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Graphical abstract



In our work, we systematically and carefully synthesized a series of metal-free electrocatalysts, i.e., pyridoxine functionalized graphene oxide (GO-VB₆), which present high catalytic active for electroreduction of CO_2 to ethanol. Besides, other four pyridine derivatives (4-hydroxypyridine, 4-aminopyridine, 8-hydroxyquionline, and 5-amino-1,10-phenanthroline) functionalized GO were also successfully synthesized and exhibit various catalytic abilities for CO_2 reduction.

Electrochemical reduction of CO₂ at metal-free N-functionalized graphene oxide electrodes

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Abstract: Exploring metal-free catalysts for electroreduction of CO_2 into value-added fuels has been a crucial challenge in nowadays society. Herein we report some metal-free electrocatalysts for electrocatalytic reduction of CO_2 to liquid products, such as ethanol and acetone. We develop functionalized graphene oxide (GO) surfaces with five pyridine derivatives: pyridoxine, 4-hydroxypyridine, 4-aminopyridine, 8-hydroxyquionline, and 5-amino-1,10-phenanthroline. Remarkably, pyridoxine modified on GO sheets with the pyridinic N content of 2.32% shows the optimum catalytic ability for electrochemical reduction of CO_2 , and the overall faradaic efficiency reaches up to 45.8%. Besides, other four pyridine derivatives functionalized GO exhibit various abilities for CO_2 reduction to ethanol and acetone. The experimental results show that N-doping can alter the electronic properties of GO for enhancing the catalytic active for CO_2 electroreduction, which is closely associated with the content of modified pyridinic N and the special structure of modified pyridine derivatives. Our work may provide inventive thought to design metal-free electrocatalysts for CO_2 reduction to useful chemical fuels.

Keywords: Electrochemical reduction of CO₂, metal-free, N-functionalized graphene oxide, pyridoxine, ethanol

1. Introduction

Atmospheric CO₂ accumulated, resulting in escalating environmental problems, has been transformed into useful chemical fuels through viable methods relying on global efforts.[1,2] Electrochemical reduction of CO₂ with high efficiency and selectivity, could potentially address the environment issues and energy crisis by utilizing renewable source, such as solar, wind and tide energy.[3,4] Over the past few decades, many researchers have been made numerous trials to explore catalysts with remarkable efficiency for CO₂ reduction reaction (CO₂RR), such as metals[5-7], metal alloys[8,9] and metal complexes[10-12]. However, these metal-containing catalysts, due to their characteristics including low abundance and high cost, have been restricted their large-scale practical application.

Compared to metal-based catalysts, metal-free electrocatalysts, as renewable and cost-effective materials, achieving comparable catalytic abilities to metal-containing catalysts, have been attracted increasing concern for CO₂RR.[13-20] Recently, heteroatom-doped carbon-based catalysts, owing to low-cost, superior stability and high catalytic ability, have been expected to replace metal-containing catalysts for CO₂RR.[17-20] For instance, Meyer and co-workers[17] demonstrated that N-doped carbon nanotubes (CNTs) as functionalized catalysts for CO₂RR in KHCO₃ aqueous solution achieved a maximum faradaic efficiency (FE) for formate of 87%. Ajayan et al.[18] revealed that CNTs, doped with N to form resident electron-rich defects, can act as highly efficient, selective and stable catalysts for the conversion of CO₂ to CO. Sharma et al.[19] found that B-doped graphene exhibits high electrocatalytic activity for the reduction of CO₂ to HCOOH at a low overpotential. Han et al.[20] showed that N-doped graphene-like materials (NGMs) are very efficient for CO₂RR to CH₄ with FE as high as 93.5% when using ionic liquids as the electrolytes.

