A versatile route to fabricate single atom catalysts with high chemoselectivity and regioselectivity in hydrogenation

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Preparation of single atom catalysts (SACs) is of broad interest to materials scientists and chemists but remains a formidable challenge. Herein, we develop an efficient approach to synthesize SACs via a precursor-dilution strategy, in which metalloporphyrin (MTPP) with target metals are co-polymerized with diluents (tetraphenylporphyrin, TPP), followed by pyrolysis to N-doped porous carbon supported SACs (M1/N-C). Twenty-four different SACs, including noble metals and non-noble metals, are successfully prepared. In addition, the synthesis of a series of catalysts with different surface atom densities, bi-metallic sites, and metal aggregation states are achieved. This approach shows remarkable adjustability and generality, providing sufficient freedom to design catalysts at atomic-scale and explore the unique catalytic properties of SACs. As an example, we show that the prepared Pt1/N-C exhibits superior chemoselectivity and regioselectivity in hydrogenation. It only converts terminal alkynes to alkenes while keeping other reducible functional groups such as alkenyl, nitro group, and even internal alkyne intact.
Single atom catalysts (SACs), with maximum atom-utilization and unique electronic and geometric properties, are becoming a thriving research field because of their enhanced catalytic performance in a wide scope of industrially important reactions, e.g., selective hydrogenation of nitroarenes, alkynes and carbonyl compounds, catalytic transformation of methanes, aqueous reforming of methanol, hydroformylation of olefins, olefin metathesis, and oxygen reduction.

Various approaches have been utilized to prepare SACs, including the methods of impregnation/ion-exchange/cocatalyst addition, defect engineering, iced-photocatalysis, atomic layer deposition, galvanic replacement, high-temperature migration, and high-temperature pyrolysis. However, developing general protocols that can be used to easily synthesize a wide variety of SACs is still highly desirable. For example, by Jung et al., theoretical calculations were conducted to predict universal principles for the electro-catalytic performance of SACs bearing various metal sites. But the difficulty arises on verifying such predictions in experiments, as there are no general routes to prepare SACs with different center metals but similar supports and coordination environment. In addition, as predicted by Beller et al., the preparation of bi-/multi-metallic SACs is regarded as a next breakthrough because of their significant importance in the domino and tandem reactions, but there are few reports for their synthesis, mainly due to the huge obstacle to keep various metallic elements with obviously different physical/chemical properties coexisting in atomically dispersed states. Furthermore, comparative studies on the catalysis of different aggregation states, e.g., single atoms (SAs), nanoclusters (NCs), and nanoparticles (NPs), like the work by Zhang et al. on the Ru catalysts for CO2 methanation, received extensive attention. But, most of these studies rely on tuning the aggregation states by changing the metal loadings, which did not conform to the single-factor-variable research method. Thus, a facile approach to regulate the aggregation states of metal species other than altering metal loading is desired.

Inspired by our previous work on the porous porphyrin polymers and the work of Jiang et al. on SACs derived from metal-organic frameworks, we report here a precursor-dilution strategy to prepare N-doped porphyrin supported SACs. It is briefly, tetraphenylporphyrin (TPP) with chelated metal cations, acting as the metal precursor, is co-polymerized with excess of free TPP as the diluent. By the dilution, the amount of free TPP is increased, preventing their aggregation during the subsequent high-temperature pyrolysis. Thus, SACs are obtained. Specially, the high chelating ability of TPP to various metal cations (Supplementary Fig. 1) empowers this method to be applicable forfabricating a wide variety of SACs. Using this strategy, we have successfully conducted the synthesis of 24 types of SACs (i.e., M1/N–C, M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Er, W, Ir, Pt, Au, and Bi), including noble metals and non-noble metals. Furthermore, by varying the preparation conditions, e.g., precursor concentrations, metal precursors, and pyrolysis temperatures, we can obtain various materials: SACs with different surface atom densities (0.002–0.034 Pt nm⁻²), bi-metallic SACs (Pt₁–Sn₄/N–C), and Pt catalysts with different aggregation states (Pt SAs, Pt NCs, and Pt NPs), respectively.

