Electrosynthesis of Cyclic Carbonates from CO_2 and Epoxides on Compacted Silver Nanoparticles Electrode

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Electrosynthesis of cyclic carbonates from carbon dioxide with epoxides has been carried out at room temperature and normal pressure in a one-compartment electrochemical cell using silver nanoparticles electrode as cathode, avoiding any additional catalysts. To optimize the reation conditions, the effects of current densities, substrate concentration, charge amount and temperature have been investigated. Moreover, the generality of silver nanoparticles electrode for electrosynthesis of cyclic carbonates has been studied. From the results, all epoxides studied in this work could be converted into the corresponding cyclic carbonates with moderate to good yields (30%-70%). In addition, this electrode is stable and reusable which could be reused multiple times without activity loss.

1. INTRODUCTION

CO_2 is an easily available, cheap and renewable carbon feedstock which has shown potential to provide an alternative for some fossil-fuel-based chemical synthesis[1-4]. In recent decades, developing effective processes for chemicals and fuels by CO_2 conversion has drawn much attention. To our knowledge, products from CO_2 such as organic carbonates[5-8], polycarbonates[9-11], oxazolidines[12], alkylidene carbonates[13,14], CH_3OH[15-17], $HCOOH$[18], CH_4[19] have been reported. Among them, organic carbonates are versatile which widely been used in organic synthesis, drug synthesis, engineering plastics, lithium ion batteries, additives and other fields[20]. Thus, the synthesis of organic carbonates is one the most promising technologies for utilization of CO_2[21-23].

For the synthesis of five-membered cyclic carbonates, a classic and atom economical methodologies is the cycloaddition reaction of epoxides with CO_2. In the past decade, a large number of catalysts including metal complexes[6,24-30], phosphine[31-33], organic base[34-36], ionic liquid[37-48] have been used to realize the above transformation. Although high yields have been obtained by some workers, while drastic conditions often have to be used to activate inert CO_2. As we all know, the use of homogeneous catalysts is unfavorable, mainly due to separation difficulties; for heterogeneous catalyst separation is easy, but often with low catalyst activity and/or selectivity[49]. It is necessary as well as important to search for efficient and economical processes for synthesis of cyclic carbonates from CO_2 under mild conditions. Fortunately, electrochemical methods just meet the requirements[50-55]. What's more, nanoelectrode may solve the problem of catalysts[56,57].

In our former work[58], we utilization of NHC-CO_2 transfers CO_2 to diols, thereby providing a new synthetic procedure to prepare cyclic carbonates. In addition, copper nanoparticles (Cu NPs) were prepared and used as cathode for the cycloaddition reaction of CO_2 with epoxides, 31% to 86% yield of cyclic carbonates were obtained[52]. In the continuity of our previous works, silver nanoparticles (Ag NPs) were prepared by the reduction $AgNO_3$ with sodium borohydride ($NaBH_4$) or hydrazine hydrate ($N_2H_4 \cdot H_2O$) in aqueous solution. A powder was obtained after centrifugation-redispersion cycles and drying which compacted into a coin and used as the cathode for the electrocatalytic cycloaddition of epoxides with CO_2 (**Fig. 1**). It should be noted that this coin was prepared from pure Ag NPs powder without a support or carrier. Both the synthesis of the Ag NPs cathode and cycloaddition were performed under very mild conditions, and no other catalyst was needed.
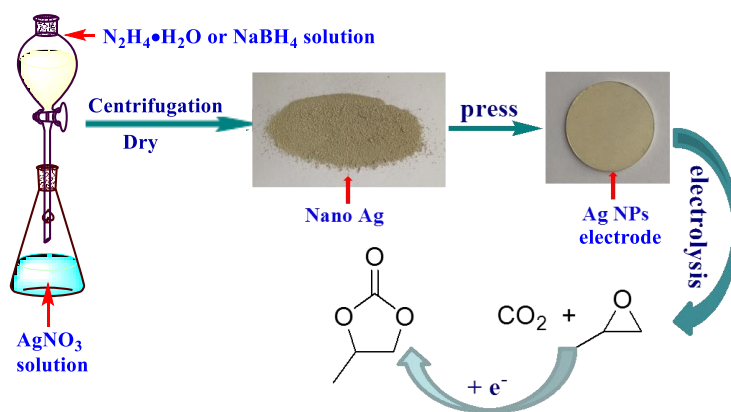
Figure 1. The synthetic procedure to prepare Ag NPs electrode and propylene carbonate.