Graphene, as unique two-dimensional carbon materials, play a very important role in the performance of the electrocatalysts, as they actually enhance the conductivity of catalysts and also provide a construct for electron capture and transport.[21-23] Nevertheless, in the process of graphene functionalization, the fact of serious π - π stacking interactions between graphene nanosheets could result in serious restacking and accumulation of graphene nanosheets, and ultimately increase the difficulty to functionalize graphene. [24]

Although graphene oxide (GO), because of variable oxygen contents, displays weak conductivity, it can tune electrical conductivity, which makes it apply to various fields of electrochemistry. [25,26] Moreover, GO, containing a good deal of hydroxyl and carboxyl, is considerably achieved easily to fabricate various structures, such as N-doped materials. Pyridoxine (Vitamin B_6 , VB₆), as an important biologically active compound, is a vital cofactor involving the metabolism of amino acids and lipids, also the synthesis of neurotransmitters, histamine and hemoglobin, and other key biologic processes. [27] Due to its low-cost, non-toxic and containing a pyridine ring, VB₆ could be modified on all most carbon material surfaces including CNT, graphene and carbon fiber. The high amounts of hydroxyl groups of VB₆ serve as a bridge linked to the carboxyl of GO in the process of catalyst functionalization. None reports have shown such an intriguing structure applied for CO₂RR.

Herein, we synthesized a series of metal-free N-functionalized GO electrodes for CO_2RR to produce liquid products, including ethanol and acetone. It was found that VB₆ functionalized GO (GO-VB₆) materials showed high catalytic active for CO₂RR and the efficiency observably relied on the pyridinic N content in the GO-VB₆. GO-VB₆ with a pyridinic N content of around 2.32% has the best catalytic performance among all considered VB₆ modified GO. For the modification part, other four pyridine derivatives, such as 4-hydroxypyridine (X-1), 4-aminopyridine (X-2), 8-hydroxyquionline (X-3) and 5-amino-1,10-phenanthroline (X-4) were modified on the GO sheets surface using the same modification procedure, displaying different catalytic properties for CO₂RR, which is attributed to the special structure of grafted pyridine derivatives.

2. Experiment section

2.1. Materials

Pyridoxine (purity> 98%) and 5-amino-1,10-phenanthroline (purity> 97%) were

obtained from Macklin. 4-Pyridinal (purity> 98%), 4-aminopyridine (purity> 98%), 8-hydroxyquionlinen (purity> 99.5%), sulfoxide chloride (SOCl₂, purity> 99%), N,N-dimethylformamide (DMF, purity> 99.5%), glacial acetic acid (purity> 99.5%) and ethyl acetate (purity> 99.5%) were purchased from Sinopharm Chemical Reagent Co.. The commercial graphene oxide was obtained from Beijing HWRK Chem Co., LTD. Nafion® 117 solution (5%) and Nafion 117 membrane were obtained from Dupont. Carbon paper (CP, HCP010) was purchased from Shanghai Hesen Electrical Co.. All chemicals were used as received without further purification.

2.2. Materials characterization

Crystal-phase X-ray diffraction (XRD) patterns were recorded using an Ultima IV X-ray powder diffractometer equipped with Cu K α radiation (k = 1.5406 Å). Microstructure was analyzed using Hitachi S-4800 field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray fluorescence spectrometer. Transmission Electron Microscope (TEM) patterns were recorded by TECNAI G²F30 transmission electron microscope. Fourier transformed infrared spectroscopy (FT-IR) was recorded by a Bruker IFS 66 V/S. The X-ray photoelectron spectroscopy (XPS) analysis was performed on the Thermo Scientific ESCA Lab 250Xi using 200 W monochromatic Al Kα radiation. The 500 µm X-ray spot was used. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing. The Raman spectra were obtained at room temperature in flame sealed capillary on a FT Bruker RFS 106/S spectrometer, equipped with a 532 nm laser, in the region from 3500 to 100 cm^{-1} with a resolution of 2 cm^{-1} . All the electrochemical experiments were performed using a CHI 660C electrochemical station (Shanghai Chenhua Instrument Co. Ltd).

2.3. Materials synthesis

2.3.1. Preparation of intermediate material: carbonyl chloride groups functionalized GO (GO-COCl)

GO (15 mg) was placed in 15 mL of DMF solution, followed by the addition of SOCl₂

(3 mL), and then refluxed at 65°C for 24 h. After filtration, the obtained solid was washed with anhydrous DMF, and dried in a vacuum oven at 40°C overnight, to give GO-COCl intermediated material.

