorption on the p-GaP surface. It is found that both the transfer of photoexcited electrons to pyridinium and pyridinium adsorption are not energetically favored, thus making very unlikely pyridinium reduction to the pyridinyl radical and the proposed mechanisms requiring this reduction step. Given this conclusion, an alternative and energetically viable pathway for pyridinium reduction on p-GaP photoelectrodes is proposed. This pathway leads to the formation of adsorbed species that could react to form adsorbed dihydropyridine, which was proposed previously to play the role of the active catalyst in this system.

The need for energy sources alternative to fossil fuels is becoming more pressing given the ever-expanding energy demand and increasing concentration of atmospheric CO_2. Photocatalytic CO_2 reduction to liquid fuels is a promising avenue toward renewable and carbon-neutral energy sources. However, reducing CO_2 is a challenging task because it requires high overpotentials and suffers losses from competing reduction reactions.[1] Hence, designing an efficient catalytic system able to operate at lower overpotentials while maintaining high selectivity is essential. Bocarsly and co-workers developed a photocatalytic system able to reduce CO_2 to methanol at underpotentials (up to 320 mV) and high selectivity (faradaic efficiency ∼100%) using a p-GaP photocathode.[2] In addition, they found lowered overpotentials (<200 mV) and good selectivity also when using metal electrodes.[3,4] In all their experiments, the addition of pyridine (Py) to the acidified (pH = 5.2) aqueous solution in the (photo)electrochemical cell proved to be essential to observe CO_2 reduction products. However, the exact mechanism of Py-catalyzed CO_2 reduction is not yet understood.

Useful mechanistic clues can be gained from experimental observations. In an earlier set of experiments using Pd electrodes, Bocarsly and co-workers found that no reduction occurred at pH values higher than 7.[3] From this observation, they concluded that the acidic environment is required for catalyzing the reduction of CO_2 using Py. More specifically, pyridinium (PyH^+), which is present in significant concentration at acidic pH given the pK_a of Py (5.3), may play an important role in the catalysis. On the basis of this experimental evidence, PyH^+ reduction to the pyridinyl radical (PyH·) has been proposed as a crucial mechanistic step in two studies: Bocarsly and co-workers conjectured that PyH· itself is the active catalyst for CO_2 reduction,[4] while Musgrave and co-workers recently proposed that PyH· will further react to form dihydropyridine (DHP) as the active (homogeneous) catalyst.[5] However, computational studies[6−9] showed that PyH^+ reduction to PyH· is energetically unfeasible in solution when using metal electrodes and under the experimentally applied potential (∼−0.6 V vs saturated calomel electrode (SCE)).[4] In contrast, Musgrave and co-workers argued that PyH^+ may be reduced to PyH· when using p-GaP photoelectrodes because the photoexcited electrons might have enough energy.[5] However, recent cluster calculations investigating the GaP(110) surface suggested that the transfer of photoexcited electrons from the GaP surface to PyH^+ is not favorable.[10] Furthermore, these calculations also showed that PyH^+ will not directly adsorb on the surface, preferring to be in solution, suggesting that the reduction process cannot be facilitated by adsorption. These are crucial findings toward elucidating the mechanism of CO_2 reduction in this promising system. However, a more accurate investigation is needed to confirm or to exclude the possibility of PyH^+ reduction to PyH· by photoexcited electrons from the p-GaP photocathode. Here, we address this point by using more accurate methods to further test the results of previous cluster calculations. In addition, we propose a new, viable reduction pathway for PyH^+ reduction on p-GaP photocathodes.

