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

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CO₂ fixation to cyclic carbonates is important but depends on the catalyst. Here, atomic zinc (1.62 at%) dispersed on graphene was synthesized as a high-performance heterocatalyst for the cyclo-addition reaction of epoxides and CO₂. High yield (99%) and high selectivity (98%) of propylene carbonate with a TOF of 2889 h⁻¹ were achieved. [ZnN_{3.76±0.2}] was the active site, which was proved by advanced characterization, including synchrotron XANES, EXAFS and XPS and comparative performance tests.

The rapidly increasing level of carbon dioxide (CO_2) in the atmosphere has raised global environmental and societal concerns. Tremendous efforts have been devoted to CO₂ fixation, regardless of the debate about the relationship between CO_2 level and global warming. Indeed, the nontoxic, nonflammable, abundant and renewable C1 feedstock features CO₂ as a green carbon source for organic transformations.1 Cyclic carbonates are industrially important as polar aprotic solvents and electrolytes in batteries, and as valuable intermediates for dimethyl carbonate, polycarbonates and other fine chemicals. Currently, the commercial production of cyclic carbonates is based on the catalyzed cycloaddition of epoxides and renewable CO₂.² Among the developed methods, greater attention has been paid to heterogeneous catalytic schemes than to homogeneous strategies due to their low cost, easy separation and recyclability benefits.3 Traditional well-defined heterogeneous catalysts mainly include metal-containing salts,⁴ poly(ionic liquid) and ionic liquid/metal/amino-supported types (with various supports: MOFs,⁵ polymers,⁶ silica,⁷ and other materials⁸). Although great efforts have been made, their complicated preparations and limited

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activity still hinder the exploration of next-generation heterogeneous catalysts for efficient CO_2 fixation. Moreover, the broad size distributions and irregular morphology of the aforementioned catalysts could bring about multiple active sites with different performances, resulting in unwanted by-products and an ambiguous catalytic mechanism.⁹ Therefore, developing a robust supported catalyst with efficient activity, uniform active sites, economic metal loading and gentle catalytic conditions for chemical transformation is imperative but challenging.

Single atom catalysts (SACs), in which metal atoms are dispersed on the support at an atomic level, featuring a theoretical maximized 100% dispersion and extremely high efficiency of metal utilization, have triggered vast attention and been applied in many heterogeneous reactions.¹⁰ Significantly, compared with conventional particle catalysts with different activities brought about by the diverse reactive sites,9 the uniform active sites with higher selectivity of SACs offer great promise for potentially making the catalytic conditions gentler with increasing energy efficiency. Recently, atomically dispersed transition metals have exhibited advances for the electrochemical reduction of CO₂ to CO.¹¹ To the best of our knowledge, the use of a SACs-catalyzed strategy in the conversion of CO₂ to value-added chemicals has not been reported. Herein, an unprecedented atomic Zn coordinated@N doped graphene (NG-aZnN) SAC was fabricated and exhibited remarkable activity for fixing CO₂ to cyclic carbonates. The NG-aZnN presents a novel and superior catalytic species for CO2 conversion via activating the epoxides and further catalyzing the reaction smoothly, with excellent TON and TOF values. The unsaturated local chemical environment of atomic Zn, coordinated with doped nitrogen atoms, was carefully characterized through electron microscopy and synchrotron spectroscopy, unveiling the key active sites for CO₂ fixation to cyclic carbonates.

Initially, Zn-based SAC was prepared as shown in Fig. 1a. Electrochemically exfoliated graphene (G) (Fig. S1, ESI⁺) was mixed with zinc–oleate complex and melamine. The N atoms would be doped on planar graphene to provide additional electron lone pairs to anchor and stabilize the metal ions in a mononuclear organometallic complex during pyrolysis, as previously reported.^{10b} Due to

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Fig. 1 (a) Schematic graph showing the synthesis of NG–aZnN, (b) TEM and (c) STEM images of NG–aZnN, and EDS colour mapping of (d) C, (e) O, (f) N and (g) Zn, respectively.

the limited doping level in graphene, the excessive metal ions would inevitably aggregate and form Zn-based nanoparticles (NG–ZnO). After acid leaching to remove oxide species and impurities, the novel single atom catalyst, namely the atomic Zn coordinated@N doped graphene (NG–aZnN), was fabricated.

