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Single Atom (Pd/Pt) Supported on Graphitic Carbon Nitride as an Efficient Photocatalyst for Visible-Light Reduction of Carbon Dioxide

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Supporting Information

ABSTRACT: Reducing carbon dioxide to hydrocarbon fuel with solar energy is significant for high-density solar energy storage and carbon balance. In this work, single atoms of palladium and platinum supported on graphitic carbon nitride (g-C₃N₄), i.e., Pd/g-C₃N₄ and Pt/g-C₃N₄, respectively, acting as photocatalysts for CO₂ reduction were investigated by density functional theory calculations for the first time. During CO₂ reduction, the individual metal atoms function as the active sites, while g-C₃N₄ provides the source of hydrogen (H*) from the hydrogen evolution reaction. The complete, as-designed photocatalysts exhibit excellent activity in CO₂ reduction. HCOOH is the preferred product of CO₂ reduction on the Pd/g-C₃N₄ catalyst with a rate-determining barrier of 0.66 eV, while the Pt/g-C₃N₄ catalyst prefers to reduce CO₂ to CH₄ with a rate-determining barrier of 1.16 eV. In addition, deposition of atom catalysts on g-C₃N₄ significantly enhances the visible-light absorption, rendering them ideal for visible-light reduction of CO₂. Our findings open a new avenue of CO₂ reduction for renewable energy supply.

1. INTRODUCTION

Because of the continuing increase in the emissions of CO₂ from human activities, the reduction of CO₂ into alternative fuels such as formic acid (HCOOH), methanol (CH₃OH), and methane (CH₄) is a critical goal that would positively impact the global carbon balance and energy storage.^{1–3} As CO₂ is an extremely stable and unreactive molecule, the conversion of CO₂ to fuels is a scientifically challenging problem that requires appropriate catalysts and high energy input.¹ The current industrial process for reducing CO₂ to methanol using H₂ is carried out at high temperature (496–573 K) and high pressure (5–10 MPa) using Cu-ZnO/Al₂O₃ as a catalyst.⁴ Tremendous efforts in both academic research and industry have been devoted to developing efficient catalysts for CO₂ reduction at a low energy cost.^{5–9}

The deposition of metal nanoclusters on substrates as heterogeneous catalysts has been widely used in many important reactions.^{10–12} The ultimate small-size limit for metal clusters is a single atom, in which isolated metal atoms are dispersed on a substrate.¹³ Using only single or a few metal atoms as active sites, such nanostructured catalysts not only minimize materials usage but also exhibit fascinating activity due to their high ratio of low-coordinated metal atoms, which usually function as active sites.^{14,15} However, isolating nanostructured clusters still remains a significant experimental challenge because the surface free energy of clusters increases

as the size of the particles decreases.¹⁶ An appropriate substrate that strongly interacts with the clusters is required in order to prevent their aggregation. Metal oxides strongly interact with single-atom/cluster metal catalysts through surface oxygen^{17–20} and have been widely used as substrates to isolate single metal atoms or clusters efficiently. In recent experiments, cluster catalysts with precise numbers of atoms, such as Cu₄ and Ag₃ clusters supported by Al₂O₃, have shown high catalytic activity toward particular reactions in both experiments and theoretical calculations.^{17–19,21} Furthermore, the experimental realization of single-atom catalysts on metal oxide substrates, including Pt₁/FeO_x,²¹ Ag₁/MgO,²² and Ru₁/Co₃O₄,²³ presages the use of these precious-metal catalysts economically. However, the oxygens of the metal oxide substrates actually partially oxidize the single atom/cluster catalyst and so diminishes the activity.^{18,24–26}

Graphitic carbon nitride (g-C₃N₄) is a promising stable, active, metal-free photocatalyst capable of efficiently splitting water into hydrogen.^{27–29} It has also been reported to be an excellent substrate for supporting catalysts.³⁰ Using g-C₃N₄ as a substrate to support noble-metal catalysts for CO₂ hydrogenation offers a number of inherent advantages, including maintaining the noble-metal atoms in their neutral state,