2.3.2. Preparation of pyridine derivatives modified GO

The similar procedures were reported by other authors. [28] Different concentrations of VB₆ (2.96, 5.92, 11.8, 19.7, 29.6 and 39.4 mM) modification on the GO sheets applied the same synthetic method, which were denoted as GO-VB₆-1, GO-VB₆-2, GO-VB₆-3, GO-VB₆-4, GO-VB₆-5 and GO-VB₆-6, respectively. For simplicity, taking GO-VB₆-4 as an example, the preparation steps are as follows. GO-COCl (15 mg) was added to DMF solution of VB₆ (19.7 mM, 15 mL) in a round-bottomed flask, and 2-3 drops of glacial acetic acid were added. Then, the mixture was refluxed at 65°C for 24 h. After cooling to room temperature, the resulting suspension was filtered and the product was obtained by washing with DMF and ethyl acetate, and dried in a vacuum oven at 40°C overnight. Similarly, other four pyridine derivatives with the same concentration of 19.7 mM functionalized GO sheets (GO-X) adopted the same modification procedure.

2.4. Electrochemical study

To prepare the GO-VB₆ and GO-X electrodes, 5 mg of the above prepared GO-VB₆ or GO-X was suspended in 40 μ L of deionized water with 20 μ L of Nafion® 117 dispersion (5 wt%) to form a homogeneous ink assisted by ultrasound. Then, the ink was spread onto the CP surface by a micropipette and then dried under room temperature. The loading of different GO-VB₆ and GO-X catalysts was 2.5 mg/cm².

The electrolysis experiments were conducted at 25°C in a gas diffusion electrode cell, which consisted of a cathode (GO-VB₆/CP or GO-X/CP electrode), an anode (Pt sheet electrode), and a saturated calomel electrode (SCE) as the reference electrode. In the experiments, the cathodic and anodic compartments were separated through a Nafion 117 proton exchange membrane. 0.1 M KHCO₃ aqueous solution was used as electrolyte. Under the continuous stirring, CO₂ was bubbled through the catholyte for 30 min before electrolysis. Then, potentiostatic electrolysis of CO₂ was carried out with CO₂ bubbling.

Linear sweep voltammetry (LSV) measurements were carried out in a single compartment cell with a three-electrode configuration, which consists of working electrode (GO-VB₆ or GO-X catalysts painted on the glassy carbon electrode), a Pt sheet electrode, and an SCE reference electrode. The electrolyte was bubbled with N_2 or CO₂ for at least 30 min to form N_2 - or CO₂-saturated solution. The LSV measurements in gas-saturated electrolyte were conducted in 0.1 M KHCO₃ solution at a scan rate of 50 mV/s. All potentials were measured against the SCE electrode and converted to the reversible hydrogen electrode (RHE) reference scale by following the equation:

 $E (vs. RHE) = E (vs. SCE) + 0.059V \times pH + 0.241V.$ (1)

2.5. Product analysis

Liquid phase products were analyzed by ¹H-NMR spectra recorded on an Ascend 400 (400 MHz, Bruker, Germany) spectrometer in D_2O with Me₄Si as an internal standard.

To confirm that the evolved products originate from CO_2 , isotopic labeling experiments were performed under the same process mentioned above, except that isotopic ¹³CO₂ (¹³C 99%, Sigma-Aldrich) replaced ¹²CO₂ as the carbon source, and the liquid products collected were analyzed by gas chromatography-mass spectrometry (GC-MS, Agilent TRACE 6890/5973N).

