Integrated CO₂ Capture and Hydrogenation to Produce Formate in Aqueous Amine Solutions Using Pd-Based Catalyst

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Abstract: Integrated CO₂ capture and hydrogenation to produce formate offers a sustainable approach for reducing carbon dioxide emissions and producing liquid hydrogen carriers (formate) simultaneously. In the current study, three different types of aqueous amine solutions including monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) were investigated as CO₂-capturing and hydrogenation agents in the presence of a Pd/NAC catalyst. The effect of amine structures on the CO₂ absorption products and formate yield was investigated thoroughly. It was found that the formate product was successfully produced in the presence of all three aqueous amine solutions, with tertiary amine TEA accounting for the highest formate yield under the same CO₂ loadings. This is due to the fact that primary and secondary amine moieties in MEA and DEA are responsible for the formation of CO₂ adducts of carbamate and bicarbonate, whereas the tertiary amine moiety in TEA is responsible for the formation of hydrogenation-favorable bicarbonate as the solo CO₂ absorption product. A high yield of formate of 82.6% was achieved when hydrogenating 3 M TEA with 0.3 mol CO₂/mol amine solution in the presence of a Pd/NAC catalyst. In addition, the physio-chemical properties of the Pd/NAC catalyst analyzed using TEM, XRD and XPS characterization were applied to rationalize the superior catalytic performance of the catalyst. The reaction mechanism of integrated CO₂ capture and hydrogenation to produce formate in aqueous amine solutions over Pd/NAC catalyst was proposed as well.

Keywords: CO₂ capture; CO₂ hydrogenation; heterogenous catalysts; Pd catalyst; formate

1. Introduction

The excessive emissions of CO₂ are regarded as a main cause for global warming, while CO₂ capture technologies and exploring clean energy replacement are the two main strategies to reduce CO₂ emissions [1–4]. CO₂ capture and utilization technology (CCU) has been widely investigated in recent years as it offers an effective way to mitigate CO₂ emissions and tackle the global warming issue [5,6]. For the traditional decoupled CCU process, CO₂ was firstly captured from fossil fuel burning points and industrial sources. The obtained pure CO₂ was then pressurized and transported to specified locations for CO₂ utilization. For a typical CO₂ capture process, CO₂ was firstly adsorbed at low temperature (40–60 °C) via exothermal chemical interaction with aqueous amine solvents, then desorbed at high temperature (100–150 °C) through an endothermic process to generate pure CO₂. The energy-intensive CO₂ desorption process is regarded as one of the main issues blocking the commercialization process of CO₂ capture process [7]. With the assistance of a suitable catalyst, the aqueous-amine-captured CO₂ can be directly hydrogenated into value-added products, which can eliminate the energy-intensive CO₂ desorption step and result in an energy-efficient integrated CO₂ capture and hydrogenation process [8].

Integrated CO₂ capture and hydrogenation to produce formate process offers a sustainable approach to reduce CO₂ emissions and produce liquid hydrogen carriers at the same
When heating up the obtained ammonium formate solution, formic acid product can be generated from thermal cleavage, which is accompanied by the regeneration of aqueous amine solvents. The concept of integrated CO$_2$ capture and hydrogenation to produce formate was firstly reported by He et al. in 2013 [9]. They reported the successful application of CO$_2$ absorption into polyethyleneimine 600 (PEI600) sorbents in methanol and in situ hydrogenation to produce alkylammonium formate with the assistance of homogeneous catalyst RhCl$_3$.3H$_2$O/CyPPh$_2$. The authors demonstrated a highest turnover number of 726, corresponding to a 55% formate yield under the reaction conditions of 40 bar H$_2$, 60 °C and a reaction time of 16 h. Later, the integrated CO$_2$ capture and hydrogenation process was extended to aqueous amine solutions as CO$_2$ capture in such solvents is most widely explored and suitable for scale-up. In 2014, Hicks et al. reported the application of a polyethylenimine-tethered iminophosphine iridium catalyst for integrated CO$_2$ capture and hydrogenation to produce formate in triethylamine solutions, with a TON of 248 achieved under reaction conditions of 20 bar H$_2$ and 120 °C [10]. An outstanding high TON value of 7375 was reported by Olah and Prakash et al. upon integrated CO$_2$ capture and hydrogenation in TMG solutions with Ru-Macgo-BH as a homogeneous catalyst [11]. In the same paper, an iron-based homogeneous catalyst was also explored as a promising candidate for CO$_2$ capture and hydrogenation in pentaethylenhexamine (PEHA) solutions with a TON of 255 obtained. Although the application of homogeneous catalysts in the CO$_2$ capture and hydrogenation process to produce formate demonstrated superior catalytic performance with high formate yields and TON values, the common issues related to homogeneous catalysts including the recycling of catalysts and the separation of products still hindered the scale-up of such a process. On the other hand, integrated CO$_2$ capture and hydrogenation to produce formate in aqueous amine solution using Pd-based catalysts is rarely reported in the open literature. One such example is reported by Lin’s group, who stated that they successfully produced formate with a product yield of 50.2% using piperidine as a CO$_2$-capturing solvent and Pd/AC as a catalyst [12]. However, the effect of amine structure on the product yield was not reported in the open literature.

