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Electrohydrogenation of Carbon Dioxide Using a Ternary Pd/Cu₂O-Cu Catalyst

Jing Li,^{‡[a,b]} Si-Xuan Guo,^{‡[a,c]} Feng Li,^[d] Fengwang Li,^[a,c] Xiaolong Zhang,^[a] Jiantai Ma,^{*[d]} Douglas R. MacFarlane,^[a,c] Alan M. Bond ^[a,c] and Jie Zhang^{*[a,c]}

[‡] These authors contributed equally to this work

Abstract: A simple one-pot method has been developed to synthesize a palladium/cuprous oxide-copper (Pd/Cu₂O-Cu) material with well-defined structure, by modification of Cu₂O-Cu with Pd through a galvanic replacement reaction. Compared to the well-known copper/cuprous oxide (Cu/Cu₂O) catalysts, the newly synthesized Pd/Cu₂O-Cu material can catalyze the electroreduction of CO₂ into C₁ products with much higher faradaic efficiencies at lower overpotentials in a CO₂-saturated 0.5 M NaHCO₃ solution. In particular, the highest faradaic efficiencies of 92% for formate, and 30% for methane were achieved at -0.25 V and -0.65 V vs. the reversible hydrogen electrode, respectively. The presence of Pd enhances the current density and reduces the overpotential for electrocatalytic CO₂ reduction. The improvement is suggested to be the result of a synergistic effect between PdH and the catalytically active copper sites during electrochemical CO₂ reduction.

Introduction

Carbon dioxide (CO₂) is a major greenhouse gas that causes serious environmental issues. However, it also provides a cheap and abundant C₁ building block for the synthesis of value added chemicals and fuels.^[1] Among all the methods reported so far, electrochemical reduction of CO₂ offers an effective way to convert CO₂ back to fuels and other valuable chemicals, provided renewable electrical energy is used.^[2] However, due to the high stability and low solubility of CO₂ in aqueous media, and the large overpotential required for its electrochemical reduction versus the

- [a] Dr. J. Li, Dr. S.-X. Guo, Dr. F. Li, Dr. X. Zhang, Prof. D. R. MacFarlane, Prof. A. M. Bond, Prof. J. Zhang. School of Chemistry, Monash University, Clayton, Victoria 3800, Australia
- E-mail: jie.zhang@monash.edu; majiantai@lzu.edu.cn [b] Dr. J. Li.

State Key Laboratory of High-efficiency Coal Utilization and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, Ningxia, 750021, P. R. China.

[c] Dr. S.-X. Guo, Dr. F. Li, Prof. D. R. MacFarlane, Prof. A. M. Bond, Prof. J. Zhang.

ARC Centre of Excellence for Electromaterials Science, Monash University, Clayton, Victoria 3800, Australia [d] Dr F. Li, Prof. J. Ma.

State Key Laboratory of Applied Organic Chemistry (SKLAOC), The Key Laboratory of Catalytic Engineering of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu, 730000, P. R. China

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ease of the competing hydrogen evolution reaction (HER), the efficiency of CO₂ reduction is low.^[3] In the past two decades, it has been demonstrated that metal catalysts, such as Ag, Au, Cu, Pb, and Sn, can be designed in a way so that they can lower the overpotential for CO2 reduction while suppressing the HER.[4] Among these catalysts, only Cu can catalyze CO₂ reduction to hydrocarbons with reasonably high faradaic efficiencies (FEs), other than products such as CO, HCOO⁻, and H₂. For example, Baturina et. al investigated four carbon-supported Cu catalysts toward CO₂ electroreduction to hydrocarbons. The ratio of C₂H₄/CH₄ faradaic efficiencies was found to be dependent on the particle size, with higher ratios observed for smaller Cu nanoparticles.^[5] Manthiram et. al demonstrated that n-Cu/C electrocatalyst exhibits an average faradaic efficiency for methane of 80% during extended electrolysis.^[6] Unfortunately, these Cu catalysts usually require a large overpotential (>0.7 V) for CO₂ reduction which limits its energy efficiency.^[7] Thus, there remains a need to design efficient copper catalysts, and to understand the mechanistic details on the catalytic surface.