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directly providing the hydrogen source, and possessing excellent solar light absorption.^{31,32} A recent advance in the use of g-C₃N₄ as a catalyst substrate made by Vilé and colleagues,³³ who showed that isolated Pd atoms could be tenaciously attached to the pyridinic nitrogen atoms of g-C₃N₄. Meanwhile, single Pt atoms supported on g-C₃N₄ were synthesized in a recent experiment that exhibited excellent photocatalytic hydrogen evolution activity.³⁴ In this work, the newly realized single-atom catalysts supported on g-C₃N₄, including Pd/g-C₃N₄ and Pt/g-C₃N₄, were investigated for the first time for the reduction of CO₂ into hydrocarbon fuels by means of density functional theory (DFT) calculations. The differential charge density demonstrated that Pd and Pt atoms form strong interactions with g-C₃N₄ by exchanging electron density, with less net electron transfer from Pd and Pt to g-C₃N₄ than to FeO_x,¹⁹ which is good for activation of the Lewis acid CO₂. The reaction pathways for CO₂ reduction on single-atom catalysts (Pd and Pt) supported on g-C₃N₄ were obtained by the climbing image nudged elastic band (CI-NEB) method. As evaluated by the reaction barriers, the preferred product of CO₂ reduction on the Pd/g-C₃N₄ catalyst is HCOOH with a barrier of 0.66 eV, while the Pt/g-C₃N₄ catalyst is able to reduce CO₂ to CH₄ efficiently with a barrier of 1.16 eV, which is smaller than that reported in ref 18. Interestingly, the optical absorption spectra demonstrate that Pt and Pd supported on g-C₃N₄ extend the absorption edge of g-C₃N₄ from 2.7 to 0.2 eV, leading to significant enhancement of the visible-light absorption efficiency.

2. COMPUTATIONAL METHODS

DFT calculations were performed by using the Vienna Ab Initio Simulation Package (VASP).^{35,36} The exchange–correlation interactions were treated within the generalized gradient approximation (GGA)³⁷ in the form of the Perdew–Burke–Ernzerhof (PBE) functional.³⁸ The van der Waals interactions were described using the empirical correction in Grimme's scheme (i.e., DFT+D3).³⁹ The electron wave functions were expanded using plane waves with a cutoff energy of 500 eV, and the convergence criteria for the residual force and energy on each atom during structure relaxation were set to 0.005 eV/Å and 10^{−5} eV, respectively. The vacuum space was more than 20 Å, which was enough to avoid interactions between periodic images. The CI-NEB method was used to find saddle points and minimum-energy paths.⁴⁰ The single-atom catalysts were modeled by depositing one metal atom on 2 × 2 × 1 supercell g-C₃N₄. The Brillouin zone (BZ) was sampled with a Monkhorst–Pack mesh with a 3 × 3 × 1 *k*-point grid in reciprocal space during geometry optimization and NEB calculations.

Hybrid functionals based on the Heyd–Scuseria–Ernzerhof (HSE06) method^{41,42} were adopted to get the exact band structures and optical absorption spectra of the Pd/g-C₃N₄ and Pt/g-C₃N₄ catalysts, with a 5 × 5 × 1 *k*-point grid in reciprocal space. VASP was used to calculate the frequency-dependent dielectric function after the electronic ground state was determined. The imaginary part of the dielectric function is determined by a summation over empty states using eq 1:⁴³

$$\epsilon_{\alpha\beta}^{(2)}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,k} 2\omega_k \delta(\epsilon_{ck} - \epsilon_{vk} - \omega) |\langle u_{ck+q} | u_{vk} \rangle|^2 \quad (1)$$

where the indices *c* and *v* refer to conduction and valence band states, respectively.

3. RESULTS AND DISCUSSION

To find the most favorable deposition sites for the single-atom catalysts, various positions on the 2 × 2 × 1 g-C₃N₄ supercell

were considered, as shown in Figure 1a and Table S1 in the Supporting Information. The optimized structures and the 3D

Figure 1. (a) Optimized structure of pristine g-C₃N₄. Positions: 1, center of the sixfold cavity; 2, corner of the sixfold cavity; 3, top of the five-membered ring; 4, edge of the sixfold cavity; 5, top of g-C₃N₄. (b, c) Plots of 3D differential charge densities of (b) Pd/g-C₃N₄ and (c) Pt/g-C₃N₄ at isosurfaces of −0.005 e/Å³ (yellow, charge accumulation) and 0.005 e/Å³ (blue, charge depletion).