**Results**

**Synthesis of Pt SACs with the precursor-dilution strategy.** In this work, we use Pt₁/N–C as an example to show the precursor-dilution strategy for fabricating SACs (Fig. 1a). First, a mixture of tetraphenylporphyrin platinum (PtTPP) and free TPP (PtTPP: TPP = 1:40, mol:mol) was dissolved in dichloromethane, and then co-polymerized by the addition of anhydrous AlCl₃ (Friedel–Crafts alkylation reactions). The as-obtained polymers were treated at 600 °C under flowing N₂ gas, and nitrogen-doped-carbon supported Pt SACs (i.e., Pt₁/N–C) were obtained.

The transmission electron microscopy (TEM) image (Fig. 1b) and high-angle annular dark-field scanning transmission electron microscopy (STEM) image (Fig. 1c) revealed that there were no observable Pt NPs in the prepared SACs. The image taken by aberration corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) showed that individual Pt atoms highlighted by yellow circles in Fig. 1d were clearly visible (no bright dots can be observed in the underlying support of nitrogen-doped carbon without metal loading (i.e., N–C), Supplementary Fig. 2), resulting from the large difference in Z contrasts of the image for Pt and N/C. Thus, this image proved the presence of atomically dispersed Pt species. The X-ray diffraction (XRD) pattern of Pt₁/N–C exhibited no peaks at 39.8°, 46.2°, and 68.5° (Fig. 1e, PDF#04-0802). This pattern resembled that for N–C, and indicated the highly dispersed state of Pt species. The aggregation state of Pt species was also probed by extended X-ray absorption fine structure spectrometry (EXAFS, Fig. 1f). There were two notable peaks at 1.7 and 2.5 Å, similar to those in the spectrum of PtTPP, which can be ascribed to the Pt–N and Pt–N–C contributions, respectively. It should be noted that the peak at 2.5 Å cannot be ascribed to the Pt–Pt bond (2.7 Å for Pt foil), which was further confirmed by the EXAFS fitting results of Pt₁/N–C (Supplementary Fig. 3, Supplementary Table 1). These fitting results were in good agreement with the original curves, and the coordination number of the Pt with surrounding N atoms was 3.4, indicating that the Pt atoms were connected with three or four N atoms. These results again corroborated the dominant presence of atomically dispersed Pt species evidenced by AC HAADF-STEM. As shown from the X-ray absorption near edge structure (XANES) spectra (Supplementary Fig. 4), the energy absorption threshold of Pt₁/N–C located between Pt foil and PtO₂, implying the presence of positively charged Pt⁵⁺ stabilized by adjacent N atoms in Pt₁/N–C. The oxidation state of Pt species was characterized by X-ray photoelectron spectroscopy (XPS, see Fig. 1g). The Pt 4f peaks located at 72.4 and 75.7 eV can be tentatively ascribed to Pt⁵⁺ with the presence of Pt–N bonds. The inductively coupled plasma optical emission spectrometry (ICP-OES) analysis revealed that the actual Pt loading was 0.43 wt% (Supplementary Table 2), slightly lower than the nominal loading (0.73 wt%) estimated by the molar ratio of PtTPP/TPP (1:40). This may be caused by metal loss in the preparation process. The result of elemental analysis (EA) revealed 5.17 wt% nitrogen content of in Pt₁/N–C (Supplementary Table 2). High BET area (595 m² g⁻¹) was found for Pt₁/N–C (Supplementary Table 2), and it was reported that high-surface-area structures could facilitate the atomic dispersion of metal species.

All the characterization results above lead to a conclusion that atomically dispersed Pt species were successfully synthesized on the support of N-doped carbon, by the precursor-dilution strategy. On the contrary, when PtTPP was used to make polymers without the diluent of free TPP, e.g., under the conditions of Pt–NPs/N–C (1:10), 100% PtTPP-based polymers and 3.31 wt% Pt loading (Supplementary Table 3), Pt NPs with 3.9 nm in diameter were formed using the same synthetic scheme (Supplementary Fig. 5). Thus, the diluent is indispensable for successful fabrication of SACs.

The versatility of the precursor-dilution strategy. The precursor-dilution strategy is of significant flexibility and...
generality for SAC fabrication, as demonstrated below. All of the synthesized catalysts were characterized fully by TEM, STEM, XRD, ICP-OES, EA, and BET (see Supplementary Figs. 6–28, 30–33 and Supplementary Tables 4–30). Among them, TEM/STEM images and XRD patterns were used to preliminarily identify the aggregation states of metal species on the supports. ICP-OES was used to reveal the content of metal species, and the EA and BET measurements were used to probe catalysts’ texture.