Intensive research efforts, both experimental (e.g. through nanostructuring, oxide-derivation etc.) and theoretical (e.g. identification of key intermediates and reaction pathways etc.), have been devoted to reducing the overpotential and improving the product selectivity of CO₂ reduction catalyzed by Cu-based catalysts.^[8] It has been shown that oxide-derived Cu films or cubes significantly lowered the overpotential and enhanced the product selectivity compared to polycrystalline Cu metal catalysts.^[9] For example, Lee et al. reported that the bi-phasic Cu₂O-Cu catalyst showed remarkable catalytic ability towards the generation of C2-C4 species in KCI electrolyte; [9a] Huan et al. reported that the addition of nitrogen-based organic compounds, such as tetramethyl cyclam, in solution significantly promoted CO2 reduction on Cu/Cu₂O-modified FTO, and produced formic acid with a FE of almost 90% at -2.0 V versus Fc⁺/Fc (Fc=Ferrocene) in a CO₂-saturated DMF/H₂O (99:1, v/v) solution;^[9b] Kas et al. reported that CO₂ reduction catalyzed by copper nanoparticles. derived from Cu₂O with optimized morphologies and surface coverages, selectively produced ~8 to 12 times more ethylene than methane.^[9c] Some other studies have suggested that the introduction of noble metals to Cu-based catalysts, e.g. AuCu nanoparticles or CuPd nanoalloys, is beneficial to breaking the scaling relation and stabilizing the intermediates, and thus lowers the overpotential and improves the product selectivity.^[10] For example, the ordered CuPd catalyst prepared by Kenis et al. can produce CO with a faradaic efficiency over 80% at a potential of about -0.55 V vs. the reversible hydrogen electrode (RHE).[10b] Other forms of PdCu materials, such as PdCu alloy, Pd-Cu bimetallic aerogel, Cu-modified Pd nanoparticles, and Cu

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overlayers on tetrahexahedral Pd nanocrystals with high-index facets have also shown promising CO_2 reduction activity and selectivity.^[11]

Encouraged by the above literature results, in this study, we report a facile one-pot synthesis of a new ternary Pd/Cu₂O-Cu catalyst which has excellent electro-catalytic activity for CO₂ reduction and achieves selective formation of C₁ species in an applied potential range of -0.15 V to -0.75 V vs. RHE in a CO₂-saturated 0.5 M NaHCO₃ solution. In particular, electrolysis at -0.25 V produces formate with ~ 92 % faradaic efficiency, while at -0.65 V, 30% FE for methane is obtained. The origin of the synergistic effects of Pd modification and the Cu₂O-Cu structure, which result in much improved activity, stability, and product selectivity, was discussed.



Scheme I. Synthesis procedures of Pd/Cu₂O-Cu Nanoparticles.

Results and Discussion

Characterizations of the nanomaterials Pd/Cu_2O -Cu, Pd_{Cu} and Cu_2O -Cu.

The morphology of the Pd/Cu₂O-Cu catalyst (Fig. 1a and b) was examined by TEM under different magnifications. The low magnification TEM image (Fig. 1a) shows a uniform structure, while the high-resolution TEM image (Fig. 1c) reveals the lattice fringe spacings of 2.45 Å, 2.20 Å and 2.08 Å, attributed to the (111) facet of Cu₂O, Pd and Cu, respectively. A HAADF-STEM image together with the EDX line scans and spectrum (Fig. 1 d, e & f) were obtained to determine the elemental distribution of the Pd/Cu₂O-Cu catalyst. Both Pd and Cu elements distribute uniformly over the entire sample (Fig. 1d), however, the Cu content is higher than that of Pd when the EDX line was scanned in the sample area (Fig. 1e). The exact loading of Pd on Pd/Cu₂O-Cu is 40% (denoted as Pd40/Cu2O-Cu), as determined by ICP-AES. Elements C, Ni, Pd, Cu and O are also detected in the EDX spectrum (Fig. 1f). The C and Ni signals arise from the sample holder. Pdcu nanoparticles show similar uniform morphology as the Pd₄₀/Cu₂O-Cu catalyst, but with larger particle size, while Cu₂O-Cu catalyst shows various shapes such as cubes and spheres with different sizes, as well as irregular shapes (Fig. S3†).