2. EXPERIMENTAL

2.1. Apparatus and reagents

Galvanostatic electrosynthesis was carried out by a digital dc regulated power supply (HY3005MT, HYelec®, China). ^{1}H-NMR spectra were recorded on an Ascend 400 (400 MHz, Bruker, Germany) or AVANCE 500 (500 MHz, Bruker, Germany) spectrometer in $CDCl_3$ with Me_4Si as an internal standard. The product yield was determined by Gas Chromatography-Flame Ionization

Detector (GC-FID) (SHIMADZU, GC-2014). Microstructure and morphology of Ag NPs were analyzed using Hitachi S-4800 field emission Scanning Electron Microscope (FE-SEM). X-ray diffraction (XRD) patterns were recorded by a Ultima IV X-ray powder diffractometer using Cu Kα radiation (k= 1.5406 Å). All reagents were used as received .

2.2 Prepare compacted Ag NPs electrode

Ag NPs were prepared by the reduction $AgNO_3$ aqueous solution via a reducing agent such as $N_2H_4 \cdot H_2O$, $NaBH_4$ in the presence of surfactant (trisodium citrate/polyvinylpyrrolidone). A fine powder was achieved after centrifugation-redispersion cycles and drying. They were easily pressed into a coin and used as cathode.

Method A: 0.85 g $AgNO_3$ was dissolved in 100 mL deionized water. Then, 0.735 g trisodium citrate was added into the solution. After 5 min stirring, 6 mmol $NaBH_4$ was quickly added, and the mixture was stirred at 25°C for 4 h. Ag NPs was precipitated immediately. The products were washed and harvested with centrifugation-redispersion cycles. Then dried for 12 h at 35°C under vacuum. Ag NPs powder with the size of ~100 nm was obtained, labeled as Ag NPs_A.

Method B: Two steps including seeding and growth are undertaken. At first, silver seeds were prepared through the following steps: 0.02 g $AgNO_3$, 4.8 g polyvinylpyrrolidone was dissolved in 50 mL deionized water. After 5 min stirring, 18 μL ammonia water was added, then 0.0577 g $N_2H_4 \cdot H_2O$ (10%) was quickly added into the stirring mixture. Last, the mixture was stirred at 25°C for 2 h, sliver seeds with the size of 35 ± 10 nm were obtained. For the second step, the particle growth solution was prepared which contains 100 ml H_2O, 0.02 g $AgNO_3$, 6.8 μL ammonia water, 0.064 g hexadecyl trimethyl ammonium bromide (CTAB), 0.044g L(+)-ascorbic acid and 4 mL of silver seeds, the above solution was stirred at room temperature for 60 h. The products were washed and harvested with centrifugation-redispersion cycles. Then dried for 12 h at 35°C under vacuum. The particles with the mean diameter is about 390 ± 35 nm, labeled as Ag NPs_B.

2.3 General electrosynthesis

Typical galvanostatic electrolysis was carried out by digital dc regulated power supply in a solution of propylene oxide (PO, 0.1 M), supporting electrolyte tetraethyl ammonium iodide (TEAI, 0.1 M) and 10 mL MeCN saturated with CO_2 (1 atm) in an undivided glass cell (20 mL) equipped with a sacrificial magnesium (Mg) rod anode and Ag NPs cathode (d = 2 cm). Continuous CO_2 flow was maintained throughout the duration of the whole electrolysis process. After the consumption of 1.0 F mol^{-1} charge, the current was switched off. The electrolyte was distilled under reduced pressure, the residue was hydrolyzed with HCl (1 mol L^{-1}, 10 mL) and extracted with diethyl ether (15 mL× 4). And the organic layer was dried with anhydrous $MgSO_4$ for 5 h. After filtration and rotary evaporated, the product analyzed by GC to get the yield based on the starting substrates with *n*-decane as an internal standard. Separation of the pure products were carried out by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent.