In the current study, three different aqueous amine solutions with different amine types including primary amine monoethanolamine (MEA), secondary amine diethanolamine (DEA) and triethanolamine (TEA) were employed as CO$_2$-capturing and hydrogenation solvents in the presence of Pd/NAC catalysts. The CO$_2$ absorption product distribution together with formate yield at different CO$_2$ loadings were measured and compared between the three different aqueous amine solutions. XRD, XPS and TEM were employed to evaluate the physio-chemical properties of the Pd/NAC catalysts in order to rationalize the corresponding catalytic performance. At last, the reaction mechanism of integrated CO$_2$ capture and hydrogenation in the presence of the Pd/NAC catalyst was proposed.

2. Results and Discussion

2.1. Integrated CO$_2$ Capture and Hydrogenation to Produce Formate

Pd-based supported heterogeneous catalysts have demonstrated superior catalytic performance towards the hydrogenation of HCO$_3^-$ in aqueous phase compared with other metal catalysts of Ni, Ru, Co and Re [13]. Carbon-based materials were widely applied as supporting materials for Pd-based heterogeneous catalysts for their application in the hydrogenation of HCO$_3^-$ in aqueous phase [13–18], among which, the generation of N-containing functional groups from synthesizing a particular type of carbon-based material, including nitrogen-doped carbon (NMC) and graphitic carbon nitride (g-C$_3$N$_4$), is well-accepted as an efficient way to manipulate the interaction between a support and active metal Pd. N-containing surface groups are often recognized as electron-donating functionalities which is beneficial to anchor and increase the electron density of active metal Pd. Therefore, a nitrogen-doped activated carbon (NAC)-supported Pd catalyst was employed as the heterogeneous catalyst for the integrated CO$_2$ capture and hydrogenation process. The NAC material used herein was prepared via a simple solid mixing and thermal treatment procedure.
To investigate the effect of amine structure on the product yield, three aqueous amine solutions including MEA, DEA and TEA were employed as capturing agents for the integrated CO₂ capture and hydrogenation process. The results of integrated CO₂ capture and hydrogenation in aqueous amine solutions of MEA, DEA and TEA in the presence of a Pd/NAC catalyst are shown in Table 1. In addition, we performed the integrated CO₂ capture and hydrogenation process with 3M TEA solutions, 0.30 mol CO₂/mol amine, with NAC as the catalyst, and the NMR results showed no characterization peak for formate was formed after the reaction. As expected, the CO₂-capturing product in MEA and DEA solutions contained both bicarbonate (HCO₃⁻) and carbamate (R₁R₂COO⁻) species, as CO₂ can directly react with primary/secondary amines. Meanwhile, HCO₃⁻ was the solo CO₂ absorption product for TEA, since CO₂ cannot react directly with tertiary amine groups. It is interesting to find that the concentrations of HCO₃⁻ species appeared to be 0 after the integrated CO₂ capture and hydrogenation process in both the MEA and DEA solutions, meaning that all HCO₃⁻ species were converted into formate products. However, there were still some carbamate species left in the liquid phase after the hydrogenation process. This interesting phenomenon proves that HCO₃⁻ is a more favorable reactant for the hydrogenation process compared with the carbamate species. This agrees well with results published in the literature that show HCO₃⁻ can act directly as a reactant for the hydrogenation process; however, the direct conversion of carbamate is rather difficult due to its electron-rich nature [19]. The conversion of carbamate species can be achieved via two possible pathways including 1) the conversion of carbamate into bicarbonate then participating in the hydrogenation process, and 2) the conversion of carbamate species into gaseous CO₂ under the reaction temperature of 80 °C then participating in the hydrogenation process. However, the low solubility of CO₂ under reaction conditions makes the second pathway less possible. Therefore, the hydrogenation of carbamate species is assumed to be through the HCO₃⁻ pathway.