3. Results and discussion

3.1 Characterization of catalysts

The schematic illustration for fabrication of GO-VB₆ catalysts was shown in **Scheme S1**. XPS spectrum of GO-VB₆-4 in **Fig. S1C** shows the presence of C1s, O1s and N1s, demonstrating that the VB₆ was successfully modified on the surface of GO sheets, although N1s peak displays much less noticeable. Notably, an obvious peak at ~399.1 eV in the high-resolution of N1s spectrum for GO-VB₆-4 catalyst was observed from **Fig. 1A**, corresponding to the pyridinic N, while the bare GO sheets

and GO-COCl intermediate material reveal no peak of N species (Fig. S1A, B). It can be clearly seen from Fig. S2A that the C1s scan of bare GO sheets represents four peaks at ~284.8, ~286.7, ~287.8 and ~289.0 eV, ascribed to the C-C or C=C, C-O-C, C=O and COOH, respectively. Relatively, Fig. S2B shows an obvious peak at ~285.2 eV in the high-resolution C1s spectrum of GO-VB₆-4 catalyst, indicating the existence of C=N, which suggests VB₆ successfully modification on the GO sheets. Besides, FT-IR also confirms VB₆ was successfully grafted on the GO surface, which exhibits a small and sharp peak at 1565 cm⁻¹, attributing to the stretching vibration of C=N (Fig. 1B). Such a peak still exists for the GO-VB₆-4 catalyst after repeated washing and steeping by ethyl acetate for 24 h, which reveals that the grafted group is greatly stable in the harsh testing (Fig. S3). Raman spectra of GO, GO-COCl and GO-VB₆-4 depicted in Fig. 1C also verify the grafting of VB₆ on the GO sheets, which shows that VB₆ functionalization of the GO sheets surface results in a slight increase in the intensity ratio (I_D/I_G) of the D band (structural defects in the vicinity of 1350 cm⁻¹) over the G band (in-plane vibrations of carbon sp² bonds in the vicinity of 1580 cm⁻¹), [29] consistent with an increase of structural distortion relative to the GO frameworks. As we know, the structural distortion can generate more defects or edges introduced into GO frameworks, which can serve as catalytic sites. [30, 31] Therefore, $GO-VB_6$ sheets with larger I_D/I_G will express higher electrocatalytic activity. Furthermore, Fig. 1D gives the XRD patterns of GO, GO-COCl and GO-VB₆-4. The diffraction peak of C for the present GO-VB₆ catalyst displays more positive shift of the diffraction position, compared with the common GO and intermediate material GO-COCl, ascribed to the doping effect of electron-rich N, [32] which reconfirmed VB₆ successful modification on the GO sheets.

To obtain more information about the surface morphologies of the prepared samples, SEM and TEM were used. As seen from **Fig. 2A**, GO displays a typical wrinkled and crumpled surface. **Fig. 2B** shows surface morphology of GO after treatment by $SOCl_2$, which reveals a flexibly aggregated, crumpled nanosheets structure. Compared with GO, GO-VB₆, after grafting various concentrations of VB₆ (**Figure 2C** and **Figure S4**), are sheets like and transparent, as reconfirmed by the

TEM of GO-VB₆-4 (**Figure 2D**), which may create a large number of active sites for CO_2 conversion.

3.2 Electrochemical performance of GO-VB₆-4 catalyst

To investigate the possibility of employing $GO-VB_6-4$ catalyst for CO_2RR , LSVs were firstly measured in both N₂-saturated and CO₂-saturated 0.1 M KHCO₃ aqueous solutions (pH values 8.67 and 6.80, respectively) at a scan rate of 50 mV/s in the same scanning region using an SCE reference electrode (Fig. 3A). In order to avoid the effect of the solution of pH, we have normalized all potentials to the RHE reference scale for comparison purposes by following the equation (1). As shown in Fig. 3A, under N₂ atmosphere, a sharply increased cathodic current on GO-VB₆-4 was likely resulted from the hydrogen evolution reaction (HER), [33,34] while the higher current in CO₂-saturated solution could be defined as the reduction of pyridinic N combined with H^+ and then reaction with CO_2 through multiple electrons and protons transfer processes. [35-37] To evaluate potential catalytic roles of pyridinic N heterocycles in CO₂RR, LSV measurement was also carried out in a 0.1 M KCl solution, which presents the similar catalytic activity of GO-VB₆-4 for CO₂RR in KHCO₃ solution (Fig. S5). Interestingly, an obvious reduction peak was observed in CO_2 atmosphere, whereas lower reduction peak was displayed in Fig. S5 under N₂-saturated 0.1 M KCl aqueous solution with HCl (pH values 5.14, which is the same pH value as the CO₂-saturated 0.1 M KCl aqueous solution), demonstrating that an enhanced current was observed when CO_2 and pyridinic N are included together in the aqueous solution.