Transmission electron microscopy (TEM) was used to characterize the obtained NG-aZnN catalyst, as shown in Fig. 1b, where hollow graphitic shells were dispersed on nitrogen doped graphene (NG). The graphitic degree of raw G and NG-aZnN is shown in Fig. S3 (ESI[†]). The absence of large nanoparticles validates the successful removal of excess Zn-based nanoparticles. To further verify the composition of NG-aZnN, energy-dispersive spectroscopic (EDS) mapping was performed, as shown in Fig. 1c-g. The chemical mapping confirmed that the bright spots correspond to the presence of C, N, O and Zn, respectively. Significantly, the overlapping distribution of Zn and N signals suggests that Zn atoms could be surrounded by doped N atoms, which would be further verified via synchrotron spectroscopy. The detailed chemical composition was further obtained by XPS, ICP-OES and elemental analysis (Tables S1 and S2, ESI†). The atomic Zn loading in NG-aZnN was about 1.62 at% (ICP-OES), which is significantly higher than that reported for transition metal based SACs.¹⁰

To give direct evidence of atomic Zn coordinated@N doped graphene, sub-angstrom-resolution, high-angle annular dark field (HAADF) imaging in an aberration-corrected STEM (AC-STEM) was performed. As shown in Fig. 2a, abundant bright dots, corresponding to heavier Zn atoms, are well-dispersed on the NG surface. The measured size of these bright dots ranges from 1.2 to 2.5 Å, corresponding to the size of individual Zn atoms. Synchrotron X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at the Zn K-edge were employed to explore the metal coordination environment and unveil Zn bonding configurations in NG–aZnN, along with model samples of Zn foil and ZnO, as shown in Fig. 2b. The XANES curve of NG–aZnN shows a near-edge absorption energy between those of ZnO and Zn foil, implying isolated Zn atoms carrying positive charges. In Fig. 2c, the corresponding Fourier transformed (FT)



Fig. 2 (a) HAADF-STEM images of NG-aZnN, (b) Zn K-edge XANES spectra of Zn foil, ZnO and NG-aZnN; the inset shows the simulated Zn configuration, (c) Fourier transform k^3 -weighted $\chi(k)$ -function of the EXAFS spectra, (d) first shell fitting of NG-aZnN and corresponding EXAFS fitting curves at *R* space and *k* space (inset).

 k^3 -weighted EXAFS curves are extracted to probe the local structure. The FT-EXAFS curves show that the Zn atom in NG-aZnN displays a different local structure with neither metallic Zn nor ZnO. NG-aZnN did not present any prominent peaks at the positions of Zn–Zn (2.27 Å) or Zn–O (1.63 Å). Remarkably, a distinctive first coordination shell scattering peak at 1.56 Å for potential Zn-N bonding could be labelled, implying that most Zn atoms in NG-aZnN form Zn-N moieties, which is consistent with the previous EDS obervation.^{12a} EXAFS spectra fitting was performed to extract the structural parameters and obtain the quantitative chemical configuration of the Zn atoms (Fig. 2d). The obtained coordination number of the Zn atom is about 3.76 \pm 0.2 for NG-aZnN with an R factor of 0.006 (Table S1, ESI⁺). Moreover, the absence of Zn-Zn in NG-aZnN is in good agreement with TEM and HAADF-STEM results that show that all the Zn species are atomically coordinated without any particle aggregation. The consistency of the EXAFS spectra and the corresponding fittings shown in Fig. 2d, therefore, confirms our simulated atomic Zn bonding configurations. This Zn-N bonding could also be verified by the subtle red-shift observed in the Zn 2p3/2 region for NG-aZnN and NG-ZnO,¹² (Fig. S7d, ESI[†]) and the C/N element XPS (Fig. S8, ESI[†]).

