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# Highly Efficient Photocatalytic System Constructed from CoP/Carbon Nanotubes or Graphene for Visible-Light-Driven CO<sub>2</sub> Reduction

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Dedication ((optional))

Abstract: Visible-light-driven conversion of CO2 to CO and highvalue-added carbon products is a promising strategy for mitigating CO<sub>2</sub> emissions and reserving solar energy in chemical form. We report an efficient system for CO<sub>2</sub> transformation to CO catalyzed by bare CoP, hybrid CoP/carbon nanotubes (CNTs), and CoP/reduced graphene oxide (rGO) in mixed aqueous solutions containing a Rubased photosensitizer, under visible-light irradiation. The in situ prepared hybrid catalysts, i.e., CoP/CNT and CoP/rGO, show excellent catalytic activities in CO<sub>2</sub> reduction to CO, with a catalytic rates of up to 39,510 and 47,330  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup> in the first 2 h of reaction, respectively; a high CO selectivity of 73.1% for the former was achieved in parallel competing reactions in the photoreduction of CO<sub>2</sub> and H<sub>2</sub>O. A combination of experimental and computational studies clearly shows that strong interactions between CoP and carbon-supported materials and partially adsorbed H<sub>2</sub>O molecules on the catalyst surface significantly improve CO-generating rates.

The heavy reliance on fossil fuels for the production of energy has increased atmospheric CO<sub>2</sub> emissions, which is considered to be an important factor in anthropogenic climate change.<sup>[1]</sup> Artificial photosynthesis has therefore attracted wide attention, with specific importance attached to the development of efficient and solar-light-driven methods that reduce CO<sub>2</sub> and convert it into energy-rich carbon-based products such as CO, methanol, methane, and aliphatic hydrocarbons.<sup>[2]</sup> To combat the chemical inertness ( $\Delta_f G^\circ = 396 \text{ kJ mol}^{-1}$ ) of CO<sub>2</sub> and the associated limits of the reaction's efficiency, most efforts have focused on exploration of promising new highly active catalytic systems.<sup>[3]</sup>

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primarily on two types of catalytic material: homogeneous metal complexes<sup>[4]</sup> and inorganic semiconductors.<sup>[5]</sup> The heterogeneous semiconductor catalysts reported to date are inefficient, largely because of inadequate use of solar light, and poor catalytic activity and product selectivity in competitive reduction between CO<sub>2</sub> and H<sub>2</sub>O because of the sluggish kinetics involving multiple electrons and protons.<sup>[6]</sup> Molecular catalysts such as Fe,<sup>[7]</sup> Co,<sup>[8]</sup> Ni,<sup>[9]</sup> and Mn<sup>[10]</sup> complexes are robust and give effective reduction of CO<sub>2</sub>, but their instability and recycling issues severely restrict their practical applications in photocatalysis. The development of new photocatalytic systems for CO<sub>2</sub> reduction with good catalytic efficiencies and high quantum yields remains a grand challenge in both approaches. Among various candidates, Co compounds are one of the most promising catalysts.<sup>[11]</sup> Wang and coworkers used a Ru-based photosensitizer (PS) and a Co-containing zeolitic imidazolate framework to construct a visible-light-driven system for CO<sub>2</sub> reduction,<sup>[12]</sup> but the catalytic activity and selectivities for CO and H<sub>2</sub> were a significant challenge. This approach was developed by using Co<sub>3</sub>O<sub>4</sub> hexagonal platelets, and gave highly efficient CO<sub>2</sub> conversion with a CO yield of 2,003  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup> in the first 3 h of reaction and high selectivity of 77.1%.<sup>[13]</sup>