differential charge densities of Pd/g-C₃N₄ and Pt/g-C₃N₄ are plotted in Figure 1b,c. The sixfold cavity of g-C₃N₄ is the most stable site for the deposition of Pd and Pt atoms, and the calculated binding energies are −2.17 and −2.95 eV respectively. These results are collectively consistent with those reported in ref 33. It can be clearly seen from the differential charge densities (Figure 1b,c) that there is significant charge transfer between the metal atoms and the neighboring pyridinic nitrogen atoms for both Pd/g-C₃N₄ and Pt/g-C₃N₄, indicating a strong interaction between the lone-pair electrons of the neighboring pyridinic nitrogen atoms and the isolated metal atoms. The charge is mainly depleted in the d orbitals of Pd/g-C₃N₄, while both charge accumulation and depletion occur around the Pt atom in Pt/g-C₃N₄. Consequently, the valence (oxidation) states of Pd and Pt on g-C₃N₄ are only +0.40 and +0.27, respectively, on the basis of Bader charge analysis; these are lower than the values of +0.61 for Pd¹⁹ and +0.45 for Pt²¹ supported on Fe₂O₃. Transition metal catalysts in a lower oxidation state generally possess stronger ability to capture the adsorbate and thus have higher catalytic activity.¹⁸ Therefore, single Pd and Pt atoms supported on g-C₃N₄ are expected to be more active catalysts than Pd and Pt atoms supported on metal oxide substrates. The metal atoms will move to a corner of the sixfold cavity in g-C₃N₄ once reactant/intermediates (discussed in the following) are adsorbed on it during the reaction.

The CO₂ reduction pathways to HCOOH and CH₃OH on the Pd/g-C₃N₄ catalyst were studied in detail, as shown in Figure 2. The overall reaction of CO₂ reduction to form CH₃OH on the Pd/g-C₃N₄ catalyst in the presence of hydrogen is expressed as follows:

Although the pyridinic N atoms demonstrate high catalytic activity in hydrogen evolution, they are inert to the CO₂ reduction reaction. Herein, the Pd acts as the active site for the formation of carbon intermediates while the g-C₃N₄ provides the hydrogen source from the hydrogen evolution reaction ($\text{H}^+ + \text{e}^- \rightarrow \text{H}^*$) for the hydrogenation of CO₂.^{27,28} during CO₂ reduction. The reaction includes six elemental hydrogenation steps, which are determined by the most stable product at each step. The initial step of CO₂ reduction is the formation of HCOO*, which is followed by the hydrogenation of HCOO* to give HCOOH*. The approach of a third hydrogen induces the dissociation of HCOOH into HCO* and H₂O*. The HCO* is further hydrogenated to form CH₂O*,

Figure 2. Reaction pathways for CO₂ reduction to HCOOH and CH₃OH on the Pd/g-C₃N₄ catalyst. Under standard conditions (pH 0, $p(\text{H}_2) = 1$ bar, $U = 0$ V vs SHE), the total energies of $\text{H}^+(\text{aq}) + \text{e}^-$ and $\frac{1}{2}\text{H}_2(\text{g})$ are equal. The reference energy (the total free energy of the catalyst, isolated CO₂ and three H₂) is set to zero. The important intermediates and products are shown as well. The substrate is displayed partly in stick model. Color code for the catalyst and small molecules: Pt, green; C, gray; O, red; H, white.

Figure 3. Reaction pathways for CO₂ reduction to COOH, CH₃OH, and CH₄ on the Pt/g-C₃N₄ catalyst. Under standard conditions (pH 0, $p(\text{H}_2) = 1$ bar, $U = 0$ V vs SHE), the total energies of $\text{H}^+(\text{aq}) + \text{e}^-$ and $\frac{1}{2}\text{H}_2(\text{g})$ are equal. The reference energy (the total free energy of the catalyst, isolated CO₂, and four H₂) is set to zero. The important intermediates and products are shown as well. The substrate is displayed partly in stick model. Color code: Pd, pine green; C, gray; O, red; H, white.

CH₂OH*, and the final product, CH₃OH*. All of the intermediates and products are adsorbed on the Pd atom, reacting with the hydrogen (H*) that is bonded to the g-C₃N₄. The rate-determining step of the CH₃OH generation pathway on the Pd/g-C₃N₄ catalyst is the hydrogenation of CH₂OH*, with a barrier of 1.46 eV. The second largest barrier is around 1.43 eV for the formation of HCO*. It should be noted that these barriers are lower than that on the Cu(111) surface (1.60 eV) and comparable to that on the Cu₂₉ cluster (1.41 eV).⁵ Therefore, the Pd/g-C₃N₄ catalyst possesses an excellent catalytic activity for CO₂ reduction.

The formation of HCOOH,

follows the first two steps of the CH₃OH pathway, after which the HCOOH* desorbs directly from the Pd/g-C₃N₄ catalyst.

The rate-determining step of the HCOOH pathway is the second step, with a barrier of 0.66 eV, which is 0.80 eV lower than the rate-determining barrier for the formation of CH₃OH (1.46 eV). In addition, HCOOH is able to desorb from the Pd/g-C₃N₄ catalyst easily with a desorption energy of 0.46 eV. Therefore, the preferred product for CO₂ reduction on the Pd/g-C₃N₄ catalyst is the HCOOH pathway rather than the CH₃OH pathway.