4-Ethyl-1,3-dioxolan-2-one[58] **2b** GC-MS (m/z, %) 116 (M$^+$, 4), 87 (64), 71 (4), 57 (15), 43 (100); ^{1}H-NMR (500 MHz, CDCl$_3$): δ 1.04 (t, J = 8 Hz, 3H), 1.73-1.86 (m, 2H), 4.10 (t, J = 8 Hz, 1H), 4.54 (t, J = 8 Hz, 1H), 4.67 (q, J = 7 Hz, 1H).

4-Popyl-1,3-dioxolan-2-one[58] **2c** GC-MS (m/z, %) 129 (1), 102 (1), 87 (67), 71 (20), 57 (40), 43 (100); ^{1}H-NMR (500 MHz, CDCl$_3$): δ 0.99 (t, J = 7 Hz, 3H), 1.42-1.44 (m, 1H), 1.50-1.53 (m, 1H), 1.66-1.69 (m, 1H), 1.80-1.82 (m, 1H), 4.08 (t, J = 8 Hz, 1H), 4.54 (t, J = 8 Hz, 1H), 4.70-4.76 (m, 1H).

4-Phenyl-1,3-dioxolan-2-one[58] **2d** GC-MS (m/z, %) 164 (M$^+$, 66), 131 (1), 119 (15), 105 (32), 90 (100), 78 (71), 65 (19), 51 (25), 39 (13); ^{1}H-NMR (500 MHz, CDCl$_3$): δ 4.36 (t, J = 9 Hz, 1H), 4.83 (t, J = 9 Hz, 1H), 5.69 (t, J = 8 Hz, 1H), 7.27-7.48 (m, 5H).

4-(Chloromethyl)-1,3-dioxolan-2-one[59] **2e** GC-MS (m/z, %) 132 (M$^+$, 1), 87 (100), 64 (5), 43 (29), 28 (16) ; ^{1}H-NMR (400 MHz, CDCl$_3$): δ 3.72-3.78 (m, 2H), 4.43 (q, J = 8 Hz, 1H), 4.61(t, J = 8 Hz, 1H), 4.97-5.01 (m, 1H).

4,5-Dimethyl-1,3-dioxolan-2-one[58] **2f** GC-MS (m/z, %) 116 (M$^+$, 3), 101 (4), 86 (1), 73 (3), 57 (7), 43 (100), 38 (6), 28 (78); ^{1}H-NMR (500 MHz, CDCl$_3$): δ 1.46 (q, J = 6 Hz, 6H), 4.32-4.35 (m, 2H).

Tetrahydro-3aH-cyclopenta[d]-1,3-dioxol-2-one[52] **2g** GC-MS (m/z, %) 113 (2), 97 (12), 83 (37), 69 (100), 55 (77), 41 (89), 28 (40); ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.68-1.82 (m, 4H), 2.15-2.18 (m, 2H), 5.10 (d, J = 4 Hz, 2H).

Hexahydrobenzo[d]-1,3- dioxol-2-one[47] **2h** GC-MS (m/z, %) 128 (M$^+$, 7), 99 (4), 83 (14), 69 (3), 55 (100), 41 (20), 28 (19); ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.41-1.47 (m, 2H), 1.59-1.66 (m, 2H), 1.88 (q, J = 4 Hz, 4H), 4.67-4.72 (m, 2H).