Metal phosphide nanoparticles (NPs) have high stability and characteristics similar to those of zero-valent metals. The metallic-state compounds have been extensively studied as efficient electrocatalysts in water splitting,<sup>[14]</sup> and are highly efficient cocatalysts for photodriven H<sub>2</sub> evolution and robust catalysts for hydrolytic dehydrogenation of ammonia borane, as reported in our previous papers.<sup>[15,16]</sup> However, the use of metal phosphide NPs as catalysts for the photoreduction of CO2 is challenging because of significant interference of water reduction during photocatalysis. Generally, the transformation of CO2 is conducted in nonaqueous solvents to suppress competitive reduction of water itself to H<sub>2</sub>. In aqueous media, H<sub>2</sub> evolution by H<sub>2</sub>O reduction is kinetically and thermodynamically more favorable than CO<sub>2</sub> reduction.<sup>[17]</sup> Therefore, enhancement of the catalytic activity and product selectivity for CO<sub>2</sub> reduction by changing the catalyst morphology and size, the structure of the hybrid catalyst interface and surface-modification of catalyst NPs to promote adsorption and transformation of CO2 are effective strategies for overcoming the above drawbacks, especially in electrochemical CO<sub>2</sub> reduction.<sup>[18]</sup> Bao and coworkers found that the presence of OH groups on the catalyst surface enhanced the adsorption and activity of CO2.[19] Our previous work combining experimental studies and firstprinciples calculations also showed that the competing adsorption of OH groups and H<sub>2</sub>O molecules on CoP surfaces changes the chemical environments of catalyst surface, and remarkably causes the changes of reaction rate and initiation

period for catalytic H<sub>2</sub> generation from ammonia borane hydrolysis.<sup>[16b]</sup> We therefore expect that limiting the adsorption of H<sub>2</sub>O molecules on the catalyst surface could improve the catalytic performance in CO<sub>2</sub> photoreduction via tuning surface interactions between H<sub>2</sub>O and CO<sub>2</sub> to provide a high local CO<sub>2</sub> concentration and facilitate proton-coupled transformation of the initial Co–CO<sub>2</sub> adduct.

Here, we present for the first time a highly efficient photocatalytic system consisting of CoP modified with carbon nanotubes (CoP/CNT) or reduced graphene oxide (CoP/rGO) as the catalyst for visible-light-driven CO<sub>2</sub> to CO conversion in a mixed water/acetonitrile medium with Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (bpy = 2,2'-bipyridine) as a PS and triethanolamine (TEOA) as an electron donor. The catalytic activities and CO selectivities of CoP/CNT and CoP/rGO are better than those of bare CoP. The dependence of the photocatalytic CO<sub>2</sub> to CO transformation on the amount of H<sub>2</sub>O was studied. A mechanism of CO<sub>2</sub>-to-CO conversion based on experimental results and density functional theory (DFT) calculations is proposed.

CoP NPs were prepared using a method previously reported by our group.<sup>[16b]</sup> The hybrid Co<sub>3</sub>O<sub>4</sub>/CNT and Co<sub>3</sub>O<sub>4</sub>/rGO were synthesized by a facile scalable approach involving a hydrothermal reaction in an autoclave  $(SI)^{[20]}$  and Co<sub>3</sub>O<sub>4</sub> phosphorized with NaH<sub>2</sub>PO<sub>2</sub> to form the CoP-embedded carbonaceous materials (Scheme 1).<sup>[21]</sup>



Scheme 1. Schematic diagram of in situ preparation of hybrid CoP/CNT.

The CoP NP loadings on the CNTs or rGO were controlled to 43 and 48 wt%, respectively. The amounts were determined by elemental analysis using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The Co:P atomic ratios were 0.93:1 and 1:0.96 for the former and latter, respectively, confirming successful formation of the desired CoP NPs. Scanning transmission electron microscopy (STEM) images (Figure 1b-f) show that the average size of the CoP NPs embedded in the carbonaceous materials was 6-10 nm; bare CoP NPs are about 15 nm in diameter (Figure S1). The amounts of C, H, and N elements, determined using a Vario EL III instrument, were 34.20%, 2.59%, and 1.48%, respectively, for CoP/CNT, and 27.61%, 2.58%, and 3.17%, for CoP/rGO; this indicates the presence of N species. The lower N percentage probably originated from the ammonium hydroxide used in the initial preparation process.<sup>[20]</sup> In the X-ray diffraction (XRD) patterns of pure CoP and the hybrid CoP/CNT and CoP/rGO all the diffraction peaks from CoP can be indexed to a phosphide with an orthorhombic structure (JCPDS Card No. 29-0497;