As in previous studies, the cycloaddition of epoxides and CO₂ undergoes an electrophilic activation and nucleophilic attack synergistic catalytic mechanism.^{2a,3,6a} Therefore, NG–aZnN could potentially activate the epoxides and further initiate the reaction efficiently. Firstly, the model cycloaddition reaction of propylene oxide (PO) and CO₂ to propylene carbonate (PC) was investigated. In order to find the most suitable catalytic system and conditions, detailed experiments were performed, as listed in Table S4 (ESI†). A low PC yield was detected when only tetra-*n*-propylammonium bromide (TPAB) was used (entry 1). Interestingly, the combination of graphene or NG–aZnN with TPAB as catalyst rendered remarkable yields up to 41.5% and 75.5%, respectively (entries 2 and 3). The increase in the carbon chain in quaternary ammonium salt is also beneficial to improving the product yield (entries 3–6), which



Fig. 3 The yields of PC (**2a**) using different catalysts; reaction conditions: **1** (20 mmol), catalyst (15 mg), $(^{7}C_{7}H_{15})_{4}NBr$ (49.1 mg, 0.5 mol%), 120 °C, 1 MPa, 3 h. The inset: cycloaddition of CO₂ and PO to produce PC.

could be attributed to the enhanced solubility of the co-catalyst in the reaction system. The quantitative yield could be obtained for 3 hours under the optimized conditions (entry 7). Moreover, the increase in temperature and pressure could distinctly accelerate the reaction rate (Fig. S9 and S10, ESI†). Therefore, based on a screening of the reactive parameters, 120 °C, 1 MPa and 3 h reaction time (or 160 °C, 3 MPa, 1 h) with ($^{n}C_{7}H_{15}$)₄NBr as the co-catalyst would be the optimized conditions and were employed for the following tests.

Fig. 3 exhibits the PC yields using different graphene and zincbased catalysts (Material preparation, ESI†) under the optimized catalytic conditions. A limited yield of 47.0% was detected when only (ⁿC₇H₁₅)₄NBr was used (only co-catalyst). The addition of the following catalysts, pure G, NG and nitrogen doped carbon-zinc oxide (NC-ZnO), exhibited surprisingly negative effects on the cycloaddition reaction. This performance degradation should be attributed to the lack of active sites in either G/NG or ZnO for the electrophilic activation process during the reaction; moreover, the large lateral size and limited surface areas of G could potentially block the transport of reactive species, leading to compromised performances. The iron content also shows limited catalytic activity, exhibiting a similar yield to only co-catalyst. Interestingly, NG-Co could enhance the yield of PC to 65.1%, revealing that the cobalt species could facilitate the cycloaddition of CO₂ and propylene oxide.¹³ Comparatively, the intermediate NG-ZnO demonstrates a yield of 2a of 94.1%, which could be further improved to more than 99.0% after acid leaching to remove inactive ZnO for the zinc-based NG-aZnN SAC. It should be noted that even when the feeding ratio of zinc precursor was decreased to half of the original, the yield of 2a was still above 75.1%, indicating the excellent catalytic activity of atomic Zn coordinated@N doped graphene.

To investigate the scope of this novel atomic Zn catalyst, a series of typical terminal and internal epoxide substrates (1a–h) were examined. As shown in Table 1, under two different schemes, a variety of target cyclic carbonates 2a–d were obtained in almost quantitative yield and excellent selectivity through the reaction of the corresponding terminal epoxides bearing an aliphatic or aromatic group and CO_2 (entries 1–4). Notably, representative terminal epoxide substrates 1e–g embodying different functionalized groups were also verified, and delightfully, corresponding products 2e–g were acquired in good yields (entries 5–7).

 Table 1
 Substrate scope^a

	$R^1 \xrightarrow{O} R^2$	+ CO ₂ Catalyst	R^1 R^2 2	
Entry	Substrate 1	Product 2	Yield ^{b} (%)	Sel. ^c (%)
1	Н ₃ С 1а	H ₃ C 2a	98(98)	> 99(99)
2	Et 1b	Et 2b	97(98)	99(>99)
3	"Bu 1c	nBu 2c	98(97)	100(99)
4	Ph 1d	Ph 2d	93(97)	99(>99)
5	Y⁰ <u>, Å</u> 1e	,°,_,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	98(94)	>99(97)
6	~1f	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	98(99)	> 99(99)
7	PhO1g	Ph ⁻⁰ , -0 Ph ⁻⁰ , -0 2g	98(99)	99(99)
8	Å_1h	ے 2h	41(67)	99(98)
9		ب 2i	(39)	(99)
10	Ç 1j	چڑ 2j	(52)	(99)