First, we could extend the precursor-dilution strategy to fabricate a variety of SACs using MTPP with different metals (M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Er, W, Ir, Au, and Bi) as the precursors and free TPP as the diluent. For most of the metals, the ratio of MTPP:TPP of 1:40 was used during the catalyst synthesis. But, there were exceptions. Some MTPPs (e.g., MnTPP and FeTPP) were found to easily leach in the polymerization process (under 80 °C and in AlCl₃). Thus, the molar ratios of MTPP:TPP were increased to obtain SACs with meaningful metal loadings (>0.05 wt%). The samples with high content of Rh or Au tended to form NPs, so the molar ratios of RhTPP:TPP and AuTPP:TPP were decreased to 1:80 and 1:160, respectively, in order to obtain atomically dispersed metal species. Details of all the synthesis were provided in Supplementary Methods. AC HAADF-STEM images (Fig. 2) showed that all of the 24 SACs featured with atomically dispersed species on the supports, which were further confirmed by the corresponding EXAFS results with the absence of metal–metal bond (Supplementary Fig. 29). Among them, SACs of Cd, Bi, and Er have never been reported before, which may underpin the exploration of intriguing applications. The EA and BET results revealed some similarity of material texture among all of the catalysts, i.e., with >420 m² g⁻¹ BET areas and ~5.0 wt% nitrogen content, due to the utilization of the similar preparation protocols.

Second, we could tune the surface Pt atom density in Pt₁/N–C by changing the precursor concentrations (i.e., the molar ratios of...
Fig. 2 AC HAADF-STEM images of M$_x$/N–C. M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, W, Ir, Pt, Au, and Bi. SAs were highlighted by yellow circles. Scale bar, 2 nm
PtTPP:TPP). Using different molar ratios of PtTPP:TPP (i.e., 1:320, 1:80, 1:40, and 1:20), we prepared a set of SACs with different Pt contents (0.06, 0.21, 0.43, and 0.73 wt%, respectively) and similar BET areas (~600 m² g⁻¹, see Supplementary Tables 2 and 27–29), and thus different Pt surface densities (0.002, 0.010, 0.022, and 0.034 Pt·nm⁻², respectively)³⁹,⁴⁰, in line with the trend observed by AC HAADF-STEM (Fig. 3).

Third, fabricating bi-metallic SACs (e.g., Pt₁–Sn₁/N–C) was also achieved with the same synthesis procedure of Pt₁/N–C and the precursor molar ratio of PtTPP:SnTPP:TPP (1:1:40). The N-doped porous carbon-based materials with 0.48 wt% Pt loading and 0.35 wt% Sn loading were obtained (Supplementary Table 30). This ratio of Pt loading and Sn loading (1.4:1) was in good agreement with the nominal ratio (1.6:1), based on the molar ratio of PtTPP:SnTPP (1:1) and atomic weight ratio of Pt:Sn (195.1:118.7). The AC HAADF-STEM image for Pt₁–Sn₁/N–C revealed the metal species atomically dispersed on the porous carbon supports (Fig. 4a). Corresponding element mapping analysis of Pt₁–Sn₁/N–C revealed that both Pt and Sn species were homogeneously distributed (Fig. 4b). The results of EXAFS (no Pt–Pt bond and Sn–Sn bond, Fig. 4c, d) were also indicative of the dominant presence of isolated Pt and Sn atoms deposited on the carbon matrix. These mutually authenticated results provided compelling evidence for the preparation of Pt₁–Sn₁/N–C.

Forth, we found that the pyrolysis temperature during the materials fabrication could influence the aggregation states of dispersed metal atoms. When the samples with the same molar ratio of PtTPP:TPP (1:40) were treated in different pyrolysis temperatures (i.e., 600, 700, and 800 °C), the Pt contents and BET surface areas of them were close (~0.5 wt% and ~600 m² g⁻¹, respectively, see Supplementary Tables 2 and 31–32), while the aggregation states of Pt species were changed from SAs (Pt₁/N–C) to NCs (Pt–NCs/N–C, 1.1 nm) and NPs (Pt–NPs/N–C, 6.9 nm) (Fig. 1d, Fig. 5 and Supplementary Figs. 34–35).
To our great delight, Pt SACs illustrated as a promising solution in practical applications of Pt loading) in hydrogenation reactions, which were previously documented. The chemo-/regio-selectivity of Pt SACs in hydrogenation.