Figure 1. (a) XRD patterns of CoP, CoP/rGO, and CoP/CNT; (b) TEM image of *in situ* prepared CoP/CNT; (c) TEM image and corresponding EDX elemental mapping images of C, Co, and P for CoP/CNT; (d) HRTEM image of CoP/CNT; (e) TEM and (f) HRTEM images of *in situ* prepared CoP/rGO.

Figure 1a); the peak at about 26° confirms the presence of the carbon support.

High-resolution transmission electron microscopy (HRTEM) images (Figures 1d and 1f) show strong interactions between CoP and the carbonaceous supports. The well-resolved lattice fringes with interplanar distances of 0.19 and 0.25 nm for the CoP NPs incorporated into carbonaceous materials are consistent with the (211) and (111) planes, respectively, of the CoP crystal structure. Energy-dispersive X-ray (EDX) elemental mapping analysis in selected field (Figure 1c) suggests that Co and P in CoP/CNT are uniformly distributed on the CNT surfaces via oxide-CNT anchoring. The chemical states of Co, P, and C in CoP/CNT and CoP/rGO were further identified by X-ray photoelectron spectroscopy (XPS). Figure S2 shows that the low-energy peaks with binding energies of 779.2 and 782.2 eV for CoP/CNT (778.9 and 781.8 eV for CoP/rGO, Figure S3) are slightly positively shifted from those for metallic Co (778.1-778.2 eV), suggesting weak charge transfer from Co to P; this is consistent with the Co 2p<sub>3/2</sub> state.<sup>[22]</sup> The high-energy peaks centered at 794.1, 798.2, and 803.1 eV for the former two correspond to Co 2p<sub>1/2</sub> electrons in CoP, whereas the latter was associated with the excitation of high-spin Co2+ ions, originating from superficial air oxidation of CoP.<sup>[23]</sup> For the P(2p) region, the

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peaks located at 130.7 and 129.9 eV correspond to P  $2p_{1/2}$  and P  $2p_{3/2}$  states, respectively (Figure S2), and indicate that P is nearly charge neutral. The broad peaks centered at 134.2 and 133.3 eV can be ascribed to oxidized P species.<sup>[24]</sup> The C 1s spectrum was deconvoluted into three peaks centered at 284.8, 286.2, and 288.5 eV, corresponding to C=C, C-C, and carbon bonded to N- or O-containing species, respectively.<sup>[25]</sup> The Raman spectra of CoP/CNT and CoP/rGO show the characteristic D band (1348 cm<sup>-1</sup>) and G band (1587 cm<sup>-1</sup>) of the carbon species, and the ratios of  $I_D$  to  $I_G$  for the former and latter are 1.50 and 1.42, respectively, implying destructive coalescence of the hybrid materials (Figure S4). The high  $I_D:I_G$  suggests that the introduction of CoP leads to more structural defects and disordered structures in the carbonaceous materials, boosting the catalytic performance.<sup>[26]</sup>