Fig. 1 (a, b) TEM and (c) HR-TEM images of the Pd₄₀/Cu₂O-Cu nanoparticles; (d) HAADF-STEM image of a pile of Pd₄₀/Cu₂O-Cu nanoparticles, and HAADF-STEM-EDX elemental mapping images of O-K, Pd-K and Cu-K. (e) Crosssectional compositional line profiles of O, Cu and Pd in Pd₄₀/Cu₂O-Cu nanoparticles recorded along the line shown in the HAADF-STEM image (inset). (f) EDX spectrum of the Pd₄₀/Cu₂O-Cu nanoparticles.

The XRD patterns of the Pd_{40}/Cu_2O -Cu, Pd_{Cu} and Cu_2O -Cu catalysts are shown in Fig. 2a. In the case of Pd₄₀/Cu₂O-Cu, the five main diffraction peaks located at 29.6°, 36.5°, 42.4°, 61.3° and 73.9° are ascribed respectively to the (110), (111), (200), (220) and (311) reflections of a face centered cubic (fcc) Cu₂O crystal (JCPDS Card No. 65-3288). The three major diffraction peaks located at 40.4°, 46.7°, 68.4° are respectively indexed to the (111), (200) and (220) reflections of a fcc Pd crystal (JCPDS Card No. 01-1201), which are consistent with those of the Pd_{Cu} nanoparticle catalyst. The Cu diffraction peaks in Pd40/Cu2O-Cu is not obvious due to its low content. Quantitative analysis of compositions of the Cu₂O-Cu catalyst was carried out by analyzing the XRD data using the Relative intensity ratio (RIR) method (the calculation details are described in the ESI†),^[12] and the results showed that the Cu₂O-Cu catalyst consists of 10.35 wt % Cu and 89.65 wt% Cu₂O. The XPS Pd 3d spectrum of the Pd₄₀/Cu₂O-Cu catalyst (Fig. 2b) can be deconvoluted into two pairs of peaks, which are attributed to metallic Pd⁰ and Pd²⁺ species.^[13] In the Cu 2p region of the XPS spectrum (Fig. 2c), the peaks at 932.6 and 952.5 eV are consistent with the binding energies of Cu⁺ 2p_{3/2} and Cu⁺ 2p_{1/2}, respectively. Compared to the Cu 2p XPS spectrum of Cu₂O-Cu, a negative shift of ~0.2 eV in binding energy was observed from the Pd₄₀/Cu₂O-Cu catalyst (Fig. S4†), which confirms that charge transfer occurred between Cu and Pd and the presence of an intimate contact between them, consistent with the TEM observation (Fig. 1c). Since the binding energy values of Cu and Cu₂O are similar, it is very difficult to distinguish them by the XPS spectra based solely on the Cu 2p data. Thus, the X-raygenerated Auger Cu LMM spectrum has been obtained for a more reliable assignment for Cu and Cu₂O. As shown in Fig. 2d, the Cu LMM spectrum for the Pd₄₀/Cu₂O-Cu catalyst shows two peaks at 916.3 and 918.0 eV, which are attributed to Cu₂O and Cu, respectively, confirming their presence.^[12c] The Pd_{Cu} catalyst is also characterized by EDX and XPS measurements (Fig. S1†). The highly sensitive XPS results show the presence of residual

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Cu⁰ in the Pd_{Cu} catalyst (~ 1 %, atomic concentration, see detailed discussion in the ESI†).

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Fig. 2 (a) XRD patterns obtained for the Pd₄₀/Cu₂O-Cu, Pd_{Cu} and Cu₂O-Cu nanoparticles; XPS spectra of (b) Pd 3d and (c) Cu 2p; and (d) Cu LMM spectrum of Pd₄₀/Cu₂O-Cu..

