

Fixation of CO₂ by electrocatalytic reduction to synthesis of dimethyl carbonate in ionic liquid using effective silver-coated nanoporous copper composites

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Abstract

With high surface area, open porosity and high efficiency, a catalyst was prepared and firstly employed in electrocatalytic reduction of CO₂ and electrosynthesis of dimethyl carbonate (DMC). The electrochemical property for electrocatalytic reduction of CO₂ in ionic liquid was studied by cyclic voltammogram (CV). The effects of various reaction variables like temperature, working potential and cathode materials on the electrocatalytic performance were also investigated. 80% yield of DMC was obtained under the optimal reaction conditions.

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With global warming ascertained as a critical problem, it is exceedingly important to reduce the emission of CO₂ into the atmosphere. After separating the CO₂ from its emission source, it is necessary to fix this greenhouse gas. The use of electrochemical methods appears to consume less energy than traditional chemical fixation processes and can take place under mild condition [1–4]. It presents the possibility of recycling and transforming this raw material into high-energy compounds and useful organic chemicals. The direct electrochemical reduction of CO₂ has been researched on different electrodes, including metallic cathodes, semiconductors, and supramolecular electrode containing transition metals [5–7]. Furthermore, this process is commonly performed in organic solvents and their precious catalysts cannot be recycled easily. Metal nanoporous film, in particular, is one of the widely used materials in electrocatalytic applications due to their high surface area, good electrical/thermal conductivity, and open porosity [8,9]. Moreover, the bicontinuous porous nanocomposites by surface decoration can provide a high volume dispersion of catalyst which is uniformly distributed through a thin porous electrode.

Room temperature ionic liquids (RTILs) constitute an alternative solvent system and offer distinct advantages over traditional solvents such as monoethanolamine (MEA), which can be potentially optimized of CO₂ selectivity because of their high CO₂ solubility, high conductivity, wide electrochemical window and almost zero vapor pressure [10].

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Thus, we studied the electrochemical reduction of CO_2 using 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{Bmim}][\text{BF}_4]$) as the electrolyte at ambient temperature. In this context, we reported the electrochemical reduction of CO_2 with an electrode in $[\text{Bmim}][\text{BF}_4]$ at room temperature. Also, silver-coated nanoporous copper (NPC-Ag) was prepared as a robust and efficient electrocatalyst for the electrochemical fixation of CO_2 with methanol for the synthesis of dimethyl carbonate (DMC). DMC can be used as fuel additives, carbonylating reagents, alkylating reagents and polar solvents [11,12]. To the best of our knowledge, silver-coated nanoporous copper is the first recyclable electrocatalyst designed for the green synthesis of DMC with CO_2 .

1. Experimental

All reagents used in the experiment were of analytical grade without further purification. The detailed report on the electrodeposition of Zn on the copper surface can be seen in the literature [9]. When finished, the whole sample was transferred into deionized water and ultrasonic agitation was applied at room temperature for several minutes, and dried with nitrogen blown at room temperature. The sample was then treated at 200°C under the protection of Ar gas for 2 h. Chemical dealloying was carried out in the HCl ($\text{pH} = 4$) aqueous solution at room temperature for 24 h to format the nanoporous Cu (NPC). Finally, electroless deposition of silver was incorporated on the surfaces of film and dried at room temperature (NPC-Ag).

The X-ray diffraction (XRD) patterns were recorded using a JapanD/max2550VB + 18 kW diffractometer under Cu $\text{K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The operation voltage and current were kept at 40 kV and 300 mA, respectively. The morphology of as-prepared sample and energy dispersive spectrum was determined using a Sirion-200 scanning electron microscope.

The experiments were carried out in a conventional three-electrode electrochemical cell. The prepared electrode was used as the working electrode, and a platinum foil of convenient area was set as the counter electrode. The third electrode was an Ag wire. The electrolyte ionic liquid $[\text{Bmim}][\text{BF}_4]$, was saturated with N_2 or CO_2 . CV tests were collected on a CHI660 workstation (Shanghai, China). At the end of electrolyses, methanol was added, which was stirred for 1 h. Finally, 3-fold molar excess of CH_3I was added and stirred for 5 h. The products after distillation were determined by GC-MS (QP2010, Shimadzu, Japan).