In general, the stronger the adsorption of the intermediates on the catalyst is,^{17,18} the lower is the barrier for a chemical reaction that can be obtained. Pt is expected to have much stronger interactions with hydrocarbon reactants than Pd because of its two uncoupled electrons. In Figure 3 we present the minimum energy pathways for CO₂ reduction to HCOOH, CH₃OH, and CH₄ on the Pt/g-C₃N₄ catalyst. The pathways for the formation of HCOOH and CH₃OH on the Pt/g-C₃N₄

catalyst are found to be nearly the same as those on the Pd/g-C₃N₄ catalyst but are thermodynamically more favorable because of the stronger interactions between Pt and the reaction intermediates. It can be clearly seen from Figure 3 that the strong interactions have a significant impact on the pathway for HCOOH production on the Pt/g-C₃N₄ catalyst. The barrier for the hydrogenation of HCOO* on the Pt/g-C₃N₄ catalyst (1.01 eV) is much higher than that on the Pd/g-C₃N₄ catalyst (0.66 eV), and the desorption of HCOOH from the Pt/g-C₃N₄ catalyst possesses the largest barrier on the entire reaction pathway (1.06 eV), while the desorption energy from the Pd/g-C₃N₄ catalyst is only 0.46 eV, suggesting that the formation of HCOOH is unfavorable for CO₂ reduction on the Pt/g-C₃N₄ catalyst. However, once the HCOOH* is formed, the following steps, including the dissociation of HCOOH* to form HCO* and the hydrogenation of HCO* to afford CH₂O*, CH₂OH*, and CH₃OH* during the formation of CH₃OH on the Pt/g-C₃N₄ catalyst become more favorable than those on the Pd/g-C₃N₄ catalyst (see Figure 2). The barriers for all of the reaction steps are much lower than those on the Pd/g-C₃N₄ catalyst. The third step, i.e., the hydrogenation of HCOOH on the Pt/g-C₃N₄ catalyst, is the rate-determining step, with a barrier of 1.16 eV. The largest barrier for the formation of CH₃OH on the Pt/g-C₃N₄ catalyst is lower than those on the Pd/g-C₃N₄ catalyst (1.46 eV), the Cu₂₉ cluster (1.41 eV), Cu(111) (1.60 eV),⁵ and Cu₄/Al₂O₃ (1.21 eV).¹⁸

We also studied the reaction pathway for the reduction of CO₂ into CH₄ on the Pt/g-C₃N₄ catalyst, as shown in eq 4:

The few first reaction steps follow the same pathway as in the formation of CH₃OH up to the formation of CH₂OH*. Then the OH dissociates from CH₂OH* and bonds with hydrogen to form CH₂* and H₂O*. The barrier for dissociation of OH from CH₂OH* during the formation of CH₄ (0.82 eV) is comparable to that for the hydrogenation of CH₂OH* during the formation of CH₃OH (0.81 eV). However, CH₂* + H₂O* is more stable than CH₂OH* by 0.47 eV in total energy, indicating that the formation of CH₄ is highly feasible. Then the CH₂* is further hydrogenated to CH₃* and CH₄* with barriers of 0.38 and 0.48 eV, respectively. The rate-determining step for the formation of CH₄ is the hydrogenation of HCOOH, with a barrier of 1.16 eV, which is the same as that for the formation of CH₃OH on the Pt/g-C₃N₄ catalyst. It should be noted that such a barrier is much lower than that on Cu₄ (1.69 eV).¹⁸ Since the CH₄ product is more thermodynamically stable than CH₃OH, the formation of CH₄ is likely to be the most dominant reaction pathway on the Pt/g-C₃N₄ catalyst. For comparison, we also investigated the pathway for the reduction of CO₂ on the Cu/g-C₃N₄ catalyst. We found that the interactions between Cu/g-C₃N₄ and the reactant/intermediates are weak. For instance, the adsorption energies of HCOOH on the Pd/g-C₃N₄ and Pt/g-C₃N₄ catalysts are −0.46 and −1.06 eV, respectively, while that on the Cu/g-C₃N₄ catalyst is only −0.35 eV. The weak interactions between Cu/g-C₃N₄ and the reaction intermediates lead to a large barrier for the formation of CH₃OH on the Cu/g-C₃N₄ catalyst (1.79 eV). This suggests that the Cu/g-C₃N₄ catalyst is not promising for CO₂ reduction (more details can be found in Figure S1 in the Supporting Information).

