1 INTRODUCTION

Electrochemical reduction of CO₂ (CO₂RR) offers a promising route for mitigating the global warming and the increasing demand of various chemicals. In comparison with other reaction routes, like thermochemical reduction and photochemical reduction of CO₂, CO₂RR can proceed under ambient conditions with higher efficiency. This method uses water instead of H₂ gas as a source of reductant, which overcomes the challenge of storage and transportation of H₂. Because of the stable nature of CO₂, the major challenge of CO₂RR is the development of active and selective catalysts. Metal electrodes have been investigated for decades; however, the development of metal electrodes is limited by the high cost of noble metals and low activity of cheap metals. Carbon-based materials have also been explored with promising results. However, due to the difficulty to create uniform defects and vacancies on the carbon-based materials, the catalytic performance is not desired for real applications.

Recently, metal single-atom catalysts (M-SACs) are attracting more attentions because of their unique properties. Low-coordination states of metal atoms, quantum size effect, and strong metal-support interaction, these effects make M-SACs superior catalysts in comparison with nano materials. Various M-SACs have been proved to be active in thermochemical reactions, electrochemical reactions, and photochemical reactions. Pt SACs were used for selective hydrogenation reaction, and Pt, Co, Ni-supported SACs were used for water splitting. Among these catalysts, M-SACs on nitrogen-doped carbon materials exhibited superior activity for CO₂RR. Atomic Ni-doped carbon materials were reported with high activity and high CO selectivity. Specifically, a nickel-doped carbon membrane was reported with superior activity of CO₂RR with industry compatible current density (up to 308.4 mA/cm²). The Ni-supported N-doped graphene (A-Ni-NG) was prepared by high temperature pyrolysis method, and a CO selectivity of 97% was obtained from as-prepared sample at the overpotential of...
0.61 V. \(^{29}\) Ni supported on N-doped carbon nanotube (Ni-SAC-N-CNT) was also prepared by pyrolysis methods and reached a turnover frequency of 11.7 s\(^{-1}\) with high CO selectivity. \(^{30}\) Even though the reported Ni-SACs had high activity, the major challenge remains. In the catalyst preparation process, high temperature treatment (pyrolysis and carbonization) is widely used. \(^{31} - ^{33}\) Due to the high surface energy of isolated metal atoms, the metal atoms tend to aggregate to large particles at high metal loading. \(^{34},^{35}\) Thus, it is desired to develop a preparation method for metal-supported materials and M-SACs without high temperature treatment.

Electrodeposition is a promising process for catalyst synthesis and suitable for large scale application under ambient conditions. \(^{36},^{37}\) For example, Ni was electrodeposited on graphite electrode for the electro-oxidation of methanol in alkaline solution. \(^{37}\) The Ni electrodeposition was performed in acid solution with 1.0 mol/L NiSO\(_4\) at −1.0 V vs Hg/HgSO\(_4\)/1 mol/L \(\text{H}_2\text{SO}_4\) (MMS). The as-prepared sample had high current density of 150 mA/cm\(^2\). However, up to date, no work has been reported to prepare Ni small clusters and Ni-SACs by electrodeposition for CO\(_2\)RR. In this article, Ni clusters supported on multiwall carbon nanotubes (Ni/MWNTs) is synthesized by electrodeposition. The proper synthesis procedure and Ni loadings are investigated to achieve a promising catalytic performance.

2 | EXPERIMENTAL SECTION

2.1 | Chemicals and instruments

Nickel nitrate hexahydrate (Ni(NO\(_3\))\(_2\)-6H\(_2\)O) (Acros Organics), ethanol (Sigma-Aldrich), KOH (Sigma-Aldrich), NaHCO\(_3\) (Fisher chemical), Nafion solution (5 wt.%) (Aldrich Chemical), multiwall nanotube (MWNTs) (Nano Lab), CO\(_2\) cylinder (Air Gas), and N\(_2\) cylinder (Air Gas) are used. The deionized water (DI water) is used in all the experiments. All the chemicals and gases are analytical grade and used without further purification.

Electrochemical tests in this report were carried out using a 3-electrode electrochemical analyzer system (CHI 832c, CHI Instruments). The Pt wire (CHI Instruments) was used as the counter electrode (CE), and Ag/AgCl (Sat’d KCl) (CHI Instruments) was used as the reference electrode (RE). The samples were loaded on a rotation ring-disk electrode (RRDE) with an area of 0.0707 cm\(^2\) (RRDE-3A) as the working electrode.