Linear sweep voltammetric (LSV) studies of the Pd40/Cu2O-Cu, Pd_{Cu} and Cu₂O-Cu catalysts were conducted in a 0.5 M NaHCO₃ aqueous solution saturated with CO2 at a scan rate of 5 mV s⁻¹ without iR compensation (Fig. 3a). All data were recorded after 50 cycles of potential scan in the range from 0 to -0.8 V vs. RHE at a scan rate of 50 mV s⁻¹, to reduce CuO and the majority of Cu₂O to the thermodynamically more stable Cu⁰ and a small amount of metastable Cu⁺. Since the reduction of these copper species contribute significantly to the current response in the first few cycles of potentials, linear sweep voltammograms obtained from a freshly prepared Pd/Cu2O-Cu modified electrode were not shown to avoid confusion. The results in Fig. 3a show that the Pd₄₀/Cu₂O-Cu catalyst has the most positive onset potential (-0.1 V) and is 0.2 V and 0.5 V more positive than those of -0.3 V and -0.6 V for the Pd_{Cu} and Cu_2O -Cu catalysts, respectively. The current density increases rapidly when the potential is more negative than -0.2 V and -0.3 V, and reaches ~ 25.5 mA cm⁻² and ~19.4 mA cm⁻² at -0.8 V, under CO₂ and N₂ atmospheres, respectively (pH values 7.2 and 8.5, respectively) (Fig. 3b).



Fig. 3 (a) Linear sweep voltammograms of Pd₄₀/Cu₂O-Cu (red line), Pd_{Cu} (blue line) and Cu2O-Cu (green line) modified GCEs in a CO2-saturated 0.5 M NaHCO3 aqueous solution, (b) Pd40/Cu2O-Cu modified GCE in a CO2-saturated (red line) and N2-saturated (brown line) 0.5 M NaHCO3 aqueous solutions. Scan rate 5 mV s⁻¹.

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The distribution of gaseous and liquid products obtained during the electrochemical reduction of CO2 using the Pd40/Cu2O-Cu catalyst under bulk electrolysis conditions in a CO2-saturated 0.5 M NaHCO3 aqueous solution (pH 7.2) in the potential range from -0.15 V to -0.75 V vs. RHE is presented in Fig. 4a. The amount of charge passed as a function of electrolysis time is provided in Fig. S5†. As the applied potential changes from -0.15 V to -0.25 V, the FE for HCOO⁻ increases from about 80% to 92%, while that for H₂ increases slightly. As the applied potential becomes more negative, the FE for HCOO⁻ decreases and is less than 10% when the potential is more negative than -0.65 V, while that for H₂ increases significantly and reaches 82% at a potential of -0.75 V. A small amount of CH₃OH is detected in the potential range of -0.35 to -0.65 V, with a maximum FE of about 6% obtained at -0.55 V. Both CH4 and CO are detected only in the potential range of -0.55 V to -0.75 V, with a maximum FE of ~30% for CH4 obtained at -0.65 V, and ~4% for CO at -0.75 V vs. RHE. No C2+ products were obtained with the Pd₄₀/Cu₂O-Cu catalyst. Although the presence of Cu₂O was reported to favor the formation of C₂H₄ during CO₂ reduction, the formation of C₂₊ products only occurs at highly negative potentials at high pH,[14] which can lower the C-C coupling energy barrier and suppress the primary competing reactions including H₂ and CH₄ formations. Furthermore, in this work, PdH is formed during the catalytic reaction, and the adsorption/desorption of CO on PdH becomes thermoneutral, thus CO adsorption is weakened and the C-C coupling reaction is unfavored.^[15] Representative NMR and GC spectra obtained are presented in Figs. S6 and S7⁺. At Pd_{cu} nanoparticles modified electrodes, a maximum FE of ~73% for HCOO- is obtained at -0.15 V vs. RHE as shown in Fig. 4b, which decreases as the applied potential becomes more negative and reaches around 2% at -0.75 V. In contrast, for the Cu₂O-Cu catalyst, HCOO⁻ could only be produced when the potential is more negative than -0.55 V with very low FEs, and a maximum FE of ~6% is obtained at -0.75 V vs. RHE. The partial current densities for HCOOproduction with different catalysts are compared in Fig. 4c. The partial current density of HCOO⁻ reaches ~4.2 mA cm⁻² with Pd₄₀/Cu₂O-Cu and ~1.5 mA cm⁻² with Pd_{Cu} at -0.25 V vs. RHE, respectively. From Fig. 4d, it can be seen that the partial current density for H₂ production remarkably increases when the applied potential becomes more negative (since the H₂ partial current densities below -0.35 V are low, a broken Y-axis presentation was used for convenient comparison in the whole potential range), indicating that the rate of H₂ production accelerates at more negative applied potentials. An earlier study by Li and Kanan,^[16] using a thick Cu₂O film on Cu as the electrode, achieved ~38% FE for HCOO⁻ at -0.55 V and ~42% FE for CH₄ at -0.97 V vs. RHE, respectively. Recently, Melchionna et al. demonstrated that CO2 could be converted to HCOOH at near zero overpotential in an aqueous solution using an electrode modified with Pd@TiO₂/single walled carbon nanoHorns.^[17] Data reported with other catalysts are summarized in Table S1⁺, which show that the Pd₄₀/Cu₂O-Cu catalyst has excellent electrocatalytic performance for CO2 reduction in terms of product selectivity at low overpotentials, particularly with respect to HCOO- and CH₄.

