Supporting Information

Atomic zinc dispersed on graphene synthesized for active CO₂ fixation to cyclic carbonates

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1. General Experimental Methods

General materials

Graphite (99.95% purity) was obtained from Qingdao Huarun Graphite Co., Ltd., Chemically pure hydrochloric acid (HCl, 37%), sodium oleate (Na-Oleate), oleic acid (OA), zinc chloride (ZnCl₂), cobalt chloride (CoCl₂), ferric chloride (FeCl₃), ethanol, hexane and melamine were purchased from Sinopharm Chemical Reagent Co., Ltd. All aqueous solution was prepared by deionized water. Unless otherwise noted, carbon dioxide (99.99%) was employed. Commercially available epoxides and $({}^{n}C_{n}H_{2n+1})_{4}NBr$ (n = 2-4 and 7), 3,4-Epoxytetrahydrofuran (96% purity) and 4-vinyl-1-cyclohexene-1,2-epoxide (mixture of two isomers, 98% purity) were purchased from Aladdin and used as received. All reactions were carried out without any special precautions against air. All chemicals were used without further purification.

Material preparation

The zinc–oleate complex was prepared by reacting zinc chloride and sodium oleate as described elsewhere.^[S1] Briefly, 24 mmol ZnCl₂ and 36 mmol sodium oleate was dissolved in a mixture solvent composed of 18 ml distilled water, 24 ml ethanol, and 42 ml hexane and 1 mL HCl. The resultant solution was heated to 70 °C and kept at this temperature for 4 hours under stirring and reflux. The reactant was then washed with distilled water in a separatory funnel several times and evaporated off hexane, resulting a thick milk-colored waxy zinc-oleate complex.

In a typical synthesis, 0.2 g electrochemically exfoliated graphene powder was mixed with 3 mmol zinc-oleate complex, 2 mmol oleic acid and 3 mmol melamine by using a pestle and mortar. The slurry was then heated to 800 °C at a heating rate of 10 °C min⁻¹ and kept at 800°C for two hours under argon atmosphere in quartz tube furnace. The product (*NG-ZnO*) was then washed with 10 % volume ratio HCl solution and water for the removal of resultant zinc-based nanoparticles for several times sequentially, and dried at 60°C overnight to give atomic zinc coordinated *@* nitrogen doped graphene (*NG-aZnN*). For comparison, half of zinc-oleate complex

was also employed to make *NG-aZnN-L* (*L*: low zinc content) by using the same process.

As control samples, iron-oleate complex and cobalt-oleate complex was also used to prepare Fe species coordinated @ N doped graphene (*NG-Fe*) and Co species coordinated @ N doped graphene (*NG-Co*) catalyst using the same aforementioned preparation process.

In order to evaluate the significance of graphene support, sample without the introduction of graphene was also made as NC-ZnO using the same preparation process. Moreover, pure graphene (G) and nitrogen doped graphene (NG) was also prepared and evaluated.

Instrumental characterization

Scanning electron microscopy (SEM) images were obtained on a field-emission SEM JSM-7001F (FESEM) operating at 10 kV. X-ray diffraction (XRD) was recorded from 5 to 80° at a scan rate of 0.02° s⁻¹ using the Cu Ka 1.5406 Å radiation. Transmission electron microscopy (TEM) images were taken with FEI, TECNAI G2 F20 microscopy at acceleration voltage of 200 kV. HAADF-STEM was performed on a JEM ARM200F equipped with double aberration correctors in Institute of physics, Chinese Academy of Sciences, and a cold field emission gun operated at 200 kV. STEM images were recorded using a HAADF detector with a convergence angle of 25 mrad and a collection angle between 70 and 250 mrad. Under these conditions, the spatial resolution is ca. 0.08 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed using Thermo ESCALAB 250 spectrometer, employing an Al-KR X-ray source with a 500 µm electron beam spot. The Brunauer-Emmett-Teller (BET) specific surface area was deduced from the N₂ physical adsorption measurement data that were obtained using an ASAP 2010 Accelerated Surface Area and Porosimetry System. X-ray absorption near-edge structure (XANES) measurements at Zn K-edge in transmission mode were performed at the BL14W1 in Shanghai Synchrotron Radiation Facility. The electron beam energy was 3.5 GeV and the stored current was 230 mA (top-up). The raw data

analysis was performed using IFEFFIT software package according to the standard data analysis procedures. ¹H NMR spectra was recorded on Bruker AVANCE III 400 MHz spectrometers using CDCl₃ as solvent referenced to CDCl₃ (7.26 ppm). ¹³C NMR was recorded at 100.6 MHz in CDCl₃ (77.00 ppm). Multiplets were assigned as singlet, doublet, triplet, doublet of doublet, multiplet and broad singlet. High resolution mass spectrometry was conducted using a Bruker micrOTOF-Q III by ESI technique.