The photocatalytic systems for CO<sub>2</sub> reduction were assembled using as-prepared CoP, CoP/CNT, and CoP/rGO as catalysts, and Ru(bpv)<sub>3</sub>Cl<sub>2</sub> as a PS in a CO<sub>2</sub>-saturated TEOA/CH<sub>3</sub>CN/H<sub>2</sub>O (v/v, 1/2/1) mixed solvent. To verify that the CO originated from CO<sub>2</sub>, isotopic labeling experiments were conducted using <sup>13</sup>CO<sub>2</sub> in a gas chromatography-mass spectrometry (GC-MS) system under identical catalysis conditions. Figure S5 proves that CO was formed by reduction of CO<sub>2</sub>, and precluded possible degradation of organics used. The photoreduction gas products were identified using GC, with Ar as the carrier gas. Further control experiments showed that no CO was generated if any of the following components were absent: light, the PS, or the catalyst. In Ar, the system generated a large quantity of hydrogen without any CO evolution. In addition, the solution after the photoreaction was analysed by ion chromatography, only trace amounts of HCOOH were detected, CO was therefore the sole carbon-containing product. The generation rates of CO and H<sub>2</sub> were evaluated as a function of catalyst concentration at fixed amounts of PS at ambient temperature (Figure 2a and 2c, Figure S6). In the case of CoP, the photoreduction yields of CO<sub>2</sub> increased with increasing catalyst concentration, and reached a limiting value, with a CO selectivity of 61.1% (Figure 2a). When the amount of CoP was further increased, the total CO2-to-CO conversion and H<sub>2</sub> liberation decreased because of a lightshielding effect and aggregation of catalyst during photoreduction. Under the same reaction conditions, the optimal CO and H<sub>2</sub> evolution rates on CoP/CNT were significantly better than the CO<sub>2</sub> reduction rate on CoP (Figure S6). The enhanced performance is attributed to CNT introduction improving the electronic conduction paths and preventing NPs aggregation.<sup>[27]</sup> The maximum CO generation rate, 122.6 µmol, and an average selectivity of 70.5% were achieved after 2 h of visible-light irradiation over the applied catalyst range (Figure S6). At higher catalyst concentrations, decreases in CO and  $\mathsf{H}_2$  production analogous to those for CoP as the cocatalyst were observed. The PS dependences of CO<sub>2</sub> and H<sub>2</sub>O photoreduction were also studied under identical conditions; the obtained data showed a curve-shape change with increasing PS concentration (Figure 2b). A comparison with the results for the dependence of photoreduction rates on concentration of CoP/CNT (Figure S6) and PS shows that the selectivity decreased slightly (Figure 2b, average value of 63.8%) with increasing PS concentrations because of the increasing contribution of PS itself to H<sub>2</sub> evolution. The results in Figure 2c clearly show that in the presence of

CoP/rGO (in the range used, i.e., 1 to 8 mg), a negative dependence of generated CO<sub>2</sub> and H<sub>2</sub> on the hybrid catalyst content appeared, because of both adsorption of PS molecules on rGO and a light-shielding effect. The selectivity for CO varied from 62.3% to 68.3% (66.7%, 0.5 g CoP/rGO) when CoP/rGO amounts from 1 to 8 mg were used. As shown in Figure 2d, a comparison of the yields for photocatalytic conversion of CO<sub>2</sub> to CO indicates that the as-prepared hybrid CoP/rGO is an excellent catalyst; this is because of synergistic coupling between CoP and the carbon support, and the catalytic rate reached 47,330  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup> in the first 2 h of the reaction. These observations are in good agreement with the particle size CoP and interfacial interactions between CoP and of carbonaceous materials. The order of the selectivity for CO over competing  $H_2$  generation is CoP < CoP/rGO < CoP/CNT; CoP/CNT gave the highest CO selectivity, i.e., 73.1% (a catalytic rates of up to 39,510  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup>), implying that other factors such as changes in the chemical environment around CoP significantly affect the competitive reaction pathways.



Figure 2. Effect of (a) CoP and (c) CoP/rGO catalyst content on catalytic performance in CO<sub>2</sub> reduction in 20 mL of CO<sub>2</sub>-saturated TEOA/CH<sub>3</sub>CN/H<sub>2</sub>O (v/v, 1/2/1) solvent containing [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (5 mg) under irradiation with stirring for 2 h at 298 K. The total volume of the quartz reaction tube was 60 mL (300 W Xe lamp with 400 nm filter); (b) PS dependence of photoreduction of CO<sub>2</sub> at fixed amount (2 mg) of CoP/CNT under similar conditions as in (a) and (c); (d) yields of CO and H<sub>2</sub> after irradiation of suspension containing [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (5 mg) and catalyst (1 mg) for 2 h under identical conditions to those in (a), (c), and Figure S6.