3. RESULTS AND DISSCUSION

3.1. Characterization of Ag NPs

The material was characterized by FE-SEM and XRD (Fig. 2). Fig. 2f displays the XRD patterns of Ag NPs, which shows four peaks at 2*θ* values of 38.1º, 44.2º, 64.4º, and 77.8º. These peaks were indexed as the (111), (200), (220) and (311) planes of the Ag fcc structure. It is also notable that no trace of other substance crystal faces were observed. Some typical morphologies of silver nanoparticles obtained are shown in Fig. 2a-e. Incidentally, nanoparticles of Fig. 2a-c were synthesized by method A, while nanoparticles of Fig. 2d,e were synthesized by method B. Fig. 2a,b indicated that Ag NPs_A has a hierarchical structure composed of metal nanograins. These elementary particles were gathered into particles of ~100 nm often exhibiting a rod-like shape and aggregated further into a macroporous solid. The Ag NPs_B of Fig. 2d often exhibiting a spheres-like shape were obtained by seed-mediated growth of silver seeds (Fig. 2e) in the presence CTAB.
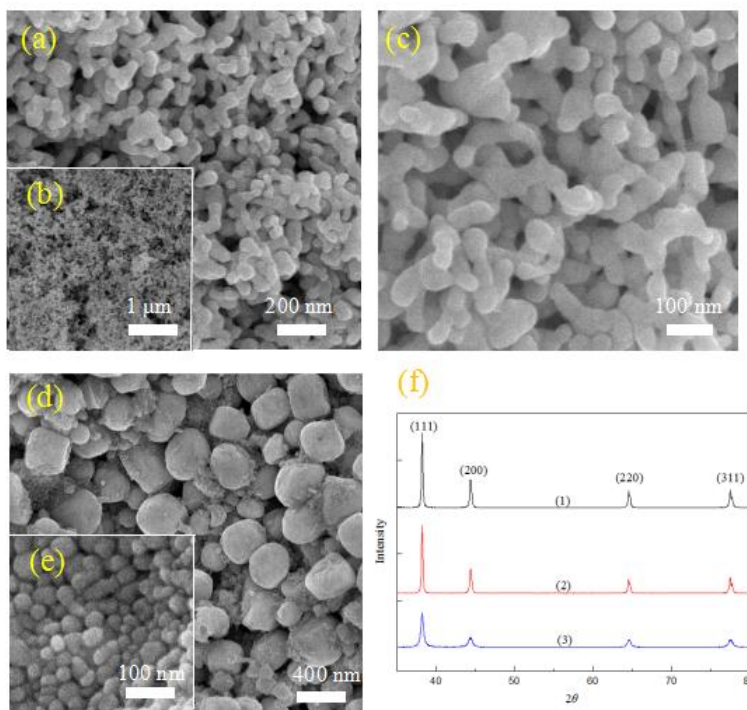
Figure 2. FE-SEM patterns (a-e) and XRD patterns (f) of Ag NPs_A as prepared (a-b, f-1) or reused for 10 times (c, f-2), Ag NPs_B (d, f-3) and sliver seed (e).

3.2. Electrosynthesis of propylene carbonate (PC) from CO_2 with PO

Firstly, PO (1a) was chosen as the model substrate to be investigated, and the optimized conditions were then applied to other epoxides. Galvanostatic electrolysis was carried out in CO_2-saturated MeCN containing 0.1 mol L^{-1} 1a in an undivided glass cell with Mg anode and Ag NPs cathode. The reactions were interrupted after consuming a specific amount of electricity. Then, PC (2a) was obtained as the main product (Fig. 1).

Before optimizing the procedure, the effectiveness of Ag NPs cathode was studied (Table 1, entries 1-4). Parallel experiments were performed under the same conditions, expect for the cathode. 24% yield of PC was got at Ag flake cathode (Table 1, entry 1), whereas 58% yield was achieved on Ag NPs_A cathode (Table 1, entry 2). It can be clearly seen that the Ag NPs electrode is superior to the Ag flakes. In order to prove this conclusion, Ag NPs with similar crystal form but different particle size (Fig. 2d,e) were prepared and used for the same reaction, 56% yield of PC (Table 1, entry 3) with Ag NPs_B and 60% yield with Ag seeds were obtained (Table 1, entry 4). These results agree with the above conclusion, which may be attributed to the far higher surface area of Ag NPs electrode. Since the morphology of silver nanoparticles synthesized by method A is regular and a larger amount of nanoparticles could be synthesized at one time, so the compacted Ag NPs_A electrode with the size of ~100 nm as the working electrode in the following experiments.

To optimize the procedure, the effects of different factors during the experiment such as current densities, the concentration of substrate, charge amount and temperature were studied. The results of the electrolysis are summarized in Table 1.