Procedure for the cycloaddition of CO_2 and propylene oxide according to the following Scheme



Take cycloaddition of CO_2 with propylene oxide 1a as an example: the reaction was carried out in a stainless steel autoclave (50 cm³ inner volume) with a stir bar. NG-aZn (15 mg, 0.12 mol%Zn content on the basis of substrate 1), (ⁿC₇H₁₅)₄NBr (49.1 mg, 0.5 mol%) and propylene oxide (1.40 mL, 20 mmol) was successively introduced and sealed at zero temperature (ice-water mixture). The pressure was adjusted to 1 MPa at the preset temperature and the autoclave was heated at that temperature for the preset time. After the reaction was completed, the reactor was cooled in ice-water bath, and then excess of CO₂ was carefully vented. The mixture was diluted with ethyl acetate, and the yield of cyclic carbonate was determined by gas chromatograph (Agilent 6890) equipped with a capillary column (HP-5 30 m \times $0.25 \mu m$) using a flame ionization detector using biphenyl (0.20 g) as the internal standard. Then, the residue was obtained by removing the solvent under vacuum and further purified by column chromatography with ethyl acetate-petroleum ether as the eluent to obtain the desired product. All cyclic carbonates have been reported previously and the characterization data are all in good agreement with literature value.

2. Supplementary Experimental Results



Fig. S1 TEM images of electrochemically exfoliated graphene sheets.



Fig. S2 TEM images of intermediate product of NG-ZnO.



Fig. S3 Raman spectra of graphene and NG-aZnN.

Fig, S3 shows the Raman spectra of graphene and NG-aZnN, in which D (~1340 cm⁻¹) and G (~1560 cm⁻¹) peaks reflect the population of structural defects and the index of graphitization, respectively. The extent of defects could be quantified by calculating the relative intensities of these two peaks (I_D/I_G). It is clearly shown that after the thermal pyrolysis, NG-aZnN own more introduced defects, which could benefit for the anchoring and stabilization of atomic Zn atoms.



Fig. S4 SEM images of (a) directly pyrolyzed NG-ZnO and (b) acid washed NG-aZn.



Fig. S5 (a) high-angle annular dark field image of NG-aZnN and (b) corresponding bright-field STEM image, the bright spots on left and dark spots on right are corresponding to isolated Zn atoms.



Fig. S6 Fourier transform k^3 -weighted χ (k)-function of the EXAFS spectra of metallic Zn foil and ZnO and corresponding first shell fitting at (a, c) R space and (b, d) k space.



Fig. S7 (a) XRD patterns of graphene, NG-ZnO and NG-aZnN, (b) N2 adsorption/desorption isotherm of graphene and NG-aZnN, inset pore size distributions, (c) Long range XPS spectra of NG-ZnO and NG-aZnN, (d) spectra of Zn 2p3/2 region for NG-ZnO and NG-aZnN.



Fig. S8 The XPS spectra of (a) C 1s and (b) N 1s of NG-aZnN with the deconvolution.



Fig. S9 Investigation of temperature effect on the cycloaddition of CO_2 and propylene oxide. ^{*a*}

^{*a*}Reaction conditions: propylene oxide (1.16 g, 20 mmol), NG-aZnN (15 mg), $({}^{n}C_{7}H_{15})_{4}NBr$ (0.5 mol%), 1 MPa CO₂, 1 h. ^{*b*}GC yield.



Fig. S10 ^{*a*}Reaction conditions: propylene oxide (1.16 g, 20 mmol), NG-aZnN (15 mg), (${}^{n}C_{7}H_{15}$)_4NBr (0.5 mol%), 120 °C, 1 h. ^{*b*}GC yield.



Fig. S11 Recyclability of NG-aZnN for cycloaddition of CO_2 and propylene oxide under 120 °C, 1 MPa, 3 h.



Fig. S12 HAADF image of NG-aZnN after the recyclability test.