2.2 | Electrodeposition of Ni on MWNTs

MWNTs were loaded on RRDE using the similar method reported previously. \(^{38}\) In a specific process, MWNTs ink was prepared by mixing 6 mg of MWNTs powder into a solution containing 2500 \(\mu\)L ethanol and 10 \(\mu\)L Nafion. 7 \(\mu\)L of the ink was coated onto the surface of the prepolished Nafion with a diameter of 3 mm. The sample was then dried in air for 30 minutes before electrodeposition. After drying in air, Ni was electrodeposited on MWNTs in a Ni(NO\(_3\))\(_2\) solution with different concentrations (100 \(\mu\)mol/L Ni\(^{2+}\), 50 \(\mu\)mol/L Ni\(^{2+}\), and 25 \(\mu\)mol/L Ni\(^{2+}\)). The linear sweep voltammetry (LSV) was used for electrodeposition and scanned from 0.1 V to −0.4 V with a scanning rate of 10 mV/s. The as-prepared samples are labeled as Ni/MWNTs-x-y; here, x and y represent the Ni concentration and the number of cycles of electrodeposition conducted, respectively. After electrodeposition, the sample was washed in DI water to remove undesired Ni\(^{2+}\) ion. Then, the sample was dried in air for different time.

2.3 | Characterizations

X-ray powder diffraction (XRD) was carried out on Philips PW3040-X-Ray diffractometer with Cu K\(_\alpha\) radiation.

Cyclic voltammetry (CV) was carried out to determine the characteristic properties of the samples in a 0.1 mol/L KOH electrolyte.

2.4 | CO\(_2\)RR

The CO\(_2\)RR performance of the sample was tested in 0.1 mol/L NaHCO\(_3\) solution at room temperature and atmospheric pressure with a rotating rate of 1500 rpm. The solution was saturated by CO\(_2\) for half an hour to remove dissolved air before the test. The LSV was scanned continuously from 0 V to −1.8 V with a scanning rate of 10 mV/s for CO\(_2\)RR. The overall current of CO\(_2\)RR was recorded with an online computer.

3 | RESULTS AND DISCUSSION

To optimize the sample preparation procedure, the effect of drying time after electrodeposition was investigated. The catalytic performance is shown in Figure 1. The sample after 60 minutes drying gives a higher current density in comparison with the samples dried for less time. The curves for Ni/MWNTs-50-1-60 and Ni/MWNTs-50-1-90 overlap due to the similarity of the activity. The plateau at −1.73 V is due to the test limitation of our detector which is 1 mA or −14.1315 mA/cm\(^2\) after normalized by the area of RRDE (0.0707 cm\(^2\)).

The current densities at −1.6 V are compared in the last column of Table 1. Ni/MWNTs-50-1-60 gives the highest current density (−10.09 mA/cm\(^2\)) at −1.6 V, compared to the
samples with less or longer drying time. In comparison with Ni/MWNTs-50-1-60, Ni/MWNTs-50-1-90 has a similar density compared with Ni/MWNTs-50-1-60, indicating 60 minutes is an optimum drying time. During the drying process after electrodeposition, Ni is oxidized to a higher oxidation state.39 Yang et al29 reported that Ni can be oxidized during the CO₂ chemisorption; thus, a higher oxidation state of Ni may be preferred in the reaction. Recently, Cu with higher oxidation state was reported to be more active for CO₂RR than metallic Cu foam, indicating a higher oxidation state of metal is preferred for CO₂RR.40 Therefore, the maximum amount of Ni was oxidized after 60 minutes drying which resulted in the better reaction performance of Ni/MWNTs-50-1-60.

To investigate the effect of Ni loadings on the performance of CO₂RR, different metal loadings are achieved by adjusting the concentration of Ni in the electrolytes. The samples were dried for 30 minutes before electrodeposition. Electrodeposition was then conducted in 100, 50, or 25 μmol/L Ni²⁺ electrolyte for one cycle, and the samples are noted as Ni/MWNTs-100-1, Ni/MWNTs-50-1, and Ni/MWNTs-25-1. After electrodeposition, the samples were washed in DI water and dried in air for 60 minutes. Figure 2 shows the catalytic performance of Ni/MWNTs with different metal loadings. The best performance is obtained on Ni/MWNTs-50-1 possibly due to the largest amount of small clusters of Ni on the surface. Higher Ni loadings lead to form Ni particles and result in lower activity for CO₂RR. Small clusters are formed on both Ni/MWNTs-50-1 and Ni/MWNTs-25-1 samples. Compared with Ni/MWNTs-50-1, Ni/MWNTs-25-1 may have less amount of Ni, thus a lower activity. To further clarify the current density from CO₂RR, a reference test was carried out with Ni/MWNTs-50-1 in 0.1 mol/L NaHCO₃ with purging of Ar (Figure 2, black). The current density from the reference test is similar to that of pristine MWNTs support (Figure 2, red), indicating the current density we measured is from the CO₂RR. Clearly, Ni/MWNTs-50-1 exhibits superior activity of CO₂RR.