Compared with MEA and DEA, TEA often demonstrated the highest formate yield under the same CO₂ loadings. For example, at the CO₂ loading of ~0.3, a formate yield of 82.6% was achieved when employing TEA as the CO₂-capturing and hydrogenating solvent, while formate yields of only 40.8% and 50.3% were achieved when employing MEA and DEA as CO₂-capturing and hydrogenating solvents. The fact that a higher formate yield was often achieved in TEA solutions under the same CO₂ loading was attributed to

### Table 1. Results of integrated CO₂ capture and hydrogenation to produce formate in aqueous amine solutions of MEA, DEA and TEA in the presence of Pd/NAC catalyst.

| Entry | Capturing and Hydrogenation Solvent | CO₂ Loading | Captured CO₂ Concentration (M) | Hydrogenation Results of CO₂ Species Concentration (M) | Formate Yield (%) |
|-------|------------------------------------|-------------|--------------------------------|---------------------------------------------------|------------------|
|       |                                    |             | HCO₃⁻ | R₁R₂COO⁻ | HCO₃⁻ | R₁R₂COO⁻ | HCOCO⁻ |                      |
| 1     | MEA                                | 0.15        | 0     | 0.45     | 0     | 0.31     | 0.14   | 30.8                 |
| 2     | MEA                                | 0.31        | 0.14  | 0.79     | 0     | 0.55     | 0.38   | 40.8                 |
| 3     | MEA                                | 0.46        | 0.25  | 1.13     | 0     | 0.63     | 0.75   | 54.1                 |
| 4     | MEA                                | 0.72        | 1.19  | 0.97     | 0     | 0.89     | 1.27   | 58.8                 |
| 5     | DEA                                | 0.16        | 0     | 0.48     | 0     | 0.29     | 0.19   | 35.1                 |
| 6     | DEA                                | 0.31        | 0.17  | 0.76     | 0     | 0.5      | 0.43   | 50.3                 |
| 7     | DEA                                | 0.48        | 0.45  | 0.98     | 0     | 0.71     | 0.72   | 46.3                 |
| 8     | DEA                                | 0.78        | 0.70  | 1.64     | 0     | 1.16     | 1.18   | 60.6                 |
| 9     | TEA                                | 0.15        | 0.45  | 0        | 0.14   | 0        | 0.31   | 68.5                 |
| 10    | TEA                                | 0.30        | 0.9   | 0        | 0.16   | 0        | 0.74   | 82.6                 |
| 11    | TEA                                | 0.46        | 1.38  | 0        | 0.51   | 0        | 0.86   | 62.5                 |
| 12    | TEA                                | 0.60        | 1.8   | 0        | 0.84   | 0        | 0.96   | 53.2                 |

Reaction conditions: 80 °C, 5.0 mL 3M amine solutions, 6 MPa H₂, 100 mg catalyst and reacting time of 8 h.

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the favorable hydrogenation when HCO$_3^-$ species were the solo CO$_2$-capturing adducts in the TEA solutions.

Among all tested amine solutions with different CO$_2$ loadings, the highest formate yield of 82.6% was achieved when using TEA as the CO$_2$-capturing and hydrogenation agent with CO$_2$ loading of 0.30 mol CO$_2$/mol amine. For the TEA solution, the concentration of formate product increased with the increase in CO$_2$ loading. However, the formate yield increased with CO$_2$ loading when CO$_2$ loading was below 0.3 mol CO$_2$/mol amine and decreased with the increase in CO$_2$ loading when CO$_2$ loading was above 0.3 mol CO$_2$/mol amine.