Pd/Cu₂O-Cu catalysts with different Pd loadings on Cu₂O-Cu (20 wt. % and 60 wt. %, denoted as Pd20/Cu2O-Cu and

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Pd₆₀/Cu₂O-Cu, respectively) were tested to investigate its influence on the product distribution of CO₂ reduction. The distribution of gaseous and liquid products obtained under the same electrolysis conditions are presented in Fig. S8⁺. When the loading of Pd is 20 wt. % and 60 wt. %, the FE for HCOO⁻ is ~80 % and ~65 % respectively at -0.25 V, which is inferior to Pd₄₀/Cu₂O-Cu. Furthermore, a maximum FE of ~7 % for CH₄ was obtained at -0.65 V on the Pd₂₀/Cu₂O-Cu catalyst, while no CH₄ was detected on Pd₆₀/Cu₂O-Cu. Based on the above observations, it is concluded that the synergistic effect is optimal when the loading of Pd is 40 wt. %.



Fig. 4 CO₂ reduction activities over the Pd₄₀/Cu₂O-Cu, Pd_{Cu} and Cu₂O-Cu catalysts in a CO₂-saturated 0.5 M NaHCO₃ solution. (a) FEs of gaseous and liquid products obtained using Pd₄₀/Cu₂O-Cu as the catalyst; (b) FEs of HCOO⁻ obtained on different catalysts; (c) HCOO⁻ and (d) H₂ partial current densities obtained on different catalysts.

It has been reported that the product selectivity in CO2 reduction was influenced by the oxide phase of the Cu-based catalysts, as well as the structure of metallic copper. [16, 18] In order to explore this issue, XRD measurements were undertaken after controlled potential electrolysis with 10 C of charge at -0.25 V and -0.75 V vs. RHE using the Pd40/Cu2O-Cu catalyst. As shown in Fig. 5a, peaks located at 30° and 42.4° ascribed to the (110) and (200) facets of Cu₂O are clearly observed, although their intensities are weak. The (110) diffraction peaks of Cu₂O shift to slightly higher 20 compared to those of the original Pd40/Cu2O-Cu catalyst, suggesting the formation of compressed lattices of Cu₂O during the electrolysis process. It seems that only a small amount of charge was used to reduce Cu⁺, resulting in no significant diffraction peaks of Cu in the XRD. In the XPS spectra (Fig. 5b), some Cu2+ appears whereas no XRD pattern associated with CuO was observed. This fact suggests that the Cu²⁺ peak is most likely from the CuO surface layers generated after electrolysis due to the oxidation of Cu in air. The Cu⁺ peaks observed in the XPS spectra imply that the non-reduced Cu₂O layer exists after electrolysis. The morphology of the Pd40/Cu2O-Cu particles become more regular (Fig. 6) after electrolysis. A slight increase in the lattice spacing of Pd (2.20 Å) is attributed to the formation