Our computational approach uses both finite cluster calculations and periodic boundary condition (PBC) calculations to model the GaP(110) surface and possible adsorbates, with a focus on PyH^+. As discussed in previous work, the GaP(110) surface was selected because it represents the most stable surface of GaP.[11] Cluster calculations were used to compute adsorption energies on neutral and negatively charged GaP(110) surface models and to calculate reduction potentials. All cluster calculations were carried out with the ORCA[12] software package and density functional theory (DFT)[13,14] using the B3LYP

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exchange−correlation functional.[15−17] Grimme semiempirical D2 dispersion corrections[18] were added and solvation effects were modeled using the continuum solvation model based on solute electron density (SMD).[19] (See Supporting Information (SI) for further details of the computational setup.) PBC calculations were used to further explore the postulated electron transfer between the PyH· radical and the GaP(110) surface observed in the previous study using cluster models. All PBC calculations were carried out with the VASP code.[20−22] We used DFT with both PBE[23] and PBE0[24] exchange−correlation functionals for charge density difference analysis and for charge analysis performed with Bader's topological partition of the electron density.[25,26] We also applied Grimme's semiempirical D2 dispersion corrections[18] in these calculations. Finally, band edge positions for GaP were computed using the nonself-consistent GW method (G_0W_0)[27] which gives more accurate results than DFT. The calculation details specific to each kind of application are partly discussed in the following and are fully reported in the SI.

Previous work employed a simple density difference plot to propose that reduction of PyH^+ to PyH· by photoexcited electrons from the GaP electrode is unlikely to occur.[10] The electron from PyH· spontaneously moved to GaP, with no minimum found for it to stay on PyH·. Here, we conducted the same density difference analysis with both our cluster approach and PBC calculations (Figure 1). The cluster approach is typically used because it allows one to easily simulate solvation effects with a continuum solvation model. However, it has the intrinsic drawback of failing to describe the electronic structure of a periodic crystal, which is a serious issue when studying electron transfer from or to solid materials. This motivated us to verify the cluster calculation result with PBC calculations. Our cluster calculation result (Figure 1a) is identical to the one reported in previous work[10] despite the difference in solvation model (previous work used the CPCM solvation model)[28] and cluster geometry (see the SI for more details). This indicates that conclusions drawn from these results are robust. Most importantly, the density difference plot generated using DFT PBC calculations with the PBE functional (Figure 1b) also yields the same result: a net decrease of electron density surrounding PyH· and an increase of electron density at the GaP surface. The only difference between the two plots is the degree of localization of the electron density at the GaP surface upon transfer of the electron from PyH·. While in the plot generated with the cluster model (Figure 1a) the electron is localized around a single Ga atom at the edge of the cluster, in the plot generated with the periodic approach (Figure 1b) the electron is delocalized around surface atoms close to the PyH· radical. Overall, our PBC calculations confirm the result of previous and current cluster calculations: PyH· transfers its electron to the GaP(110) surface.

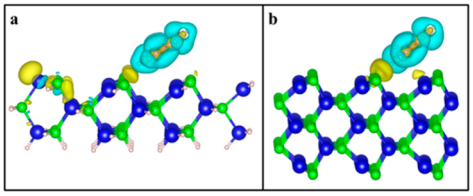

Figure 1. Density difference plots showing formation of pyridinium and transfer of an electron to the GaP(110) surface simulated with (a) a cluster model and (b) a periodic slab. Ga atoms are represented in blue, P atoms in green, C atoms in violet, N atoms in light blue, and H atoms in white. Increase in charge density is represented in yellow while decrease is represented in light blue. Isosurface level = (a) 0.002 and (b) 0.001 e/bohr^3.

To further support the result obtained with the density difference analysis, we performed a Bader charge analysis on the periodic (GaP-PyH)· system represented in Figure 1b. For this analysis we solved for the ground-state density using both PBE and PBE0 functionals. Pure DFT notoriously overestimates the extent of charge transfer due to its lack of exact exchange energy. Thus, the hybrid functional PBE0 was used to ensure that our conclusions are not affected by spurious results obtained with the pure PBE functional. Bader charge analysis, performed with both functionals, reveals a net transfer of 0.45e negative charge from the PyH· radical to the GaP slab, independent of functional. This finding suggests that the electron could somehow be shared between the adsorbate and the slab. Further investigation (see SI) reveals that the adsorbate/surface Bader volumes heavily overlap such that this evaluation must be considered a lower bound on the degree of charge transfer. Consistent with this finding, both Mulliken and Löwdin charge analyses of our cluster model give rise to respectively 0.97e and 1.00e charge transfer from the adsorbate to the surface. We therefore conclude that the direct evidence provided by density difference plots for electron transfer from PyH· to GaP(110) is confirmed by several different electron population analyses.