2.2. Catalyst Characterization

To rationalize the catalytic performance with the physical–chemistry properties of the Pd/NAC catalyst and propose the reaction mechanism, XRD, XPS and TEM measurements were performed on the catalyst. The XRD pattern of the Pd/NAC catalyst is shown in Figure 1. The diffraction peaks at 2θ of 40.1°, 46.7° and 68.1° corresponded to the (111), (200) and (220) crystalline planes of Pd (PDF# 46-1043). This certainly indicates the existence of crystalline Pd in zero valence (Pd$^0$), which is well-believed to be the active site for the dissociative adsorption of H$_2$ in heterogeneous hydrogenation processes.

Particle size is often believed to be one of the crucial features governing the catalytic performance of supported metal catalysts in heterogeneous reactions [20,21]. For example, the optimized Pd nanoparticle size appeared to be within the range of 1.8−3.5 nm in an aqueous phase formic acid dehydrogenation reaction process. For the hydrogenation of bicarbonate in aqueous solutions, the reported mean particle size of Pd nanoparticles with decent catalytic activity falls in the range of 1.6 to 3.1 nm. Cao et al. reported the application of a 5 wt% Pd/r-GO catalyst with a mean particle size of 2.4 nm for the hydrogenation of 4.8 M KHCO$_3$ solution under conditions of 100 °C and 40 bar H$_2$; a formate yield of 66.3% was obtained after 10 h of reaction [16]. Zhang et al. investigated the application of Pd/AC and Pd/MNC catalysts in a system of the hydrogenation of 4 M KHCO$_3$ solutions at 353 K [17]. A high formate yield of 69.7% was obtained after a reaction time of 2 h in the presence of the Pd/MCN catalyst with a mean particle size of 2.4 nm, while a low formate yield of 43.2% was obtained after a reaction time of 3 h in the presence of the Pd/AC catalyst with a particle size of 3.1 nm. Therefore, the TEM technique was employed to obtain information on nanoparticle size in the Pd/NAC catalyst. The measured TEM image and corresponding particle size distribution plot of the Pd/NAC catalyst are presented in Figure 2a,b.
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Figure 2. TEM image (a) and corresponding particle distribution plot (b) of Pd/NAC catalyst.

As can be seen from Figure 2a, the Pd nanoparticles were uniformly distributed on the NAC catalyst. The mean sizes and standard deviations of the Pd nanoparticles were calculated using 100 individual nanoparticles. The calculated average diameter of the Pd nanoparticles was 2.8 ± 0.2 nm. The obtained mean particle size of Pd nanoparticles on the Pd/NAC catalyst fell into the decent-activity nanoparticle size range of 1.6 to 3.1 nm, which was likely to facilitate the hydrogenation of HCO$_3^-$ in the integrated reaction process.

The XPS technique is a useful tool to examine the valence states and surface composition of metal-based catalysts [22–24]. Therefore, to further acquire information on the chemical state of Pd and surface N-containing groups, XPS measurement was performed for the Pd/NAC catalyst. The XPS spectra of Pd 3d and N 1s core level of Pd/NAC catalyst were measured and are presented in Figure 3a, b.