To get an in-depth understanding of the improved photoreduction performance, the yields of CO and  $H_2$  were measured in this study as a function of irradiation time. The results, shown in Figure 3, clearly show changes in the relative amounts of the products from both competing pathways over time. Initially, a higher  $H_2$ -generating rate was observed. The photocatalytic reaction for the conversion of CO<sub>2</sub> to CO became more crucial with increasing reaction time, and rapid acceleration of the CO-generating rate occurred after irradiation for 30 min. The crossing points occurred at about 1.4, 1.0, and 1.2 h during irradiation for the CoP, CoP/CNT, and CoP/rGO catalysts, respectively; this is consistent with the selectivity for CO seen in Figure 2d. This means that in the initial period species formed by the interaction between molecules in reaction

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system and surface on catalyst tunes the competing catalytic pathways, and changes the catalytic properties of the catalyst surface.<sup>[16b]</sup> If this speculation is correct, the interactions between H<sub>2</sub>O and atoms on the catalyst surface may be important. The dependence of the CO-generating rate on the H<sub>2</sub>O content in CO<sub>2</sub> photoreduction on CoP/CNT was therefore studied as a function of various H<sub>2</sub>O contents. The results clearly demonstrate that the amount of H<sub>2</sub>O on the catalyst surface plays a significant role in improving the catalytic efficiency and selectivity in CO<sub>2</sub> transformation. In the absence of H<sub>2</sub>O, the catalyst shows a lower CO-generating activity, but the rate of CO production increases sharply with addition of H<sub>2</sub>O (Figure 3d), and reaches the limiting values after adding 5 mL of H<sub>2</sub>O. Subsequent addition leads to low catalytic efficiency (inset in Figure 3d), and  $H_2$  generation shows a similar trend (Figure S7), which indicates that the interactions between H<sub>2</sub>O molecules and atoms on the catalyst surface accelerate the CO- and H<sub>2</sub>generating reactions and excess H<sub>2</sub>O decreases the catalytic activity. The former effect is beneficial for proton transfer and increasing the local CO<sub>2</sub> concentration, but the latter results in a decrease in the number of active catalytic sites because the catalyst surface is covered by H<sub>2</sub>O.



**Figure 3.** CO and H<sub>2</sub> evolution as function of irradiation time for visible-light catalytic performance in 20 mL of CO<sub>2</sub>-saturated TEOA/CH<sub>3</sub>CN/H<sub>2</sub>O (v/v, 1/2/1) solvent containing [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (10 mg) and (a) CoP (2 mg), (b) CoP/CNT (2 mg), and (c) CoP/rGO (2 mg) at 298 K. (d) Dependence of CO-generating rate in CO<sub>2</sub> photoreduction on H<sub>2</sub>O content in 15 mL of CO<sub>2</sub>-saturated TEOA/CH<sub>3</sub>CN (v/v, 1/2) solvent at fixed amounts of CoP/CNT (2 mg) and [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (10 mg); inset: CO evolution weakened with increasing H<sub>2</sub>O amount from 5 to 7 mL, and then to 9 mL.