Next, we sought to verify whether the result of the charge density difference and Bader charge analyses is consistent with the reducing power of the photoexcited electrons produced at a GaP photocathode, with respect to PyH^+ reduction to PyH·. For this purpose, we compare the position of the GaP conduction band minimum (CB_{min}), i.e., the expected energy of the photoexcited electrons produced at an illuminated p-GaP photocathode, to the reduction potential value for PyH^+ reduction to PyH· (Figure 2).

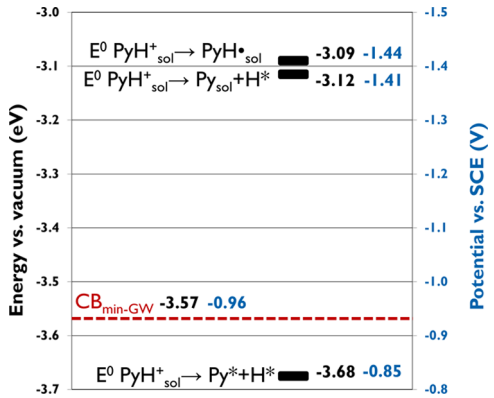

Figure 2. Comparison of computed relevant energies, relative to the vacuum level (values reported in black), and relevant potentials, relative to the SCE (values reported in blue): GaP conduction band minimum computed with G_0W_0 calculations (CB_{min}, red dashed line) and reduction potential values (E^0) for different solvated PyH^+ reduction pathways (black rectangles). These pathways are: reduction to PyH· ($PyH^+_{sol} \rightarrow PyH\cdot_{sol}$), reduction to an adsorbed hydrogen atom and solvated Py ($PyH^+_{sol} \rightarrow Py_{sol} + H^*$) and reduction to an adsorbed hydrogen atom and adsorbed Py ($PyH^+_{sol} \rightarrow Py^*+H^*$). * indicates adsorbed species and the subscript "sol" indicates species in solution. E^0 $PyH^+_{sol} \rightarrow PyH\cdot_{sol}$ is taken from previous work.[7] Values on the vacuum scale were converted to the SCE scale and vice versa by using the absolute value of the standard hydrogen electrode −4.281 V[29] converted to the SCE value −4.525 V (see SI for more details).

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Accurate band edge positions for GaP were calculated using the method proposed by Toroker et al.[27] Details regarding this method and its application in this work are discussed in the SI. The comparison between our calculated band gap from G_0W_0 calculations (2.47 eV) and the experimental value (2.22 eV[30]) suggests that the uncertainty in the computed band edge positions is ∼0.1 eV, because the computation of these values requires the half band gap rather than the band gap. The half band gap is used to derive the energy shift of the band edges with respect to the band gap center (see ref 27 for more details).

The CB_{min} position obtained with DFT-PBE calculations (−4.04 eV) is lower in energy than the reduction potential of PyH^+ to PyH· relative to the vacuum level (−3.09 eV)[7] by ∼1 eV. This suggests that photoexcited electrons cannot be transferred from the GaP surface to PyH^+ to form PyH·, in agreement with our charge density difference and Bader charge analyses performed using DFT with the PBE functional. Most importantly, this result is confirmed by the CB_{min} position obtained with more accurate G_0W_0 calculations (−3.57 eV). Note that even if we take the most conservative approach of assuming the uncertainties in the computed band edge positions (∼0.1 eV) and in the computed reduction potential (∼0.3 V, see ref 7 and references therein) act in the same direction, the position of CB_{min} will still be lower than the reduction potential of PyH^+ to PyH·. Furthermore, as discussed in the SI, our computed band edge positions are at the pH of zero charge, which we consider equal to pH 7. The band edges of any semiconductor are affected by the pH of the solution in contact with the semiconductor surface, as the pH will determine the nature of the charged adsorbates (H^+,OH^-) that will in turn shift the band edges. Thus, CB_{min} at the experimental pH (5.2) will be even lower in energy (∼ −3.67 eV), and PyH^+ reduction to PyH· will be even more unfavorable. Note that while CB_{min} position is affected by pH, the reduction potential of PyH^+ to PyH· is not affected by it, as this reduction process does not involve protonation of the reactant. Overall, on the basis of the values reported in Figure 2 (CB_{min} and E^0 $PyH^+_{sol} \rightarrow PyH\cdot_{sol}$) and their respective uncertainties, we conclude that PyH^+ reduction to PyH· by photoexcited electrons from the GaP electrode is very unlikely.