To further explore the influence of electrolytic potentials, potentiostatic electrolysis of CO_2 on GO-VB₆-4 are represented in **Fig. 3B**. The liquid products are ethanol and acetone, detected by ¹H NMR (**Fig. S6**). As shown in **Fig. 3B**, the FEs of ethanol and acetone ascend with the negative shift of applied potential, reaching the maximum value for ethanol and acetone (36.4% and 8.9%, respectively) at -0.40 V vs. RHE and subsequently decrease at more negative potentials due to an increase in competing with HER. [33,34] Thus, -0.40 V vs. RHE as the best reaction potential, was applied in the subsequent tests. The absolute value of current density (J),

symbolizing the production rate, is further studied. In contrast to total J_{Total}, partial J of ethanol (J_{Ethanol}) and acetone (J_{Acetone}) are illustrated in Fig. 3B. The J_{Total} increases with the negative shift of applied potential, however, J_{Ethanol} shows a volcanic shape depending on the applied potentials, while that of acetone increases slowly. In order to determine that evolved products originate from CO₂, multiple control tests were carried out. When the electrolyte was purged with N2, no liquid products were detected at the same potential range (Figure S7). Moreover, a ¹³C-labeling isotopic experiment was carried out, in which 13 CO₂ replaced 12 CO₂ as the carbon source. Fig. S8 and S9 show the GC-MS spectrum after electrocatalytic conversion of ${}^{12}CO_2$ and 13 CO₂ respectively. The GC-MS full spectra of **Fig. S8** and **S9** display the existence of H_2O solvent, ethanol and acetone. When ${}^{13}CO_2$ was used as the reactant, the signals of ${}^{13}CH_3{}^{13}CH_2OH (m/z = 47, 48) \text{ and } {}^{13}CH_3{}^{13}CO{}^{13}CH_3 (m/z = 61) \text{ were detected, which}$ were significantly different from the signals for ${}^{12}CH_3{}^{12}CH_2OH$ (m/z = 45, 46) and ${}^{12}CH_3{}^{12}CO^{12}CH_3$ (m/z = 58) when ${}^{12}CO_2$ was used. This is solid evidence to prove that the evolved product comes exclusively from CO₂ and not from any other carbon source.

To better illustrate the electrochemical reduction of CO_2 on metal-free carbon material, a graphite sheet electrode was replaced the Pt sheet as the counter electrode. The electrolysis was carried out on GO-VB₆-4 at a variety of constant potentials from -0.2 to -0.6 V vs. RHE in CO₂-saturated aqueous 0.1 M KHCO₃ solution. These results were presented in **Figure S10**, which exhibits exactly the same electrocatalytic ability obtained using the Pt counter electrode. This phenomenon suggests that the anodic was just inducing water oxide whether using a Pt sheet or a graphite sheet as the counter electrode.

3.3 Influence of the VB₆ amounts for CO₂RR on various GO-VB₆ catalysts

To deeply explore the influence of modified amounts of VB_6 on the GO sheets surface, we have selected different concentrations of VB_6 functionalized on the GO sheets surface using the same synthetic method. The total N contents (N_T) were exhibited in **Table 1**, which were analyzed by elemental analysis, and the total input concentrations of VB_6 were also provided in this table. The N contents of the GO-VB₆

are closely connected with the concentrations of VB_6 . Generally, the N contents increase with increasing the concentrations of VB_6 to 19.7 mM, however, following to increase the concentrations of VB_6 , the N contents acquire an obvious plateau, which is around 2.32%. Hypothetically, the N contents can deeply affect the catalytic active

