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Short Communication

Electrocatalysis of CO_2 Reduction on Nano Silver Cathode in Ionic Liquid $BMIMBF_4$: Synthesis of Dimethylcarbonate

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Nano silver particles deposited on conductive glass was prepared by cyclic voltammogram. This obtained electrode was used to catalyze electroreduction of carbon dioxide for synthesize dimethylcarbonate. Results show that the process of electrochemical reduction of CO_2 on nano silver particles electrode in 1-butyl-3-methylimidazoliumtetrafluoborate ($BMIMBF_4$), is step by step, which is proved by two reduction peaks at -1.8 V and -2.2 V (vs. Ag). Under mild conditions, electrolyses experiments were carried out in an undivided cell at -1.8 V without any toxic solvents, catalysts and supporting electrolytes, yielding the dimethyl carbonate with yield of 83%. Moreover, no other product was found in liquid product.

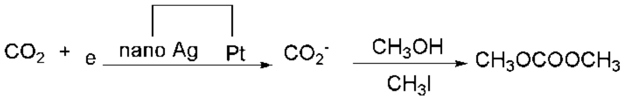
Keywords: Electrocatalytic, Nano silver, CO_2, Dimethylcarbonate, Ionic liquid

1. INTRODUCTION

Dimethyl carbonate (DMC) has an extensive application because of its excellent properties and low toxicity as a solvent; it is a substitutive intermediate for highly toxic phosgene or dimethylsulfate.[1,2] Ionic liquids is a kind of molten salt, with low melting points, which obtained by combination of organic cations with anions. Recently, ionic liquids are used to be green reaction median due to their wide electrochemical potential window, high ionic conductivity, good solvating ability and low vapour pressure. [3,4]

Chemical conversion of CO_2 is of great interest, because it can utilize the CO_2 as a carbon source. CO_2 has very low reactivity because of its linear structure. Various methods have been proposed to convert CO_2. [3] Electrochemical reduction of CO_2 is attractive, extensive research has been carried out on a variety of electrode surfaces, including bulk metal, modified metal, metal alloys and so on. Among all the materials, copper and silver are the most promising electrodes to CO_2 reduction. However, the electrochemical reduction of CO_2 on metal electrodes (such as copper and silver) requires a high overvoltage and the system conversion efficiency suffers. [4]

To compete with alternative processes successfully, electro-reduction CO_2 must take place with high efficiency and selectivity at low potential. This process requires cathode material have highly efficient electrocatalyst. Recently, metal nano metals is a research focus, due to their large surface area, high electrostability and facile preparation.[1,5,6] In this paper, nano structure silver was prepared and characterized through SEM, X-ray diffraction. Cyclic voltammogram (CV) and potentiostatic electrolyses (Scheme 1) were used to evaluate the performance of the nano silver electrode for electro-reduction CO_2 to synthesis of DMC in ionic liquid 1-butyl-3-methylimidazoliumtetrafluoborate ($BMIMBF_4$).



Scheme 1

2. EXPERIMENTAL

2.1 Chemicals

Ionic liquid $BMIMBF_4$ (purity, 99%) was dried under vacuum at 120 ^{o}C 24 h prior to use. The purity of CO_2 and N_2 was 99.99%. Unless otherwise noted, the reagents and solvents were used as received from commercial suppliers.

2.2. Preparation and characterization of the nano Ag electrode

Approximately 760 mg silver nitrate was dissolved in 500 mL deionized water. The nano silver electrode was obtained by CV scanning at a scanning rate of 0.01 Vs^{-1} for 50 cycles between -0.8 V to 0.8 V vs. Ag. The experiments were conducted with conductive glass as cathode, Pt foil as anode and Ag wire as reference electrode. Then obtained electrode was dried under vacuum at 60 ^{o}C for 12 h.[7-9]

The size and morphology of the nano Ag electrode was characterized by scanning electron microscopy (SEM, Sirion 200, Holland). X-ray diffraction data was collected on a RigakuD/max $2550VB^+$ 18 kW under Cu Kα radiation, scan range from 10° to 90°.

2.3. Electrocatalytic reduction of carbon dioxide for synthesis of DMC

Prior to the experiments, all electrodes were polished mechanically with sand paper and then were sonicated in ethanol for 5 min. Finally, the electrodes were cleaned with diluted hydrochloric acid and double distilled water and then were dried.