To further explore the effect of metal loadings on the reaction performance, more cycles of electrodeposition were conducted in 25 μmol/L, 50 μmol/L, and 100 μmol/L Ni²⁺ electrolytes. Specifically, electrodeposition was conducted for 2 and 3 cycles in 25 μmol/L and 50 μmol/L Ni²⁺ electrolyte and the samples are noted as Ni/MWNTs-25-2, Ni/MWNTs-25-3, Ni/MWNTs-50-2, and Ni/MWNTs-50-3, respectively. Electrodeposition was also conducted for 3 and 5 times in 100 μmol/L Ni²⁺ electrolyte and the samples are noted as Ni/MWNTs-100-3 and Ni/MWNTs-100-5. After electrodeposition, the samples were washed in DI water and dried in air for 60 minutes. The catalytic performance is shown in Figure 3. For the Ni/MWNTs-25-1 samples, the sample treated with 2 cycles has a better performance than the samples treated with 1 or 3 cycles. For both Ni/MWNTs-50-1 and Ni/MWNTs-100-1 series of samples, electrodeposition with more cycles lead to a lower activity. The Ni/MWNTs-25-2 and Ni/MWNTs-50-1 samples give the similar, but the highest current densities among all the samples. The result demonstrates that there is not enough active small Ni clusters on Ni/MWNTs-25-1, while extra loadings obtained with high Ni concentrations or more electrodeposition cycles result in relatively larger Ni clusters that are not active for CO₂RR.

To clarify the origin of promising activity of the catalysts, the XRD was conducted on Ni/MWNTs-50-1, Ni/MWNTs-100-1, and pure MWNTs. The Ni was electrodeposited on MWNTs sheet with the MWNTs sheet used as the working electrode. As shown in Figure 4, the peaks at 25.7, 40, and 43 degree are the characteristic peaks for MWNTs sheet, no peaks are assigned to NiO or Ni. Even though, according to

![FIGURE 1](image_url)  
**FIGURE 1** Effect of drying time after electrodeposition, the current density was normalized by the area of RRDE.

| Sample name        | Drying time before electrodeposition (min) | Drying time after electrodeposition (min) | Current density (mA/cm²) at −1.6 V vs Ag/AgCl (Sat’KCl) |
|--------------------|--------------------------------------------|------------------------------------------|----------------------------------------------------------|
| Ni/MWNTs-50-1-0    | 30                                         | 0                                        | −3.44                                                    |
| Ni/MWNTs-50-1-30   | 30                                         | 30                                       | −7.50                                                    |
| Ni/MWNTs-50-1-60   | 30                                         | 60                                       | −10.09                                                   |
| Ni/MWNTs-50-1-90   | 30                                         | 90                                       | −10.07                                                   |
the database, the peak around 43 degree overlapped with the characteristic peaks for NiO (PDF 00-044-1159). The missing of other two characteristic peaks around 37.2 and 62.8 degree implies no NiO large particles are observed from the XRD patterns. The XRD results demonstrate that the Ni clusters from electrodeposition synthesis are too small to be detected by the XRD techniques, even with the sample synthesized in high Ni concentration (Ni/MWNTs-100-1), confirming the formation of small Ni clusters or Ni single atoms.

To further clarify the origin of the superior activity of Ni/MWNTs-50-1 than Ni/MWNTs-100-1, CV was conducted on Ni/MWNTs-100-1 and Ni/MWNTs-50-1 in 0.1 mol/L KOH solution. As shown in Figure 5, two characteristic peaks are observed for Ni/MWNTs-100-1 at 0.386 V and 0.467 V, respectively. The redox peaks are attributed to the transformation of Ni(OH)$_2$ and NiOOH in alkaline solution: Ni(OH)$_2$ + OH$^-$ → NiOOH + H$_2$O + e$^-$. The formation of Ni(OH)$_2$ is due to the instability of large Ni clusters or particle in alkaline solution: Ni + H$_2$O → Ni(H$_2$O)$_{ads}$ → Ni(OH)$_2$ + H$^+$ + 2e$^-$. However, no redox peak is observed on Ni/MWNTs-50-1, which implies the formation of very small Ni clusters or atomically dispersed Ni on Ni/MWNTs-50-1, that do not go through the same redox reactions as for large Ni clusters or particles.
Based on the above results, very small Ni clusters or atomically Ni atoms are formed on as-prepared sample which is confirmed by electrochemical characterization in alkaline solution. Ni/MWNTs-50-1 sample has the highest amount of small Ni clusters (or atomically Ni atoms) on the surface and therefore a better reaction performance. The results from the as-prepared Ni/MWNTs in this work are comparable to those in the literatures. 47,48

4 | CONCLUSION

Small nickel clusters (or atomically Ni) on MWNTs are synthesized by electrodeposition method. The sample drying time and Ni metal loadings are investigated and found to affect the catalytic performance significantly. Optimized sample preparation procedure is explored for the optimum of active small Ni clusters on the surface. As-prepared sample has a promising activity for CO$_2$RR. This work provides a novel catalyst preparation procedure, demonstrating the feasibility of preparing small metal clusters or even M-SACs by electrodeposition.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

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