2. Results and discussion

Fig. 1 presents a typical diffraction pattern of Cu_5Zn_8 alloy (a) and nanoporous copper after dealloying (b). All the peaks (a) can be well indexed as cubic phase of Cu_5Zn_8 with cell parameter $a = 8.854 \text{ \AA}$, which was in good agreement with the values from the standard card (JCPDS No. 65-3157). XRD pattern of the etched sample (b) matched well with Cu (JCPDS No. 04-0836). This reveals that Zn in the Cu–Zn alloy has been completely etched off after immersion in HCl solution for 24 h. In Fig. 1c, all the peaks can be respectively assigned to Cu–Ag solid solution after electroless deposition of silver on the nanoporous copper.

The morphology and size of as-prepared NPC and NPC-Ag were investigated by scanning electron microscopy (SEM). As shown in Fig. 2a, the morphology with uniform pores and hollow channels of around 200 nm can be obtained through dealloying of the Cu_5Zn_8 alloys. It is generally recognized that ideal bicontinuous nanoporous structures are observed from binary alloys with a single-phase solid solubility across all compositions by chemical/electrochemical dealloying [9].

The representative microstructures of silver-plated nanoporous copper (NPC-Ag) are shown in Fig. 2b. It can be seen that the silver-plated films uniformly covered the internal surface of nanoporous copper. The analysis of the micrographs suggests that silver atoms are homogenous dispersed on the surface, and the copper atoms inside and keep the original nanostructure. The chemical composition of the as-prepared sample which analyzed with EDS, are shown in Fig. 2c. The strong peaks for copper and silver were observed in the spectrum.

Fig. 3 presents the cyclic voltammograms of using NPC-Ag as working electrode in N_2 - or CO_2 -saturated ionic liquid $[\text{Bmim}][\text{BF}_4]$ at the potential scanning rate of 50 mV s^{-1} . As shown in Fig. 3b, no redox peaks observed in the sweeping region (-0.8 V to -2.2 V) in the absence of CO_2 . After addition of CO_2 into the solution, a single reduction peak was found at -1.7 V , indicating the complete irreversibility of the electrochemical reaction on the NPC-Ag electrode. The shape of curves has been ascribed to one electron reduction of CO_2 , which produced an anion radical of CO_2 ($\text{CO}_2^{\bullet-}$) [1].

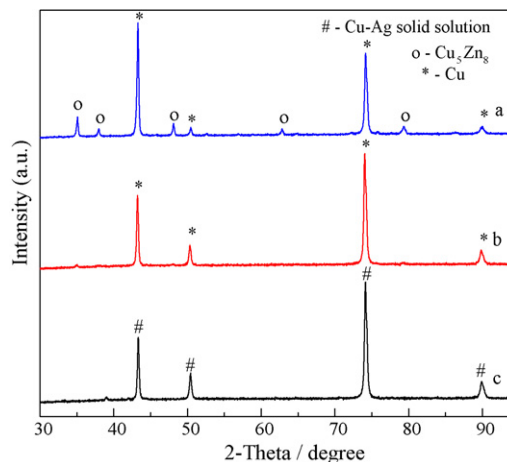


Fig. 1. XRD patterns of the as-prepared alloys (a), nanoporous copper after dealloying for 24 h (b) and electroless deposition of silver on the nanoporous copper for 10 min (c).

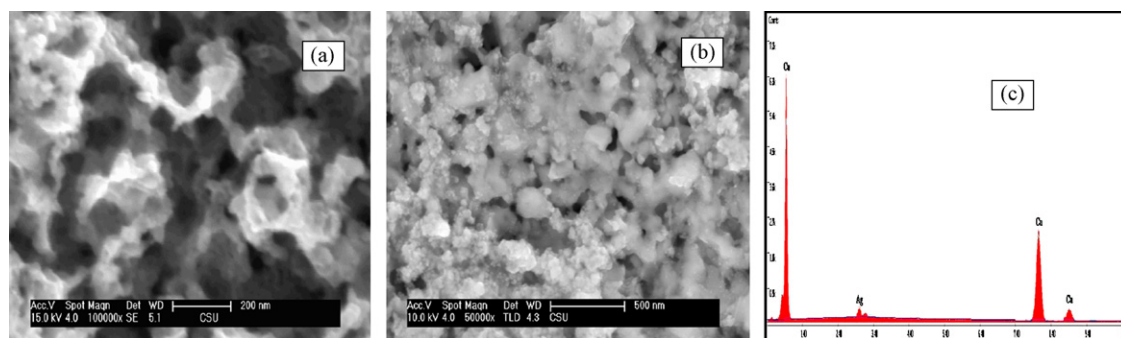


Fig. 2. SEM images of NPC (a) and NPC-Ag (b) and EDS pattern of NPC-Ag (c).