DFT calculations show that the adsorption energies for  $CO_2$ on the CoP (010) surface without and with P defects are -0.012 and -0.223 eV, respectively. During  $CO_2$  photoreduction these surface defects facilitate the approach of carbon atoms of  $CO_2$ molecules to Co atoms, resulting in the configuration of the  $CO_2$ molecule changing from linear to V-shaped, and C-Co and O-Co distances of 1.955 and 1.968 Å, respectively (Figure 4). The C=O bond lengths of 1.211 and 1.280 Å in the V-configuration are considerably longer than those of 1.172 and 1.169 Å in the linear molecule (Figure S8). The calculation results indicate that high catalytic activity arises from P defects on the CoP surface.<sup>[28,29]</sup> When the H atom of a proton donor far from the P atom of the CoP surface (6.682 Å) approaches a P····H distance of 1.410 Å, the interaction between the H atom and the O atom of CO<sub>2</sub> is accompanied by a H···O distance of 3.705 Å, and energy of 3.73 eV is released. The transition state TS1, in which the H atom is closer to O, is generated by overcoming an energy barrier of 2.42 eV. For TS1, the C-O bond length of 1.34 Å is close to that of a typical single bond (ca. 1.34 Å), and it undergoes an energetically downhill transformation to the intermediate OCOH\*. Afterwards, the change in the C ··· OH distance from 2.316 in TS2 to 3.681 Å is also energetically downhill. This shows that the HO-CO bond was split to give an OH group and a stable intermediate with a Co···CO distance of 1.786 Å; the H–O and C=O bond lengths are 0.972 and 1.158 Å, respectively. It was noted that generation of CO as the final product from Co····CO requires overcoming of a slightly lower energy barrier (1.50 eV) than the activation energy of TS1, suggesting that the key kinetic step in photoreduction CO<sub>2</sub> is the proton transfer step. Figures S9 and S10 show that the activation energy for TS1 in the presence of H<sub>2</sub>O is 0.99 eV lower than that in the presence of H<sup>+</sup>. The lower reaction barrier for the rate-determining step reveals that CO<sub>2</sub> photoreduction is favored in the presence of H<sub>2</sub>O; this is in good agreement with the experimental results. In addition, it can be seen from Figure S11 that the CoP/rGO catalyst retained about 97% of its initial activity after five cycles, and XPS analysis shows that the peak profiles of the recovered catalysts were almost unchanged (Figures S12 and S13). The slight drop in activity could be ascribed to the breaking away of CoP from the carbon materials because of violent stir during the catalytic reaction.



Figure 4. Relative energy change diagram for  $\text{CO}_2$  reduction to CO catalyzed by CoP in system containing proton donor.

In summary, coupled CoP/CNT and CoP/rGO catalysts show higher catalytic activities and CO selectivity for CO<sub>2</sub>-to-CO in the presence of a Ru-based PS under visible-light irradiation compared with those for CoP alone. A catalytic rate of 47,330  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup> (CoP/rGO) and 73.1% (CoP/CNT) selectivity for CO<sub>2</sub> conversion to CO were achieved in parallel with water reduction. The effects of interactions between CoP and carbonaceous materials, P defects on the CoP surface, and partially adsorbed H<sub>2</sub>O molecules, which lowers the activation

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energy of the rate-determining step, on the catalytic rate and selectivity for CO were unambiguously shown by experimental results and calculation data. This work represents a new strategy for highly effective photodriven  $CO_2$  reduction and offers a complementary approach to the development of advanced catalysts for  $CO_2$  transformation into value-added carbon products.

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Ru-based photosensitizer

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## COMMUNICATION

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Photocatalytic Reduction of CO<sub>2</sub> to CO

## COMMUNICATION

New systems for visible-light-driven reduction of CO<sub>2</sub> to CO catalyzed by hybrid CoP/CNT or CoP/rGO with a Ru-based photosensitizer in a mixed aqueous medium were constructed. A catalytic rate of 47,330  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup> and 73.4% CO selectivity were achieved. Strong interactions between CoP and carbonaceous materials and partially adsorbed H<sub>2</sub>O molecules on the catalyst surface greatly improved the CO-generating rates.



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Highly Efficient Photocatalytic System Constructed from CoP/Carbon Nanotubes or Graphene for Visible-Light-Driven CO<sub>2</sub> Reduction