To verify the above guess, Fig. 4A reveals a dramatic difference in the amounts of VB_6 contents in the overall CO_2 electrocatalytic reduction activity of $GO-VB_6$. For GO catalyst, as shown in Fig. 4A and S11, much higher reduction current was observed in CO₂-saturated solution than that in N₂-saturated solution, but none reduction peak appeared. In sharp contrast, VB₆ functionalized GO catalysts exhibit obvious catalytic abilities for CO_2RR . Fig. 4A suggests that increasing the VB₆ contents in the GO-VB₆ catalysts facilitates CO₂RR, leading to the enhanced activity of CO2 reduction. The activities of GO-VB6-1 and GO-VB6-2 got worse performance than all other catalysts in term of the reduction peak potentials and currents, which resulted from the low contents of VB₆ modified. Noteworthily, GO-VB₆-4, GO-VB₆-5 and GO-VB₆-6 showed similar performances, due to the almost same content of N doping. The reduction peak potentials of GO-VB₆-3, GO-VB₆-4, GO-VB₆-5 and GO-VB₆-6 displayed almost the same value, about -0.40 V vs. RHE, however, the peak currents of GO-VB₆-4, GO-VB₆-5 and GO-VB₆-6 revealed the nearly identical trend, which were higher than the one of $GO-VB_6$ -3. The results clearly indicate that an optimum content of VB_6 in the GO-VB₆ catalysts is required to achieve the maximum activity for CO₂RR.

The electrocatalytic reduction of CO_2 over different GO-VB₆ sheets electrodes employed a typical potential of -0.40 V vs. RHE were examined (**Fig. 4B**). As expected, the raw material GO exhibited very poor catalytic property for CO_2RR because of lack of the active center – pyridinic N. By contrast, after grafting VB₆ on the GO sheets surface, all of the prepared GO-VB₆ samples showed superior performance improvements for CO_2RR . From **Fig. 4B**, GO-VB₆-4, GO-VB₆-5 and GO-VB₆-6, due to the similar contents of pyridinic N, showed almost no different catalytic activities for CO_2RR , as consisted with the results of LSV. The increased FEs of ethanol and acetone on the GO-VB₆ sheets indicate that the enhanced catalytic activity is affected by an appropriate amount of VB_6 modified on the GO surface. The catalytic activities for CO_2RR on $GO-VB_6-4$, $GO-VB_6-3$, $GO-VB_6-2$ and $GO-VB_6-1$ gradually decline, ascribed to gradually decrement of pyridinic N contents. The results indicate that low modification amounts of VB_6 lead to not only the drop of N% in GO-VB₆, but also clearly weaken catalytic abilities in the CO_2RR .

On account of the above results, we could assume that the pyridinic N species is the main active species for electrocatalytic of CO_2 to ethanol. The effect of the active pyridinic N species on the catalytic active was exhibited in **Fig. S12**, which clearly shows the relationship of the active N contents (calculated from **Table 1**) and the products FEs. The FE_{ethanol} significantly rises from 7.5% to 36.4%, as increasing the contents of active N species from 0.521% to 2.314%, whereas the FE_{acetone} slightly increases from 2.7% to 8.9%. Interestingly, the FE_{Total}, FE_{Ethanol} and FE_{Acetone} are all positively related to the contents of pyridinic N for various GO-VB₆ catalysts, which suggests that the active pyridinic N species content plays a vital role for the high catalytic ability of CO₂RR to ethanol and acetone.

3.4 Material and electrochemical characterization of various pyridine derivatives modified GO catalysts

For sake of investigate whether other pyridine derivatives modified GO also work on the CO₂RR, a variety of pyridine derivatives including 4-pyridinal, 4-aminopyridine, 8-hydroxyquionline and 5-amino-1,10-phenanthroline (the structures of these pyridine derivatives are recorded in **Table S1**) with the same input concentration of 19.7 Mm to modify GO, were explored. XPS characterized (Fig. S13) and element analysis (Table S2) showed that these pyridine derivatives were successfully grafted on the GO sheets surface. In addition, Raman spectra of GO-X-1, GO-X-2, GO-X-3 and GO-X-4 were investigated, as seen from Fig. S14. The intensities of I_D/I_G for GO-X distinctly exceed the one of GO ($I_D/I_G=0.88$), demonstrated once again that the N heteroatoms were modified on the GO surface. We also studied the electrochemical performance using the different GO-X electrodes in 0.1 M KHCO₃ solution and the results were provided in Fig. S15. GO-X catalysts revealed different electrochemical activities towards CO₂RR in 0.1 M KHCO₃