CVs experiments were conducted in $BMIMBF_4$ by CHI660B electrochemical station in an undivided cell equipped with as-prepared nano Ag electrode (area= 0.5 cm^2) as cathode, Pt foil (area= 1 cm^2) as anode and Ag wire as reference electrode. The electrolyte was saturated with N_2 and CO_2 before experiment, respectively. Potentiostatic electrolyses experiments were also conducted in a standard three electrode cell with gas inlet and outlet. At this condition, the area of the as-prepared nano Ag cathode and Pt foil anode is 5 cm^2 and 6 cm^2, respectively. When the electrolyse was interrupted, the CH_3OH (0.12 mol/L) was added, stirred for 1.0 h, after that 3 fold molar CH_3I was added, refluxed for 5 h. The products after distillation were determined by GC-MS. The yield of DMC was based on the starting methanol.

3. RESULTS AND DISCUSSION

3.1. Silver nano particles characteristics

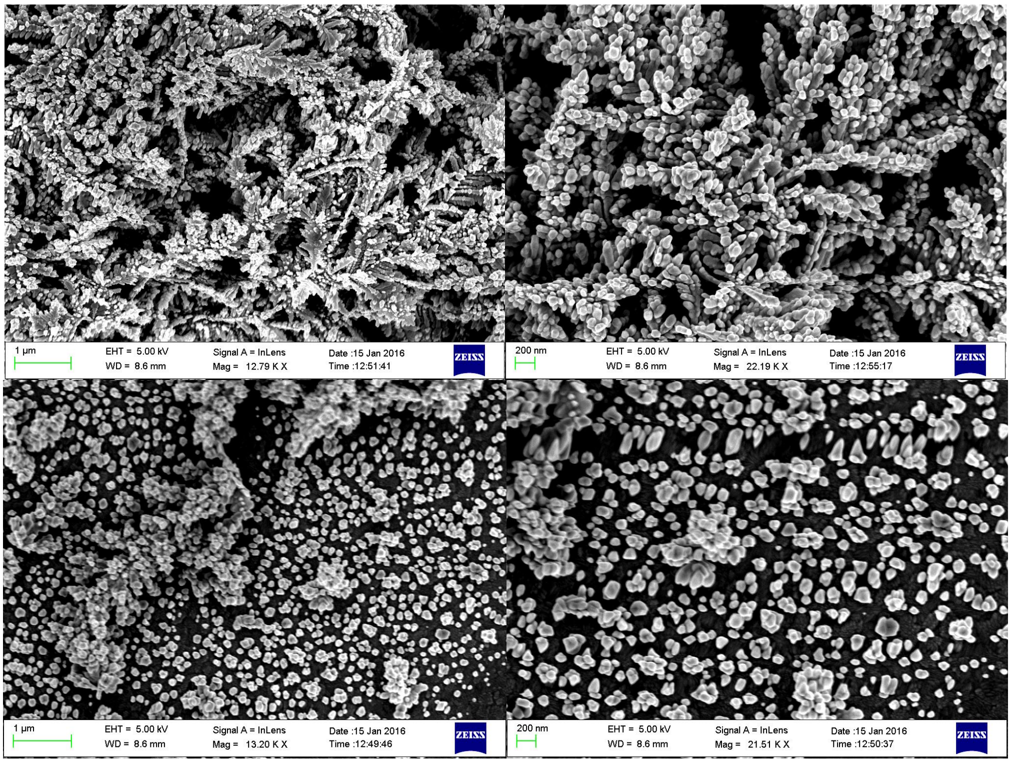


Figure 1. SEM image of as-prepared nano-silver (a) no PEG or PVP, (b) enlarged detail (a), (c) polyethylene glycol (PEG), and (d) PVP

The SEM images of the obtained samples are shown in Fig. 1. Results showed that the synthesized nano silver particles presented a coral polyps form, and the size was 90 nm. The coral polyps are composed of the nano silver particles (Fig. 1a, b). Fig. 1a, Fig. 1c and Fig. 1d were demonstrated that the prepared nano silver particles were well distributed in presence of polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP). When the addition is PVP, the particles size distribution is more uniform. This is because the PVP molecules can not only prevent the agglomeration of nano silver particles but also reduce the rate of silver deposition on the cathode surface through the combination between Ag^+ ions and PVP molecules.[10] This result agree with the literature that with PVP, the size of the prepared nano silver particles was 20~80 nm, and the nano silver particles dispersed well. [11]

The XRD patterns are illustrated in Fig. 2. These results are in good agreement with the standard card (JCPDS NO.89-3722), demonstrating the forming of the silver nanoparticles. The prominent peaks on 2θ scale are 38.4, 44.6, 64.8, and 77.6° representing the (111), (200), (220), and (311) reflections of the face centered cubic structure of the metallic silver, respectively. The well defined intense peaks showed excellent crystallinity of nano silver particles. Furthermore, peaks of Fig. 2a are stronger and sharper than Fig.2b, indicating that PVP is conducive to silver nanoparticles formation.[12,13] The average crystals size was obtained based on the Scherrer's equation, and the size was in the region of 88 nm. This result agrees with the SEM.