Previous work has demonstrated that pure g-C₃N₄ can be a potential photocatalyst for hydrogen production²⁹ and the reduction of CO₂.⁴⁴ However, g-C₃N₄ shows only minimal

visible-light absorption because it has a relatively large band gap (2.7 eV).⁴⁵ The deposition of isolated Pt and Pd atoms on g-C₃N₄ is expected to significantly modify its electronic structure and might enhance the visible-light response. Figure 4 presents

Figure 4. (a–c) Band structures and (d) optical absorption spectra of g-C₃N₄, Pd/g-C₃N₄, and Pt/g-C₃N₄. For the purpose of comparison, the contributions of the metal atom in the band structures are distinguished by red coloring, and the top of the valence states in pristine g-C₃N₄, Pd/g-C₃N₄, and Pt/g-C₃N₄ have been shifted to zero.

the calculated band structures (a–c) and optical absorption spectra (d) of pristine g-C₃N₄, Pd/g-C₃N₄, and Pt/g-C₃N₄ using a state-of-the-art hybrid functional. The band gap of g-C₃N₄ was calculated to be 2.98 eV, which is in good agreement with the experimental value.⁴⁵ With Pd/Pt atoms deposited on the g-C₃N₄, we found that the occupied d bands of the metal atoms lie in the gap of the band structure of g-C₃N₄. Consequently, the band gaps of Pd/g-C₃N₄ and Pt/g-C₃N₄ are significantly reduced to 0.64 and 0.72 eV, respectively. In addition, the conduction-band minima for Pd/g-C₃N₄ and Pt/g-C₃N₄ are located around −0.91 and −0.90 V, respectively, with respect to the normal hydrogen electrode (NHE), which are more negative than the standard electrode potentials of CO₂/HCOOH (−0.61 V vs NHE), CO₂/CH₃OH (−0.38 V vs NHE), and CO₂/CH₄ (−0.24 V vs NHE).⁴⁶ As the valence-band maxima of Pd/g-C₃N₄ (−0.27 V vs NHE) and Pt/g-C₃N₄ (−0.18 V vs NHE) are located above the potential for the production of O₂ (1.23 V vs NHE), a proper sacrificial electron donor may be required to promote the hydrogen evolution reaction.³²

Most interestingly, the narrower gaps of Pd/g-C₃N₄ and Pt/g-C₃N₄ compared with pristine g-C₃N₄ lead to a red shift of the optical absorption spectra and thus enhance the visible-light harvesting, as shown in Figure 4d. As can be seen, the main light absorption peak of pure g-C₃N₄ is located at around 4.5 eV, and the absorption edge ends at 2.7 eV. With a Pd or Pt atom deposited on g-C₃N₄, a new absorption peak appears at 0.7 eV and the absorption edge extends to 0.2 eV, which could be ascribed to the electron excitation from the d band of the metal atom to the conduction band of g-C₃N₄. Therefore,

single atom (Pd/Pt) supported on g-C₃N₄ is also able to harvest visible and infrared light with a higher solar conversion efficiency compared with the pure g-C₃N₄ material. In the presence of a proper sacrificial electron donor,³² the photo-generated electrons will be transferred to the conduction band of g-C₃N₄ and participate in proton reduction to provide the hydrogen source (H*) for CO₂ reduction. Therefore, the reaction pathways shown in Figures 2 and 3 may be better promoted by visible light.

4. CONCLUSIONS

Single metal atoms, including Pd and Pt, supported on g-C₃N₄ as photocatalysts for CO₂ reduction by hydrogen were investigated by DFT calculations. During the reaction, the noble atom functions as the active site while the g-C₃N₄ provides the hydrogen source from the hydrogen evolution reaction. A single-atom catalyst not only can maximize the efficiency of noble-metal atoms but also exhibits excellent activity for CO₂ reduction. As evaluated by the reaction barriers, the preferred product of CO₂ reduction on the Pd/g-C₃N₄ catalyst is HCOOH with a barrier of 0.66 eV, while the Pt/g-C₃N₄ catalyst is able to reduce CO₂ to CH₄ efficiently with a barrier of 1.16 eV. In addition, the single metal atoms supported on g-C₃N₄ significantly enhance the visible-light absorption, making these materials potential photocatalysts for visible-light-promoted reduction of CO₂. Our results provide a new clue for experimental validation to convert CO₂ into fuel using solar energy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b02692.

Binding energies of Pt and Pd on g-C₃N₄ at different adsorption sites shown in Table S1, elemental steps for the formation of HCOOH, CH₃OH, and CH₄, and reaction pathways for CO₂ reduction to HCOOH and CH₃OH on the Cu/g-C₃N₄ catalyst (Figure S1) (PDF)

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Notes

The authors declare no competing financial interest.

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