Sample	C (at. %)	N (at. %)	Zn (at. %)	O (at. %)
NG-ZnO	70.93	11.13	8.62	9.32
NG-aZnN	78.41	10.11	1.57	9.91

 Table S1. Element compositions obtained XPS.

Table S2. Element compositions obtained via ICP-OES (Zn) and elemental analysis (C/N/O)

Sample	C (at. %)	N (at. %)	Zn (at. %)	O (at. %)
NG-ZnO	75.09	12.09	3.99	8.83
NG-aZnN	85.07	9.11	1.62	4.2

Table S3. EXAFS fitting obtained via IFEFFIT software package.

Sample	Path	N	R(Å)	$\sigma^{2}(\times 10^{-2} \text{ Å}^{2})$	$\Delta E_0(eV)$	R-factor
Zn Foil	Zn-Zn	6	2.64	1.55	3.18	0.08
ZnO	Zn-O 1	1	1.97	0.01	2.12	0.05
	Zn-O 2	3	2.07	6.2	3.13	
NG-aZnN	Zn-N	3.76	2.01	0.83	1.87	0.006

Table S4. Effect of Reaction Parameters on the Cycloaddition of CO₂ and Propylene Oxide ^a

$H_{3}C$ + CO_{2} Catalyst O + $H_{3}C$ $H_{3}C$ 2a						
Entry	Catalyst	Co-catalyst	T(°C)	P(MPa)	Time (h)	Yield (%) ^b
1	-	ⁿ Pr ₄ NBr	120	1	2	18.1
2	Graphene	ⁿ Pr ₄ NBr	120	1	2	41.5
3	NG-aZnN	ⁿ Pr ₄ NBr	120	1	2	75.5
4	NG-aZnN	Et ₄ NBr	120	1	2	61.5
5	NG-aZnN	ⁿ Bu ₄ NBr	120	1	2	83.8
6	NG-aZnN	$({}^{n}\mathrm{C}_{7}\mathrm{H}_{15})_{4}\mathrm{NBr}$	120	1	2	94.6
7	NG-aZnN	(ⁿ C ₇ H ₁₅) ₄ NBr	120	1	3	>99(85) ^c
8	NG-aZnN	("C7H15)4NBr	160	1	1	84.1
9	NG-aZnN	$(^{n}C_{7}H_{15})_{4}NBr$	160	3	1	97.9(96) ^c
10	NG-aZnN	$({}^{n}\mathrm{C}_{7}\mathrm{H}_{15})_{4}\mathrm{NBr}$	160	3	0.5	91.7

^{*a*} Reaction conditions: propylene oxide (1.16 g, 20 mmol), or NG-aZnN (15 mg), ^{*n*}R₄NX (0.5 mol%). ^{*b*} Determined by GC using biphenyl as the internal standard. ^{*c*} Recovered catalyst for the second run.

3. Characterization Data of the Products



4-Methyl-1,3-dioxolan-2-one (**2a**) Colorless liquid. ¹H NMR (CDCl₃, 400 MHz) δ 4.84-4.92 (m, 1H), 4.58 (t, *J* = 8.4 Hz, 1H), 4.04 (t, *J* = 8.4 Hz, 1H), 1.49 (d, *J* = 6.0 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) δ 155.1, 73.7, 70.7, 19.4 ppm.



4-Ethyl-1,3-dioxolan-2-one (**2b**) Colorless liquid. ¹H NMR (CDCl₃, 400 MHz) δ 4.62-4.69 (m, 1H), 4.51 (t, J = 8.2 Hz, 1H), 4.05-4.09 (1H), 1.68-1.86 (m, 2H), 1.01 (t, J = 7.6 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) δ 155.1, 78.0, 69.0, 26.9, 8.4 ppm.



4-*n***-Butyl-1,3-dioxolan-2-one (2c)** Colorless liquid. ¹H NMR (CDCl₃, 400 MHz) δ 4.66-4.73 (m, 1H), 4.52 (t, *J* = 8.0 Hz, 1H), 4.06 (dd, *J* = 7.3 Hz, *J* = 8.0 Hz, 1H), 1.63-1.85 (m, 2H), 1.30-1.49 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) δ 155.1, 77.0, 69.4, 33.5, 26.4, 22.2, 13.8 ppm.