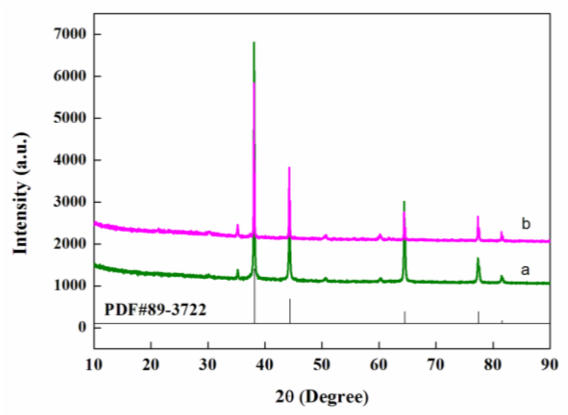


Figure 2. X-ray diffraction patterns as-prepared nano Ag cathode (a) PEG (b) PVP

3.2. Cyclic voltammogram behavior of CO_2 on nano-Ag in $BMIMBF_4$

Cyclic voltammogram (CV) behavior of CO_2 at the scan rate of 10 mV s^{-1} in $BMIMBF_4$ on nano silver electrode (area = 0.1 cm^2) was measured in an undivided cell at 25 °C with Pt (area =1 cm^2) as the counter electrode. The references electrode was Ag wire. All potentials are given with respect to this reference electrode. Fig. 3 shows the typical curves. It is not to consider IR-drop.

Fig. 3a shows that in neat $BMIMBF_4$ there is no reduction peak from -0.5 V to -2.7 V, and the current starts to increase at -2.4 V, due to the polarization of the $BMIMBF_4$.

In Fig. 3b, in CO_2 saturated $BMIMBF_4$, the CV displays two wide peaks at -1.8 V and -2.2 V, respectively. The -1.8 V peak is attributed to a single electron electroreduction of CO_2 to high energy intermediate CO_2•─.[2] The peak at -2.2 V is ascribed to further reduction of CO_2•─ with CO_2 adsorbed on the electrode surface. [3]

Fig. 3b also shows that on the nano Ag electrode, the process of electrochemical reduction is step by step. The Ep of one electron reduction of CO_2 is positive than the potential of further reduction of CO_2•─. Therefore, the electroreduction of CO_2 could obtain more CO_2•─ without interference from further reduction of CO_2•─ in this potential window. A number of research groups have dedicated their efforts to fundamental studies the electroreduction of CO_2 on a variety of electrode surfaces, and the results indicated that the CV of CO_2 is a signal peak. As we known in this potential range, electroreduction of CO_2 is a multistep reaction, a signal reduction peak illustrate that many kinds of CO_2 reduction reaction were not distinguished. So, there is always competition between one electron reduction of CO_2 and further reduction of CO_2•–, which results in low yield of DMC. In general, on the nano-Ag electrode, due to those nanostructure, one electron reduction of CO_2 and further reduction of CO_2•− was distinguished, which lead to less side reaction and the high yield of DMC.

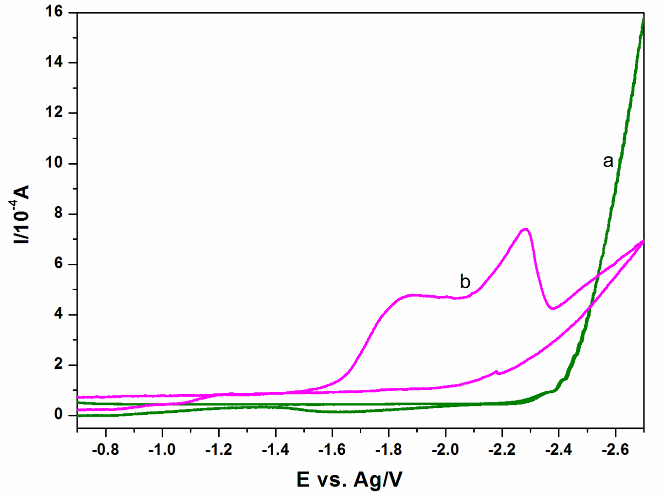


Figure 3. Cyclic voltammograms recorded with as-prepared nano Ag cathode (a) neat $BMIMBF_4$; (b) $BMIMBF_4$ saturated with CO_2.