There are two main doublets that could be observed in the deconvoluted XPS spectra of the Pd 3d region (Figure 3a), which indicates the existence of two different Pd chemical states of Pd$^0$ and Pd$^{2+}$. The two intense doublets observed at 336.2 and 341.5 eV were attributed to the characteristic peaks of metallic Pd (Pd$^0$). The other residual weak peaks at 338.0 and 343.3 eV were attributed to the characteristic peaks of Pd$^{2+}$. By integrating the corresponding peak areas for the Pd$^0$ and Pd$^{2+}$, the ratio between surface Pd$^0$ and Pd$^{2+}$ appeared to be 71.4:28.6. This result suggests the formation of a large amount of metallic Pd on the surface of the Pd/NAC catalyst, which is assumed to be the active site for H$_2$ adsorption and dissociation. The amount of metallic Pd is highly related to the reactivity of the hydrogenation reaction; hence, a potential increase in the hydrogenation reactivity can be achieved via further increase in the Pd$^0$ amount on the surface of the catalyst. As can be seen in Figure 3 (b), four types of N-containing functionalities were identified on the surface of the Pd/NAC catalyst containing pyridine (N1, 398.7 eV), nitrile (N2, 399.3 eV), pyrrole (N3, 400.3 eV) and quaternary N (N4, 400.9 eV) [25,26]. As
reported by Lee et al., the sp² nitrogen site appears to have more diffuse orbitals and more negative charges, which are likely to interact with the Pd²⁺ in the precursor and benefit the reduction of Pd²⁺ into Pd⁰ in a subsequent reducing procedure [27]. The abundant amount of surface N-containing groups are believed to be electron-donating functionalities which can increase the electron density of Pd⁰ on the surface of the Pd/NAC catalyst. The electron-enriched Pd nanoparticle was often accompanied with decent catalytic activity in the hydrogenation of bicarbonate; therefore, decent catalytic performance was observed when using the Pd/NAC catalyst for the hydrogenation of CO₂-captured amine solutions. The used catalyst was collected following a filtration, water wash and dry process in order to examine the chemical state of Pd after the reaction. The XPS spectra of the Pd 3d core level of the used Pd/NAC catalyst can be found in Figure S1 of the Supporting Information, demonstrating a minor change in the chemical state of Pd on the surface of the catalyst with a similar Pd⁰ and Pd²⁺ ratio compared with the fresh catalyst.

![XPS spectra of Pd 3d (a) and N 1s (b) core level of Pd/NAC catalyst.](image)

**Figure 3.** XPS spectra of Pd 3d (a) and N 1s (b) core level of Pd/NAC catalyst.

### 2.3. Reaction Mechanism

Based on the understanding of Pd nanoparticle size and its corresponding chemical state on the surface of the Pd/NAC catalyst, the reaction mechanism of the integrated CO₂ capture and in situ hydrogenation to produce formate in aqueous amine solutions with Pd/NAC catalyst was proposed and is illustrated in Figure 4. Firstly, CO₂ was adsorbed into aqueous amine solutions with R₁R₂NCOO⁻ and HCO₃⁻ as the main CO₂-capturing products in primary/secondary amine solutions and HCO₃⁻ as the solo main CO₂-capturing product in tertiary amine solutions. Secondly, HCO₃⁻ was acting as the main hydrogenation reactant in all amine solutions, while the carbamate species R₁R₂NCOO⁻ was transformed into the form of HCO₃⁻ through an equilibrium reaction before participating in the hydrogenation process. The following procedure was the hydrogenation of bicarbonate into a formate product, which follows the insertion mechanism as
reported in the open literature [17,28]. As indicated from the XPS results, the Pd nanoparticles were in the electron-enriched state, which was beneficial for the following HCO$_3^-$ hydrogenation process. The residual free amine molecules in the solutions were also recognized as electron-donating species, which would increase the electron-enriched state of Pd and benefit the subsequent hydrogenation process. Basically, the HCO$_3^-$ species was adsorbed on the surface of the NAC support and H$_2$ was adsorbed and activated on the Pd site to form surface Pd-H species. The Pd-H species then attacked the positively polarized carbon in HCO$_3^-$ to form formate product. Lastly, the formate product desorbed from the surface of the catalyst, followed by the regeneration of the fresh Pd/NAC catalyst for the adsorption and activation of HCO$_3^-$ and H$_2$ reactants.

3. Materials and Methods

Preparation of catalyst: The N-doped activated carbon (NAC) was prepared by a simple solid mixing and thermal treatment procedure using melamine as the nitrogen source. Activated carbon was initially washed with HCl solution (1 M, 500 mL) at 75 °C for 2 h. The obtained activated carbon was then filtered and washed with distilled water and dried at 110 °C for 2 h (sample AC). Then, 5 g of AC was mixed evenly with 5 g of melamine in a porcelain boat. Then, the mixture was calcined at 700 °C for 2 h at a heating rate of 3 °C·min$^{-1}$. There was no gas during the heating up process and the first 90 min of the keeping stage. In the last 30 min, N$_2$ was passed into the tube furnace with a flow of 30 mL·min$^{-1}$. The obtained N-doped AC sample was named NAC. An ultrasonic-assisted method was applied to deposit Pd on NAC, and the pretreated NAC was grinded to achieve a sample size less than 0.1 mm before the deposition. Then, 0.5 g NAC was suspended in 50 mL of deionized water, and the mixture was immersed into an ultrasonic instrument filled with water (by changing the water frequently to maintain the reaction temperature between 30 and 35 °C) for 30 min so that NAC could be dispersed to a uniform suspension. After that, 8.6 mL of PdCl$_2$ aqueous solution (2.9 mg/mL) was added into the N-doped