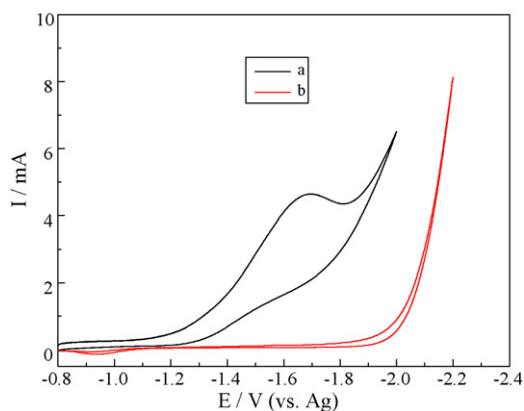


Fig. 3. Cyclic voltammograms of the NPC-Ag electrode in ionic liquid [Bmim][BF₄] saturated with CO₂ (a) and N₂ (b), $\nu = 50$ mV/s (vs. Ag).

Furthermore, a much higher catalytic peak current ($I_p > 4$ mA) of CO₂ reduction was obtained on NPC-Ag electrode, which was higher than that had been reported in this issue by Zhang et al. [2], indicating that nanoporous structure could increase a great deal of active centers where the reduction of CO₂ carried on. The transfer of electron to the adsorbed CO₂ molecule might be much easier and faster. In other words, the NPC-Ag electrode exhibits excellent catalytic activity.

Table 1

Reaction conditions and results of electrosynthesis of demethyl carbonate in [Bmim][BF₄].^a

Entry	Temperature (°C)	Cathode	Potential (V) vs. Ag	Yield (%)
1	20	NPC-Ag	−1.7	29
2	30	NPC-Ag	−1.7	37
3	40	NPC-Ag	−1.7	65
4	50	NPC-Ag	−1.7	80
5	50	NPC-Ag (reusing 5 times)	−1.7	74
6	60	NPC-Ag	−1.7	71
7	70	NPC-Ag	−1.7	53
8	50	NPC-Ag	−1.5	57
9	50	NPC-Ag	−1.9	61
10	50	NPC-Ag	−2.1	49
11	50	NPC-Ag	−2.3	34
12	50	Silver	−1.7	59
13	50	NPC	−1.7	35

^a Saturated with CO₂ in [Bmim][BF₄] until 1.0 F/mol of charge was passed under atmospheric pressure.

The results using methanol for electrosynthesis of DMC are reported in Table 1. No other byproduct was detected by GC–MS for all the experiments. The influences of temperature, working potential, cathode material on the yield were investigated. Appreciate differences in the yield of DMC were obtained at different temperature (entries 1–7). The highest yield (80%) was achieved (entry 4) at 50 °C, which is higher than that reported by Zhang et al. [2]. The temperature influences the viscosity of the ionic liquid and the solubility of CO₂ in the ionic liquid. The yield of DMC strongly depended on the working potential (entries 8–11). More positive potential will not be effective for CO₂ reduction, also, the ionic liquid [Bmim][BF₄] will polarize at more negative potential, which is harmful for CO₂ reduction. The yield of DMC using silver or NPC cathode material (entries 12 and 13) is remarkable lower than that using NPC-Ag cathode material, demonstrating that nanoporous structure could increase a great deal of active centers where the reduction of CO₂ took place, and showed the better electrocatalytic activity for CO₂ reduction. Furthermore, the yield tends to be constant at 74% after reusing NPC-Ag electrode for five times (entry 5). It demonstrates that the NPC-Ag electrode has a benign stability during the electrochemical reduction of CO₂.

In summary, novel silver-coated nanoporous copper composite electrocatalysts were prepared and firstly employed in electrosynthesis of DMC, which combined the advantages of high surface area, open porosity and highly efficient of catalysts. We trust that our experimental results will trigger more intense research in electrocatalytic synthesis of DMC. Further improvement in DMC yield may offer a practical approach to CO₂ utilization.

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