To investigate the effect of current density, experiments were carried out from 2 to 6 mA cm^{-2}, the 2a yield reaching a maximum (58%) at 3 mA cm^{-2} (Table 1, entries 2, 5-7). These results show that both low and high current densities would led to lower yields. That's because the electrochemical generation of the CO_2 radical anion requires a suitable potential[60,61]. The larger the current density was, the more negative the electrode potential would be, then other undesirable reactions (such as production of CO, oxalate) would be engendered. The relative amounts of oxalate and CO depend upon current density[62]. The smaller the current density was, the more difficult for CO_2 reduction[60,63], since direct electrochemical reduction of CO_2 occurs at rather negative potentials in most solvents[60].

Table 1. Electrosynthesis of PC from CO_2 with PO on Ag electrode[a]

Entry	Cathode	j (mA cm^{-2})	C (mol L^{-1})	Q (F mol^{-1})	T (^oC)	Yield[b] (%)
1	Ag flake	3.0	0.1	1.0	25	24
2	Ag NPs_A	3.0	0.1	1.0	25	58
3	Ag NPs_B	3.0	0.1	1.0	25	56
4	Ag seeds	3.0	0.1	1.0	25	60
5	Ag NPs_A	2.0	0.1	1.0	25	53
6	Ag NPs_A	4.0	0.1	1.0	25	48
7	Ag NPs_A	6.0	0.1	1.0	25	35
8	Ag NPs_A	3.0	0.05	1.0	25	44
9	Ag NPs_A	3.0	0.15	1.0	25	52
10	Ag NPs_A	3.0	0.2	1.0	25	46
11	Ag NPs_A	3.0	0.1	0.8	25	48
12	Ag NPs_A	3.0	0.1	1.5	25	67
13	Ag NPs_A	3.0	0.1	2.0	25	70
14	Ag NPs_A	3.0	0.1	2.5	25	71
15	Ag NPs_A	3.0	0.1	2.0	15	50
16	Ag NPs_A	3.0	0.1	2.0	35	56

[a] Electrolyses carried out in undivided cell, MeCN-TEAI = 0.1 mol L^{-1}, CO_2 pressure = 1atm;
[b] GC yield based on **1a**.

In the reaction, PO is one of the main raw materials, its concentration would affect the speed and extent of reaction. Thus, it is expected that the yield of **2a** will be different with various concentrations. To verify this speculation, four different concentrations 0.05 mol L^{-1}, 0.1 mol L^{-1}, 0.15 mol L^{-1} and 0.2 mol L^{-1} have been tried here (Table 1, entries 2, 8-10), 44%, 58%, 52%, 46% yield of 2a was obtained respectively. These results are consistent with what we expected. At lower concentration the contact opportunity of PO and CO_2 decreased resulted in lower yield[64]. With the increased of the substrate concentration, electrolytic time would be increased. Mg^{2+} plays an important role in cycloaddition of epoxides with CO_2[50,51]. As the reaction progresses, Mg anode is constantly being sacrificed to form magnesium salts attached to the Mg electrode, thus hindering the further cycloaddition of epoxides with CO_2. Continued electrolysis may lead to side effects[65], resulting in

lower yield. So the optimized PO concentration is 0.1 mol L^{-1}.

In order to test the influence of the charge amount and temperature, other experiments have been performed. The yield of **2a** increased with increasing the charge amount. It reaches a peak value at 2.0 F mol^{-1} (Table 1, entry 14). The temperature influences the reaction rate as well as the solubility of CO_2[66], which is a factor of key. Increased temperature from 15°C to 25°C favored the reaction (Table 1, entries 13, 15), but further increased temperature resulted in lower yield (Table 1, entry 16). The highest yield (70%) was achieved at 25°C.