Figure 4. Scheme of reaction mechanism of integrated CO$_2$ capture and hydrogenation in aqueous amine solutions catalyzed by Pd/NAC.
carbon suspension under ultrasonication, allowing the chelate adsorption of Pd$^{2+}$ on NAC. After being ultrasonicated for 1 h, 25 mL of NaBH$_4$ aqueous solution (4 mg/mL) was added dropwise, and the resulting suspension was maintained under ultrasonication for 2 h to allow a complete reduction of metallic salt. The slurry at last was filtered, washed with deionized water several times and dried under vacuum at 70 °C overnight.

Integrated CO$_2$ capture and hydrogenation: The CO$_2$ capture process was performed at room temperature via bubbling CO$_2$ into 3 M amine solutions, and the CO$_2$ content in the solutions was weighted to determine the CO$_2$ loading. The CO$_2$ flow rate was controlled at 80 mL/min. The subsequent hydrogenation was carried out in a high-pressure micro reactor. Typically, 5.0 mL of CO$_2$-loaded amine solution and Pd/NAC catalyst was placed in the reactor. Then, the reactor was sealed, and H$_2$ gas was charged after the internal air was scrubbed completely by using H$_2$ at room temperature. The stirrer (1000 rpm) was started until the desired reaction temperature of 80 °C was reached. After a certain reaction time, the reactor was placed in cool water, and the gas was carefully released. Afterwards, the reaction mixture was centrifuged to collect liquid products. The liquid products were then measured using $^{13}$NMR.

The formate yield was calculated via the concentration of formate product divided by the concentration of total captured CO$_2$ concentration.

$$\text{Yield} = \frac{\text{mole of formate product}}{\text{mole of amine Captured CO}_2} \times 100\%$$ (1)

Catalyst characterization: The JEOL JEM-1200EX electron microscope operated at 200 kV was applied to measure the transmission electron microscopy (TEM) images of the Pd/NAC catalyst. In order to increase the conductivity, the catalyst was gold-plated before acquiring the TEM images. X-ray photoelectron spectroscopy (XPS) measurements were obtained on an ESCALAB 250XI spectrometer with 24.2 W of Al Kα radiation.

4. Conclusions

In the current paper, three aqueous amine solutions were evaluated as CO$_2$-capturing and hydrogenating agents and successfully produced formate product in the presence of a Pd/NAC catalyst. Among the three tested aqueous amine solutions, tertiary amine TEA proved to be the best-performing candidate with highest formate yield. The reason for the superior formate yield in TEA solutions was attributed to the presence of HCO$_3^-$ as the sole CO$_2$ absorption product since HCO$_3^-$ is more favorable to the hydrogenation process compared with carbamate species. As for the MEA and DEA solutions, the CO$_2$-capturing products mainly included HCO$_3^-$ and carbamate species. The carbamate species was assumed to be hydrogenated via the HCO$_3^-$ pathway as it can transform into HCO$_3^-$ through equilibrium. The small mean particle size of 2.8 nm with a high content of Pd$^0$ on the surface of the catalyst and abundant amount of surface N-containing groups are the main reasons for the decent catalytic performance in the integrated CO$_2$ capture and hydrogenation process in the presence of the Pd/NAC catalyst. Finally, the reaction mechanism of integrated CO$_2$ capture and hydrogenation in aqueous amine solutions in the presence of Pd/NAC catalyst was proposed. The reusability, Pd leaching test and other physical–chemical characterizations of catalysts after the reaction are within the research scope of our plans to further advance the integrated CO$_2$ capture and hydrogenation process to large scales.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12080925/s1, Figure S1: XPS spectra of Pd 3d core level of the used Pd/NAC catalyst.

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**Data Availability Statement:** The data that support the findings of this study are available from the corresponding author (Li, L.), upon reasonable request.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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