4-Phenyl-1,3-dioxolan-2-one (**2d**) White solid. ¹H NMR (CDCl₃, 400 MHz) δ 7.44 (d, ³*J* = 6.4 Hz, 3H), 7.36 (d, *J* = 7.6 Hz, 2H), 5.70 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.35 (t, *J* = 8.4 Hz, 1H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) δ 157.7, 154.7, 129.6, 121.9, 114.6, 74.1, 68.8 66.2 ppm.



4-*i***-Propoxy-1,3-dioxolan-2-one (2e)** Colorless liquid. ¹H NMR (CDCl₃, 400 MHz) δ 4.82 (m, 1H), 4.50 (t, *J* = 8.0 Hz, 1H), 4.38 (dd, *J* = 8.0 Hz, *J* = 15.6 Hz, 1H), 3.58–3.70 (m, 3H), 1.16 (t, *J* = 6.4 Hz, 6H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) δ 155.2, 75.3, 72.9, 67.1, 66.4, 21.9, 21.8 ppm.

4-((Allyloxy)methyl)-1,3-dioxolan-2-one (2f) Colorless liquid. ¹H NMR (CDCl₃, 400 MHz) δ 5.81-5.91 (m, 1H), 5.20-5.30 (m, 2H), 4.79-4.84 (m, 1H), 4.37-4.52 (m, 2H), 4.03-4.06 (m, 2H),

3.59-3.70 (m, 2H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) *δ* 154.9, 133.6, 117.9, 75.0, 72.6, 68.8, 66.2 ppm.

4-Phenoxymethyl-1,3-dioxolan-2-one (**2g**) White solid, mp: 99-100 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.31 (t, J = 8.0 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 5.02-5.04 (m, 1H), 4.62 (t, J = 8.4 Hz, 1H), 4.55 (dd, J = 8.4 Hz, J = 6.0 Hz, 1H), 4.24 (dd, J = 3.6 Hz, J = 10.8 Hz, 1H), 4.16 (dd, J = 4.4 Hz, J = 10.8 Hz, 1H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) δ 157.8, 129.7, 122.1, 114.7, 74.1, 66.9, 66.3 ppm.



Hexahydrobenzo[1,3]dioxol-2-one (2h) Slight yellow liquid. ¹H NMR (CDCl₃, 400 MHz) δ 4.67 (m, 2H), 1.88 (d, J = 5.4 Hz, 4H), 1.56-1.65 (m, 2H), 1.36-1.45 (m, 2H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) δ 155.3, 75.7, 26.7, 19.1 ppm.



Tetrahydrofuro[3,4-d][1,3]dioxol-2-one (2i) White solid. ¹H NMR (CDCl₃, 400 MHz) δ 5.17-5.21 (m, 2H), 4.18 (d, 2H), 3.49-3.55 (m, 2H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) δ 154.4, 80.1, 72.8 ppm. HRMS (ESI): C₅H₆O₄Na⁺ for [M+Na]⁺ calculated 153.0158, found 153.0154.



5-Vinylhexahydrobenzo[d][1,3]dioxol-2-one (2j) (mixture of isomers) Colorless liquid. ¹H NMR (CDCl₃, 400 MHz) δ 5.67-5.78 (m, 1H), 4.98-5.07 (m, 2H), 4.62-4.80 (m, 2H), 1.96-2.35 (m, 3H), 1.53-1.83 (m, 3H), 1.12-1.40 (m, 1H) ppm. ¹³C NMR (CDCl₃, 100.6 MHz) δ 155.1, 140.9 (140.8), 114.3 (114.0), 75.6 (75.5), 75.1, 36.4, 33.8 (33.5), 31.6, 26.6, 25.8 (25.7), 25.0 ppm. HRMS (ESI): C₉H₁₂NaO₃⁺ for [M+Na]⁺ calculated 191.0679, found 191.0695.

4. NMR Spectrum of the Products





^o/_{"Bu} **2c** ¹H NMR (CDCl₃, 400 MHz)







-0.00



2e ¹H NMR (CDCl₃, 400 MHz)



2f ¹H NMR (CDCl₃, 400 MHz)





7.7 7



 \checkmark **2h** ¹H NMR (CDCl₃, 400 MHz)



 $2i^{1}H$ and ^{13}C NMR

- 7.26 - 7.26 - 7.26 - 7.19



2j (mixture of isomers) ¹H and ¹³C NMR



Reference

[S1] Wang, C.; Zhang, H.; Zhang, Y.; Cheng, M.; Zhao, H.; Wang, J. Chem. Mater. **2017**, *29*, 9915-9922.