3.3. Reuse of compacted Ag NPs electrode

Ag NPs could be reused in the next run after simply polishing and cleaning that used in the previous run. The reuse of Ag NPs_A was studied under optimized conditions of Table 1, entry 13. As shown in Fig. 3, the PC yield maintained at around 70% for 10 times. This indicates that Ag NPs electrode as cathode could be reused in electrosynthesis of cyclic carbonates. In order to further study the stability of Ag NPs electrode, it was characterized by XRD before (Fig. 2f-1) and after (Fig. 2f-2) the electrosynthesis for 10 times. According to XRD patterns, the component of Ag NPs_A electrode had not been changed during the electrosynthesis procedure. In addition, its particle size and structures had been maintained (Fig. 2c). Therefore, the Ag NPs_A electrode is highly stable and reusable.
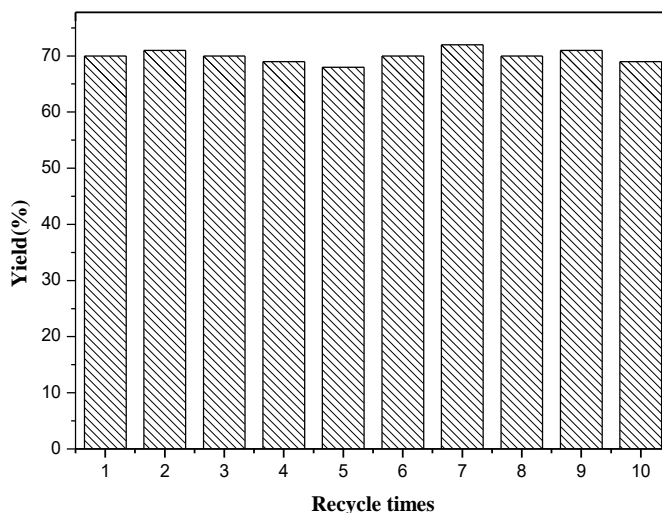
Figure 3. Reuse of Ag NPs_A electrode in the electrosynthesis of PC. Reaction conditions as Table 1 entry 13.

3.4. Electrosynthesis of other cyclic carbonates on Ag NPs electrode

To test the applicability of this methodology, the investigation was extended to other epoxides, mono substituted epoxides such as 1-butene oxide (**1b**), 1-pentene oxide (**1c**), styrene oxide (**1d**), epichlorohydrin (**1e**), disubstituted epoxides such as 2-butene oxide (**1f**), cyclopentene oxide (**1g**), cyclohexene oxide (**1h**). The results of these electrolyses carrying out under the previous optimized

conditions (Table 1, entry 13) are reported in Table 2. In all case, the corresponding cyclic carbonate was obtained. The results indicate that the size of the substituent of the epoxide influenced the reaction yield, as the substituent varies from methyl, ethyl, and propyl (entries 1-3), the yield decreases in the order 2a>2b>2c. The yield of 2d (entry 4) is approximated to that of 2b (entry 2) and higher than that of 2c (entry 3), which might be attributable to the weakening of the benzylic C-O bond of the oxirane ring of 1d by conjugation to the phenyl ring[52]. Generally, mono substituted epoxides gave better yield than that of disubstituted epoxides except for 1e. The low yield of 2e (entry 5) might due to secondary reactions including the CH$_2$Cl substituent. The CH$_2$Cl substituent in epichlorohydrin is weakly electron withdrawing, which should have little effect on its reactivity. Possible side reactions with epichlorohydrin could give propanol and a hydroxylactam. The lowest yields were obtained with the disubstituted epoxides 1f, 1g, and 1h (entries 6-8) probably attributable to the intrinsic lower reactivity but also might be due to the size of the substituent.

Table 2. Electrosynthesis of cyclic carbonates on Ag NPs_A electrode[a]

Entry	Substrate		Product		Yield (%)[b]
1		1a		2a	70
2		1b		2b	57
3		1c		2c	50
4		1d		2d	56
5		1e		2e	34
6		1f		2f	39
7		1g		2g	35
8		1h		2h	30

[a] Electrolysis were carried out under the same conditions as **Table 1**, entry 13.
[b] Mass yield, determined by GC.

4. CONCLUSIONS

In conclusion, a compacted Ag NPs cathode was prepared via simple chemical reduction without any supporter or carrier, which was effective for the electrocatalytic cycloaddition of epoxides

with CO_2. Under optimized conditions, propylene carbonate with 70% yield was obtained, moderate to good yield of cyclic carbonates could also be achieved with other epoxides without any metal-catalyst additive. Moreover, this Ag NPs cathode has remarkable stability and reusability.

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