solution, yet from **Fig. 5**, the reduction peak potential on GO-VB₆-4 was about -0.40 V vs. RHE, which was more positive than those on all GO-X catalysts. Among these materials, the absolute value of current on GO-VB₆-4 catalyst (0.745 mA at -0.40 V vs. RHE) was higher than those on GO-X-1 (0.350 mA), GO-X-2 (0.349 mA), GO-X-3 (0.312 mA) and GO-X-4 (0.104 mA). Potentiostatic electrolysis of CO₂ were then performed using different GO-X as electrodes and KHCO₃ solution as the electrolyte at the applied potential of -0.40 V vs. RHE. The liquid products (ethanol and acetone) were detected by ¹H NMR. The FEs of the products were calculated and summarized in **Table 2**, which are in consistent with the results of LSV for different GO-X catalysts. GO-X-1 and GO-X-2 owing to the similar structures grafted on GO, get the approximated pyridinic N% of 2.764% and 2.540% and lower total FEs of 17.9% and 16.4% than the one of GO-VB₆-4, respectively. Other pyridines modified GO with large branches like X-3 and X-4 also demonstrate reduced total FEs of 14.3% and 3.1%, respectively.

VB₆, as a low-cost, wide distribution and environment friendly pyridine derivative, was grafted on the GO sheets surface, providing a relatively high efficiency towards CO₂RR to ethanol. This molecule, containing some strong electron donating groups, such as -OH and -CH₃, can lead to the increase for electronegativity of the pyridinic N, and then easily absorb or react with CO₂. Although other pyridine derivatives, such as X-1 and X-2, also have one strong electron-donating group (e.g. -OH or -NH₂), these groups disappeared in the process of material synthesis and translated into the groups of -COO- or -CONH-, as reconfirmed by the XPS spectra of GO-X-1 and GO-X-2 (Fig. S13a, b). Similarly, the GO-X-3 and GO-X-4 catalysts are observed the above finding. Unfortunately, both X-3 and X-4 pyridine derivatives have an extra benzene ring that linked to the pyridinic N. The benzene rings in the X-3 and X-4 molecular have ability to disperse the electrons, leading to further attenuation of electronegativity for pyridinic N. Such complex structures for GO-X-3 and GO-X-4 catalysts can weaken the abilities of CO₂ adsorption and then reduce CO₂ reduction abilities. In summary, the FEs are closely related to the pyridinic N contents and the structure of grafted pyridine derivatives for different GO-VB₆ and GO-X catalysts.

A detailed comparison on heteroatom doped carbon materials (especially N-doped carbons) that have been recently studied as catalysts for CO_2RR was summarized and compared in **Table S3**. Numerous reports have been made to CO_2RR to produce gas and C1 products, such as H₂[15], CO [18], CH₄[20] and HCOOH [17], on metal-free N-doped carbon nanofibers, N-doped CNT, NGM and N-doped carbon nanomaterials. To the best of our knowledge, few reports have been further investigated on CO_2RR to ethanol using metal-free N-functionalized graphene material. [38,39] Our work was the first finding to combine GO and VB₆ forming metal-free carbon materials, which can produce ethanol with reasonable FE.

3.5 Mechanism analysis

According to previous reports based on density functional theory, the key initial step for CO₂RR is the formation of COOH* or CO* intermediates through proton-electron transfer on the electrodes surface, and CO* dimerization forming $*C_2O_2$ intermediate is a rate-determining step for the reduction of CO₂ to ethanol.[39,40] N-doped carbon materials can facilitate the proton-electron transfer in the CO₂RR.[41,42] The active pyridinic N sites uniformly distributed on the surface of GO sheets, due to electron withdrawing effects, are more electronegative than carbon atoms, subsequently inducing the adjacent carbon atoms to be positively polarized. Such a special structure can efficiently supply the electrons for the dimerization of the CO* intermediates to produce ethanol, [43] analogous to previously reported catalysts, such as N-doped graphene quantum dot [38] and N-doped mesoporous carbon [39]. Moreover, the pyridinic N retains a lone pair of electrons, which could bind CO₂, and exhibits low reaction energy for CO* formation [44] that can be stabilized to some extent by the order layer structure with high electron density, hindering the formation of CO as a product [39]. Wu et al [38] have reported that the pyridinic N is believed to be active to induce C-C bond formation, which leads to a higher yield of C2 and C3 products. Therefore, the pyridinic N in N-doped GO materials are indicated as the active sites for electrocatalytic CO₂ reduction to ethanol and acetone in our works, but it is a complex process. Numerous experimental data and theoretical calculations are still needed to investigate deeply

and detailedly in the near future.