The reduction potential for PyH^+ reduction to PyH· (E^0 $PyH^+_{sol} \rightarrow PyH\cdot_{sol}$) reported in Figure 2 is for a homogeneous process. Adsorption of PyH^+ on the GaP surface could catalyze the reduction of this species to PyH·, thus decreasing its reduction potential as previously proposed on Pt(111).[8] Furthermore, even if this reduction process is not catalyzed, adsorbed PyH^+ could represent a relevant species for CO_2 reduction catalysis at p-GaP photoelectrodes. For these reasons, we investigated the adsorption of PyH^+ and other relevant species on both the neutral and negatively charged GaP(110) surface with our cluster models and using continuum solvation to account for water solvation effects. Given the similarity of our results on cluster and periodic slab models,[10] we expect the cluster models to be reliable. We considered CO_2, H_2O, and Py, as they are all present under experimental conditions.[2] Furthermore, we considered one possible isomer of DHP, *o*-DHP, because adsorbed DHP has been proposed to play the role of the active catalyst in this system.[31−33] p-GaP is used as a photocathode in the experiments, with a small negative applied potential, and thus is negatively charged. Therefore, modeling the negatively charged surface is important. Furthermore, electrostatic attraction could likely be the key to a more favorable adsorption for a positively charged species like PyH^+ compared to other neutral species. The negatively charged surface of the photocathode was simulated by simply adding extra electrons to the cluster model. We found that PyH^+ and CO_2 do not adsorb on the neutral GaP(110) surface (surface charge = 0 in Figure 3), while H_2O, *o*-DHP, and Py do, in agreement with previous work.[10]

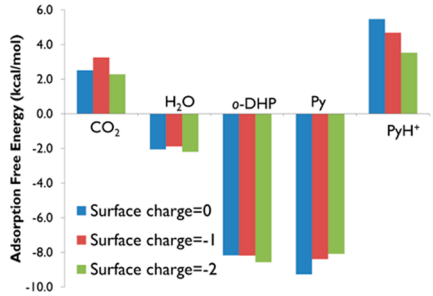
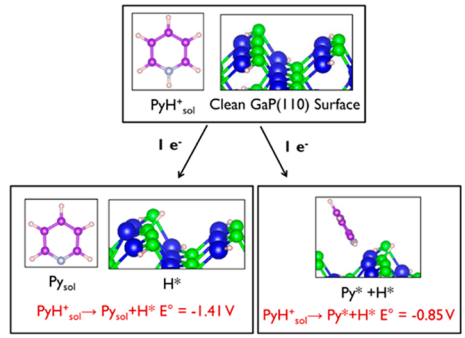


Figure 3. Adsorption free energy values at room temperature in kcal/mol for different species on the neutral (surface charge = 0) and charged (surface charge = −1,−2) GaP(110) surface simulated with cluster models in the presence of continuum solvation (water solvent).

Furthermore, these conclusions are unaltered when the surface is negatively charged (surface charge = −1,−2 in Figure 3). Overall, the results of this adsorption free energy study on the neutral and negatively charged GaP(110) surface suggest that PyH^+ reduction to PyH· cannot be catalyzed by adsorption on the surface and adsorbed PyH^+ cannot play a role in CO_2 reduction catalysis. Therefore, Py and DHP remain the only Py-related species that could play the role of adsorbed cocatalysts.