^{*a*} Reaction conditions: **1** (20 mmol), NG–aZnN (15 mg, 0.12 mol% Zn content on the basis of substrate **1**), $({}^{n}C_{7}H_{15})_{4}NBr$ (49.1 mg, 0.5 mol%); protocol A (120 °C, 1 MPa, 3 h); protocol B (160 °C, 3 MPa, 1 h), the data in the parenthesis are obtained *via* protocol B. ^{*b*} Isolated yield. ^{*c*} Determined by GC using biphenyl as the internal standard.

However, the internal epoxides such as cyclohexene oxide exhibited limited reactivity, probably owing to the steric effect, and meanwhile the rise in temperature is beneficial to improving the efficiency (entry 8).

To further validate the efficaciousness of SAC and the methodology, a TON/TOF test was performed with a lower catalyst amount (Scheme 1). As a result, a quantitative yield of **2a** was obtained with a high TON of up to 8666 and a TOF of up to 2889 h^{-1} . Comparatively, other analogous heterocatalysts such as graphitic carbon nitrides and nitrogen doped carbons gave the target product with low TOF values (100–600).¹⁴ Moreover, with a lower catalytic loading, the higher TON was reached together with a high yield. These results confirmed the highly catalytic efficaciousness of an atomically dispersed zinc catalyst. The recyclability of



Scheme 1 TON/TOF experiments. (1) Reaction conditions: **1a** (11.6 g, 0.2 mol), 3 h; results: **2a**, 21 g, >99% yield, TON = 8666, TOF: 2889 h⁻¹. (2) Reaction conditions: **1a** (23.2 g, 0.4 mol), 9 h; results: **2a**, 36.2 g, 89% yield, TON = 15380, TOF: 1710 h⁻¹.



Scheme 2 Plausible atomic [ZnN] based reaction mechanism.

NG-aZnN was further examined (Fig. S11, ESI \dagger); the resultant decreased PC yield could be attributed to surface partial Zn aggregation after the reaction, as shown in Fig. S12 (ESI \dagger).

On the basis of previous reports and experimental investigation in this work, a tentative mechanism for the NG-aZnN-catalyzed cycloaddition reaction of CO₂ and epoxides could be plotted. It should be noted that for simplicity, a [ZnN₄] unit is schematically shown in Scheme 2. Initially, the functional site, *i.e.* $[ZnN_4]$ in NG-aZnN, interacts closely with the epoxide to polarize the C-O bond of the epoxide. Subsequently, the activated epoxide concurrently undertakes a ring-opening step upon nucleophilic attack by the bromide anion from the less-sterically-hindered carbon atom and gives an intermediate A (step 1). Next, the active site-stabilized alkoxide intermediate A is formed. Then, nucleophilic attack of the intermediate A at the CO₂ molecule generates the alkyl carbonate anion B (step 2). Finally, cyclic carbonate is produced via ring closing with regeneration of the catalytic species (step 3). In this process, the activation of epoxides and stabilization of intermediate were significantly enhanced via the functional site $[ZnN_4]$ and reactants' intermolecular interactions, leading to the excellent catalytic performances.

In summary, a novel single zinc atom catalyst was prepared through a facile pyrolysis method with an oleic zinc precursor. The atomic zinc was coordinated with doped nitrogen atoms and supported on a graphene sheet. This Zn-based SAC has demonstrated high efficiency for the synthesis of cyclic carbonates from epoxides and CO₂, with superior catalytic species for CO₂ conversion with a TON up to 8666 (TOF: 2889 h⁻¹). The unique and carefully characterized ZnN_{3.76±0.2} units were revealed as the dominant catalytic sites in the chemical transformation. We believe that our strategy can be further developed into a general approach to fabricate inexpensive heterogeneous catalysts for upgrading CO₂ through its incorporation into valuable chemicals with synergistic activation and catalysis.

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Conflicts of interest

There are no conflicts to declare.

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