of PdH (2.29 Å), where H occupies metal vacancy as a dopant to form PdH and hence changes the unit cell volume.[19] However, there is no obvious PdH diffraction peaks in Fig. 5a, because the amount of stabilized PdH is relatively small. In a control experiment, the Pd40/Cu2O-Cu was firstly fully reduced to Pd/Cu in a CO₂-saturated NaHCO₃ solution (confirmed by the XRD data shown in Fig. S9†) before being used in electrolysis. Much lower faradaic efficiencies for HCOO- were obtained over the whole potential range studied (Fig. 5c), suggesting the important role of Cu₂O in CO₂ reduction to HCOO⁻. It has been reported that Pdbased catalysts and the enzyme formate dehydrogenase can catalyze the reduction of CO₂ to HCOO⁻ at close to its equilibrium potential.^[20] Our results show that the Pd/Cu₂O-Cu catalyst can drive this CO₂ reduction reaction under moderate overpotentials. A HCOO⁻ partial current density as high as 4.2 mA cm⁻² was obtained at -0.25 V vs. RHE on the Pd40/Cu2O-Cu modified electrode, compared to that of 1.5 mA cm⁻² on the Pdcu catalyst under the same conditions. On most catalysts, the initial step for CO₂ reduction involves the transfer of an electron to CO₂ to form CO2⁻⁻ which requires a large overpotential.^[21] It has been reported that supported Pd can effectively catalyze the reduction of bicarbonate to formate in the presence of H₂.^[22] Kanan et al. have shown that Pd nanoparticles dispersed on carbon support catalyzed CO₂ reduction to formate with a partial current density as high as 10 mA cm⁻² at -0.2 V vs. RHE with a mass loading of Pd as low as 50 µg cm^{-2 [20b]} Such high activity of Pd/C was attributed to the electrohydrogenation of CO₂ to formate by the electrochemically generated PdH on the catalyst surface. In this work, the formation of PdH on the catalysts surface is confirmed by the XPS spectra taken after electrolysis at -0.25 V (Fig. S10+). In addition to the peaks at the binding energies of 335.4 and 337.5 eV corresponding to Pd⁰ 3d_{5/2} and Pd²⁺ 3d_{5/2}, respectively, the peak at 335.9 eV is attributed to PdH. The electrokinetic measurements support a rate law given by Eq. 2 where electrohydrogenation of CO₂ is the rate-limiting step. ^[20c] i=k [CO₂] exp(-*a*EF/RT) (1)

where *k* is the rate constant and *a* is the transfer coefficient and *E* is the applied potential, *R* is the gas constant and *T* is the absolute temperature. A Tafel slope of 118 mV dec⁻¹ is expected if α = 0.5. In this study, a Tafel plot was constructed in the potential range from -0.17 to -0.25 V vs. RHE, and the Tafel slope value of 135 mV dec⁻¹ was obtained (Fig. 5d). This value is close to the value of 118 mV dec⁻¹. Therefore, in the presence of Pd, CO₂ is proposed to be converted to HCOO⁻ by PdH which was generated *in situ* electrochemically. A schematic representation of the mechanism for CO₂ reduction on Pd₄₀/Cu₂O-Cu is shown in Scheme II. For the generation of CH₄, the initial formation of *CO and the following hydrogenation to *H₃CO (methoxy) are proposed, followed by the oxophilicity of the Pd₄₀/Cu₂O-Cu surface which can break the C-O bond, and the final formation of CH₄ by the hydrogenation process.^[21b, 23]

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Fig. 5 (a) XRD powder patterns of Pd₄₀/Cu₂O-Cu before and after electrolysis in CO₂ saturated 0.5 M NaHCO₃; (b) Cu 2p XPS spectra of Pd₄₀/Cu₂O-Cu after electrolysis at -0.75 V for 10 C; (c) Faradaic efficiency for HCOO⁻ (red bars) and H₂ (black bars) production at Pd/Cu as a function of applied potential. (d) Partial current density of HCOO⁻ vs. applied potential on Pd₄₀/Cu₂O-Cu. The Tafel slope is 135 mV dec⁻¹.



Fig. 6 TEM (a) and HR-TEM (b-c) images of Pd_{40}/Cu_2O -Cu after potentiostatic electrolysis at -0.75 V for a total charge of 10 C



Scheme II. Electrohydrogenation mechanism for CO_2 reduction to form formate on Pd/Cu₂O-Cu.