Given that our results suggest that PyH^+ reduction to PyH· is unlikely to occur, yet experiments suggest that PyH^+ is essential to the catalysis, we continued to investigate other possible PyH^+ reduction pathways. Specifically, we investigated possible heterogeneous reduction mechanisms using our cluster model (Scheme 1). We started by investigating a reduction mechanism analogous to the one proposed by Batista and co-workers on Pt(111).[9] In this reduction mechanism, solvated PyH^+ undergoes a one-electron reduction to an adsorbed hydrogen atom and solvated Py ($PyH^+_{sol} \rightarrow Py_{sol} + H^*$). While on Pt(111) this

Scheme 1. Alternative Pathways for PyH^+ Reduction on the GaP(110) Surface[a]



[a]Reduction potential values are expressed in V versus SCE. Ga atoms are represented in blue, P atoms in green, C atoms in violet, N atoms in light blue, and H atoms in white. * indicates adsorbed species and the subscript "sol" indicates species in solution. Note that $PyH^+ \rightarrow Py_{sol} + H^*$ is a reduction pathway analogous to the one proposed by Batista and co-workers on Pt(111).[9]

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mechanism was computationally found to have a moderate reduction potential (−0.72 V vs SCE), we found that this mechanism will require a −1.41 V vs SCE applied potential to occur on GaP(110). However, if Py adsorbed next to the adsorbed hydrogen atom was modeled as a product (PyH^+_{sol} → Py*+H*) instead of solvated Py, we found a much lower reduction potential (−0.85 V vs SCE).

In Figure 2, we compare these computed reduction potentials (E^0 PyH^+_{sol} → Py_{sol} + H* and E^0 PyH^+_{sol} → Py* + H*) to the reduction potential of PyH^+ to PyH· (E^0 PyH^+_{sol} → $PyH·_{sol}$) and to the position of GaP CB_{min} computed with accurate G_0W_0 calculations. This comparison suggests that PyH^+_{sol} → Py* + H* reduction is much more likely to occur by transfer of photoexcited electrons than the previously discussed PyH^+_{sol} → $PyH·_{sol}$ reduction, since CB_{min} is higher in energy than the reduction potential of PyH^+_{sol} → Py* + H* by ∼0.1 eV, while it is lower in energy than the reduction potential of PyH^+_{sol} → $PyH·_{sol}$ by ∼0.5 eV. This last result is crucial in the context of the proposed heterogeneous mechanism on GaP(110).[32,33] In fact, in this mechanism, adsorbed pyridine and adsorbed hydride-like species are the reactants needed for the formation of the active catalyst adsorbed DHP.[31] Therefore, PyH^+ could contribute to the active catalyst formation by being reduced to adsorbed hydrogen and adsorbed pyridine.

In conclusion, we confirmed that an electron cannot be transferred from the GaP(110) surface to PyH^+ to form PyH· using accurate periodic calculations with pure and hybrid DFT theory. Furthermore, this result was verified by comparing GaP band edge positions computed with accurate G_0W_0 calculations to the most accurate previously computed[7] one-electron reduction potential of PyH^+, which also happens to be the average value of the four independently calculated values reported in the literature.[6−9] We found that the conduction band minimum lies too low in energy to allow the transfer of a photoexcited electron from the GaP photocathode to PyH^+. PyH^+ adsorption was previously proposed to lower its reduction potential on Pt(111);[8] however, we found that PyH^+ does not adsorb on the GaP(110) surface even when simulating a negatively charged electrode surface. From this result we can also confirm that, of the possible adsorbates investigated so far, only Py and DHP can play the role of adsorbed cocatalyst, as previously suggested.[10,31] Finally, given that we found PyH^+ reduction to PyH· by transfer of photoexcited electrons from the p-GaP photocathode to be very unlikely, we investigated alternative reduction pathways. We found that reducing PyH^+ to adsorbed Py and an adsorbed hydrogen atom is favored and more likely to occur than PyH^+ reduction to PyH· under experimental conditions. Interestingly, this more favorable reduction pathway also leads to the generation of the reactants needed for adsorbed DHP formation, which is the active catalyst in a proposed mechanism for CO_2 reduction on p-GaP photocathodes[32,33] currently under investigation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08639.

Further alculation details and Cartesian coordinates of the structures (PDF)

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Notes

The authors declare no competing financial interest.

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