4. Conclusion

In summary, pyridine derivatives, such as 4-hydroxypyridine, 4-aminopyridine, 8-hydroxyquionline, 5-amino-1,10-phenanthroline and pyridoxine, were successfully grafted on GO sheets by adopting a simple and effective method, which show remarkable enhanced catalytic abilities to reduce CO₂ into ethanol. The metal-free GO-VB₆ catalysts demonstrated more superior activities for the electrochemical reduction of CO₂ to ethanol than other four pyridine derivatives modification on GO sheets. The catalytic active of GO-VB₆ was deeply affected by the pyridinic N contents in the $GO-VB_6$ catalysts. The experimental data reveal that pyridinic N is the active site for CO₂RR. Besides, the catalytic activities of pyridine derivatives modified GO exhibit distinct performances, which are not only closely related to the pyridinic N contents of the GO-X, but also the structure of grafted the pyridine derivatives. The optimal samples were observed for GO-VB₆ with an N content of around 2.32% on the surface of GO sheets, which produce the maximum FE ethanol of approximately 37%. This work could instruct us to design large amounts of novel materials with high catalytic activity, excellent selectivity and strong stability for CO_2 electrochemical conversion.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <u>https://doi.org/10.1016/j.electacta.2017.XX.XXX</u>.

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Entry	$N_{T} \left(wt\%\right)^{a}$	$C_{VB6} \left(mM \right)^{b}$
GO	0.189	0
GO-VB ₆ -1	0.521	2.96
GO-VB ₆ -2	0.972	5.92
GO-VB ₆ -3	1.562	11.8
GO-VB ₆ -4	2.314	19.7
GO-VB ₆ -5	2.317	29.6
GO-VB ₆ -6	2.321	39.4

Table 1. $N_T\%$ and C_{VB6} of different GO-VB_6 catalysts

 $^{a}N_{T}\%$ represents the total N content.

 $^{b}C_{VB6}$ represents the total input concentration of VB_6.

Table 2. Characteristics of the different GO-X catalysts with the FE for each product at an applied potential of -0.40 V vs. RHE in 0.1 M KHCO₃.

Material	FE (%)	
	Ethanol	Acetone
GO-X-1	14.2	3.7
GO-X-2	13.1	3.3
GO-X-3	11.9	2.4
GO-X-4	2.0	1.1
GO-VB ₆ -4	36.4	8.9



Fig. 1. (A) High-resolution of N1s for GO-VB₆-4; FT-IR spectra (B), Raman spectra (C) and XRD patterns (D) of GO, GO-COCl and GO-VB₆-4.



Fig. 2. SEM images of (A) GO, (B) GO-COCl, (C) GO-VB₆-4; (D) TEM image of GO-VB₆-4.



Fig. 3. (A) LSV patterns of GO-VB₆-4 catalyst on a glassy carbon electrode with saturated CO_2 (red line) and N_2 (black line); (B) Absolute value of J and FEs for CO_2 reduction products on GO-VB₆-4 catalyst at various potentials in 0.1 M KHCO₃ solutions.



Fig. 4. (A) LSV patterns of GO and various GO-VB₆ catalysts on a glassy carbon electrode with saturated CO₂ in 0.1 M KHCO₃ aqueous solution as the electrolyte and at a scan rate of 50 mV/s. (B) FEs of CO₂ reduction on different GO-VB₆ sheets surface at -0.40 V vs. RHE in 0.1 M KHCO₃ aqueous solution.



Fig. 5. LSV patterns of different GO-X catalysts and GO-VB₆-4 catalyst.