The potentiostatic *i-t* response associated with bulk electrolysis was used to evaluate the stability of the electrocatalyst. A series of *i-t* curves (Fig. 7a) obtained at applied potentials over the range of -0.15 V to -0.75 V vs. RHE show that the Pd_{40}/Cu_2O -Cu catalyst is stable on the corresponding time scale. This high stability is probably due to the fact that the work function of Pd (~5.12 eV) is higher than that of Cu₂O (~4.3 eV), facilitating the electron transfer from Cu₂O to Pd to equilibrate the electron Fermi

distribution at their interface and hence efficiently stabilizing Cu⁺ at negative applied potentials as suggested by the XPS data (Fig. S4†). At an applied potential of -0.25 V, the amounts of formate generated were measured after consuming 10 C, 20 C, 30 C and 40 C of charges (Fig. 7b). The FEs of HCOO⁻ remain essentially unchanged from 10 C to 40 C (92% at 10 C vs 89% at 40 C). XRD results (Fig. S11†) suggest that Cu₂O is present even though its content significantly decreased in comparison with that found in the pristine Pd₄₀/Cu₂O-Cu catalyst. This result agrees with those obtained by Sargent and coworkers which show that Cu⁺ is present at an applied potential as negative as -1.2 V vs. RHE for over 1 h and plays an important role in the catalytic CO₂ reduction.^[24] Controlled potential electrolysis was also undertaken in a N₂ atmosphere at -0.15, -0.45 and -0.75 V vs. RHE (Fig. S12⁺). H₂ was the main product with a faradaic efficiency of at least 90% under all conditions.



Fig. 7 (a) Chronoamperometric *i-t* data obtained for a Pd₄₀/Cu₂O-Cu modified electrode for reduction of CO₂ in a CO₂-saturated 0.5 M NaHCO₃ solution under stirring at applied potentials over the range of -0.15 V to -0.75 V vs. RHE; (b) $j_{\text{otal-time relationship}}$ (black trace) and FE of HCOO⁻ (blue triangles) obtained for the CO₂ reduction in a CO₂-saturated 0.5 M NaHCO₃ solution under an applied potential of -0.25 V vs. RHE.

Conclusions

A synergistic effect between the Cu₂O-Cu nanostructure and the introduced Pd atoms in electrocatalytic reduction of CO₂ has been recognized for the first time. We found that the modification of Cu₂O-Cu nanoparticles with Pd facilitates the formation of C₁ products at low overpotentials. The Pd/Cu₂O-Cu catalyst has been characterized in considerable detail and achieves remarkable catalytic activity and excellent stability for the reduction of CO₂ to produce C₁ species. In particular, the highest faradaic efficiencies of 92% for HCOO⁻, and 30% for CH₄ were obtained at -0.25 V and -0.65 V vs. RHE respectively. A simple one-pot synthesis provides a straightforward strategy towards the generation of this new electrocatalyst.

Experimental Section

Materials

NaHCO₃ (ACS grade), acetone (absolute GR, 99.7%), dimethylsulfoxide (DMSO), and Nafion (5 wt. %) were purchased from Merck; anhydrous copper chloride (CuCl₂), disodium tetrachloropalladate (Na₂PdCl₄, 98%), and sodium borohydride (NaBH₄) were from Sigma–Aldrich. All chemicals

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were used without further purification. Water from a Milli Q water purification system (18.2 M Ω cm) was used for the preparation of all aqueous solutions.

Synthesis of the Pd/Cu₂O-Cu catalyst

Prior to catalyst synthesis, all solvents used were purged with N_2 for 30 min to remove oxygen. The synthesis process is schematically illustrated in Scheme I. In detail, 15.73 mg of anhydrous copper chloride (CuCl₂) was dissolved in 25 mL of deionized water under magnetic stirring. Next. 30 mL of freshly prepared aqueous NaBH₄ (10 mg) solution was added dropwise until the mixture turned dark purple under vigorous stirring to form Cu2O-Cu nanoparticles. The mixture was stirred overnight to make sure all residual NaBH₄ is decomposed. Next, 1.5 mL of Na₂PdCl₄ (17.65 mg) aqueous solution was added to the mixture, and the Pd/Cu₂O-Cu catalyst was obtained by galvanic replacement which involved the reduction of PdCl42- to Pd metal and the oxidation of Cu. The entire synthesis was performed over one day with continuous stirring at room temperature under a N₂ atmosphere to prevent the oxidation of Cu by O₂ in air. Finally, the black product was filtered, washed and stored in acetone. For comparison, Pd nanoparticles were also synthesized using galvanic replacement reaction by adding excess amount of Pd2+ precursor to oxidize Cu to Cu2+, and the mixture was stirred overnight. The as-obtained Pd nanoparticles are denoted as Pd_{Cu} since it contains small amount of Cu based on XPS analysis (vide infra).