3.3. Electrochemical reduction of CO_2 synthesis of dimethylcarbonate on nano-Ag electrode in $BMIMBF_4$

The potentiostatic experiments were performed at a constant potential in CO_2 saturated $BMIMBF_4$. At the end of electrolysis, methanol and CH_3I were added for synthesis of DMC. DMC: MS(m/z,%): 90(M$^+$,8),75(1),60(9), 59(77),45(100),33(8), 31(47), 29(36),28(8),15(37).

It is well known, in ionic liquid, temperature influence the viscosity and solubility of CO_2. Based on our experimental resulted, we chose 50 °C as reaction temperature. [2,3] To optimize experimental conditions, the effect of potential and charge passed on the yield of DMC was studied. All experimental results were summarized in Table 1.

No other product was found expect DMC in liquid produc at −1.8 V. Based on the quantitative analysis, DMC was given in yield 83% (table 1-2) on the nano-Ag electrode in $BMIMBF_4$, higher than that of the pure Ag electrode (74%).[1,2] This is possibly the electrochemical reduction of CO_2 on the nano Ag electrode is step by step. The Ep of one electron reduction of CO_2 is positive than the potential of CO_2•− further reduction. Under this condition, the electroreduction of CO_2 obtain more CO_2•− without interference from further reduction of CO_2•−. Furthermore, one-electron reduction of CO_2 generates CO_2•−., CO_2•− attacks the BMIM$^+$ to afford $CO_2^{\bullet-}$-BMIM$^+$, which is stable.[1] Finally, treatment of the composite with methanol and CH_3I gives DMC.

The potential of CO_2 one electron reduction peak was at −1.8 V, and −1.6 V, −1.9 V −2.1 V and −2.3 V were also chosen as the electrosynthesis potential. The results showed that no reaction could be observed without at -1.6 V. When potential was −1.9 V, the product was dimethoxybutane. When potential was more negative than −2.1V, at -2.3V, the obtained products were butanoicacidmethylester, and butanoicacid-2-methyl-methylester. According to the experimental results, the optimized potential for this electrosynthesis is -1.8 V.

The charge passed (Q) supplied to the electrodes during the reduction of CO_2 to $CO_2^{\bullet -}$ has a great influence on the yield of DMC. The experiments were investigated under a potential of -1.8 V. As shown in table 1(6-8), it had a higher value of 83% at 1.0 F mol^{-1}. Before this point, the yield was rapidly increased, because the concentration of $CO_2^{\bullet -}$ in $BMIMBF_4$ increased with increasing the charge consumption. After this point, superabundant $CO_2^{\bullet -}$ will favour the reaction where $CO_2^{\bullet -}$ reacted itself resulting in yield decrease.[1,2]

The gas products of the potentiostatic experiments were also studied. Results showed that, the gas product was dimethyl ether at −1.6 V, −1.8 V, −1.9 V, −2.1 V and −2.3 V. Further investigations on the mechanism are in progress.

Table 1. Reaction conditions and yield of DMC

Entry	Potential (V) vs. Ag	Q(F mol^{-1})	Liquid product	Gas product	Yield (%) (DMC)
1	-1.6	1.0	no	no	0
2	-1.8	1.0	DMC	d	83
3	-1.9	1.0	a	d	51
4	-2.1	1.0	b	d	0
5	-2.3	1.0	c	d	0
6	-1.8	0.8	DMC	d	60
7	-1.8	1.0	DMC	d	76
8	-1.8	1.2	DMC	d	52

a dimethoxybutane; b butanoicacidmethylester; c butanoic acid-2-methyl-methyl ester; d dimethyl ether

Dimethoxybutane, MS(m/z,%):103(M$^+$,9),87(100),55(84), 29(58).

Butanoic acid methyl ester, MS(m/z,%):102(M$^+$,4), 87(36), 74(100), 59(24), 43(97), 27(37), 15(27).

Butanoic acid-2-methyl-methyl ester, MS(m/z,%):101(M$^+$,22),88(85),69(8), 57(100),41(54),29(68).

Dimethyl ether,MS(m/z,%):46(M$^+$,46),45(100),29(81), 15(59).

4. CONCLUSIONS

The important nano silver particle electrode was successfully prepared by cyclic voltammogram. Cyclic voltammogram and electrochemical synthesis showed that nano silver particle electrode can used for CO_2 reduction in ionic liquid. Results indicated that the process of electrochemical reduction of CO_2 on this nano-Ag electrode in $BMIMBF_4$ is step by step, under this condition, one-electron reduction of CO_2 on nano-Ag electrode generates more CO_2•−, leads to more DMC. The electrolyses were studied at different potential without any toxic solvent, catalysts and supporting electrolytes. At -1.8 V (vs.Ag) DMC was obtained in good yield (83%). Moreover, no other product was found expect DMC. Efforts are under way to explore the mechanism of electrosynthesis of DMC on this electrode.

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