Characterization of the catalysts and products of electrochemical CO_2 reduction.

Transmission electron microscopic (TEM) and High-angle annular darkfield scanning transmission electron microscopic (HAADF-STEM) images were obtained with a FEI Tecnai G2 T20 TWIN TEM Instrument. X-ray powder diffraction (XRD) data were collected with a Bruker D2 PHASER powder diffractometer (Cu Kα radiation, $\lambda = 0.15406$ nm). The relative intensity ratio (RIR) method (the calculation details are presented in the Supporting Information) was used to estimate the mass fraction of Cu and Cu₂O in the catalyst when analyzing the XRD data. The compositions of the nanomaterials were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (PerkinElmer Optima 4300 DV). The Xray photoelectron spectroscopic (XPS) spectra obtained with a PerkinElmer PHI-5702 instrument were calibrated by the position of the C 1s peak.

Gas chromatography (GC) was performed with an Agilent 7820A gas chromatography system. For H₂ and CO measurements, a thermal conductivity detector (TCD) and a HP-PLOT MoleSieve column were used; while for CH₄ detection, a flame ionization detector (FID) is used together with a HP-5 column. Helium (99.99%) was used as the carrier gas for CO analysis, while nitrogen (99.99%) was used for H₂ and CH₄ analysis. The retention times were compared with authentic compounds. The liquid products were analyzed by ¹H NMR with the water suppression mode on a Bruker DRX400 spectrometer at 400.2 MHz, with added DMSO as an internal standard.

Electrochemical CO₂ reduction experiments

All electrochemical experiments were conducted using a CHI 760E potentiostat (CH Instruments, Austin, Texas, USA) at room temperature $(25 \pm 2 \text{ °C})$. Linear sweep voltammetric (LSV) measurements were carried out in an aqueous NaHCO₃ solution (0.5 M) saturated with N₂ or CO₂ by bubbling with the relevant gas for at least 10 min in a conventional three–electrode cell. A platinum wire counter, an Ag/AgCl (3 M NaCl) reference and a catalyst modified glassy carbon (GCE, 3 mm diameter, CH

Instruments) working electrodes were employed. The Ag/AgCl reference was calibrated against the RHE reference scale following a procedure reported in the literature,^[25] and the formula given in Eq. 2 was derived (see the ESI† for details). All potentials reported herein are with respect to the RHE scale unless otherwise noted.

$$E(vs. RHE) = E(vs. Ag/AgCI) + 0.205 V + 0.059 V \times pH$$
 (2)

To prepare the catalyst modified GC working electrode, 5 mg of the catalyst was dispersed in a mixture of 2.5 mL deionized water, 1.25 mL 0.5 % Nafion solution and 1.25 mL ethanol (v:v:v = 2:1:1) by sonication for 30 min. 5 μ L of this dispersion was then drop cast onto a polished GCE and dried under an infrared lamp.

Bulk electrolysis was operated in an airtight H-shape electrolysis cell with two compartments separated by a glass frit at room temperature and pressure. A platinum (Pt) gauze counter electrode, a modified glassy carbon plate (1 cm×1 cm, loaded with 50 μ L catalyst dispersion) working electrode were utilized along with the same reference electrode used for voltammetric measurements. Before electrolysis, the solution was bubbled with CO₂ gas for at least 30 min to obtain a CO₂-saturated electrolyte solution, and then quickly sealed tightly. The solutions in both compartments were stirred during electrolysis.

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Keywords: CO₂ electroreduction • ternary nanocatalyst • palladium • copper • formate • methane

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Entry for the Table of Contents

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Ternary Pd/Cu₂O-Cu efficiently catalyzes electroreduction of CO₂ to formate and methane in bicarbonate media via an electrohydrogenation pathway.



Jing Li,[‡] Si-Xuan Guo,[‡] Feng Li, Fengwang Li, Xiaolong Zhang, Jiantai Ma,^{*} Douglas R. MacFarlane, Alan M. Bond and Jie Zhang^{*}

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