After illustrating the facile synthetic routes of SACs with great versatility, we show here the unique catalytic properties of SACs (Pt1/N C, with 0.43 wt% Pt loading) compared with NPs (Pt–NPs/N–C, with Pt–NPs of 6.9 nm in diameter and 0.52 wt% Pt loading) in hydrogenation reactions, which were previously illustrated as a promising solution in practical applications of SACs1. To our great delight, Pt1/N–C showed excellent chemoselectivity in the hydrogenation of 1-nitro-4-ethynylbenzene (with –C≡CH and –NO2) and 1-ethynyl-4-vinylbenzene (with –C≡CH and –C=CH2), as it only transformed alkyne groups to alkenyl groups and kept –NO2 and –C=CH2 intact (99% selectivity to 1-nitro-4-vinylbenzene and 99% selectivity to 1,4-divinylbenzene at ~20% conversion level, and 98% selectivity to 1-nitro-4-vinylbenzene and 97% selectivity to 1,4-divinylbenzene at ~100% conversion level, respectively (Fig.6c, d, Supplementary Figs. 36c and 36d)). However, similar hydrogenation reactions catalyzed by Pt–NPs/N–C were not selective, i.e., both terminal and internal alkynes were hydrogenated. For example, the hydrogenation of 1-ethynyl-4-(phenylethynyl)benzene catalyzed by Pt–NPs/N–C showed 13%, 12%, and 75% selectivities to 1-(phenylethynyl)-4-vinylbenzene, 1-ethyl-4-(phenylethynyl)benzene, and 1-styryl-4-vinylbenzene, respectively (Fig.6c).

It is generally accepted that there are two activation pathways for semi-hydrogenation of alkynes: (i) the terminal of the –C≡CH group interacts with metal surfaces leading to deprotonation, and then the –C≡C group becomes activated; (ii) the entire –C≡C group interacts with the metal surfaces and becomes activated42. In our system, because of possible steric hindrance effect (1.2 Å for C≡C bond length vs. 0.8 Å for Pt2+ radius43) of Pt1/N–C, the first pathway is more probable. Apparently, due to its absence of terminal hydrogen, internal alkyne cannot be activated and then hydrogenated on Pt1/N–C. On the contrary, Pt–NPs/N–C with much larger diameters than that of Pt1/N–C is able to interact with substrates with less steric hindrance effect44 and then catalyze the hydrogenation of both terminal and internal alkynes. To verify our assumption, Pt1/N–C, Pt–NPs/N–C (1.1 nm), and Pt–NPs/N–C (6.9 nm) were employed under the same reaction conditions (Supplementary Table 33). As expected, the catalytic activities (i.e., turnover frequency, TOF, based on the metal dispersion13) for the hydrogenation of internal alkynes on Pt–NPs/N–C fell between those on Pt1/N–C and Pt–NPs/N–C: 1-phenyl-1-propyne (0, 132, and 2946 h−1), 1-phenyl-1-pentyn (0, 93, and 2556 h−1), and 5-decyne (0, 2860, and 13300 h−1) on SACs, NCs, and NPs, respectively. The observation that the
activities for the hydrogenation of internal alkynes increased with the increasing size of Pt species coincided quite well with our speculation that the unique group discrimination of terminal alkynes from internal ones on Pt1/N–C can be attributed to the geometric effect (see Supplementary Fig. 37).

In addition, the stability of the Pt1/N–C catalysts in the hydrogenation of the four substrates, i.e., 1-nitro-4-ethynylbenzene, 1-ethynyl-4-(phenylethynyl)benzene, 1-(dec-1-yn-1-yl)-3-ethynylbenzene on Pt1/N–C and Pt–NPs/N–C. Reaction condition: substrate (0.5 mmol), catalyst (Pt:substrate = 1:1200, mol:mol), methanol (2.0 mL), H2 (1.0 MPa), 50 °C (a, b) or 80 °C (c, d). All the conversions were maintained at ~20%. TOF was calculated based on Pt dispersion (Pt1/N–C: 100%; Pt–NPs/N–C: 14.5%, estimated by particle size (6.9 nm) according to $D = \frac{1}{d_{Pt}}$)

Discussion

In summary, a precursor-dilution strategy was developed to synthesize a series of SACs on N-doped porous carbon supports. This strategy is facile and versatile, and thus meets the requirements of the in-depth research nowadays. The Pt1/N–C SACs prepared with this strategy showed extremely high chemo- and regioselectivity towards terminal alkynes in hydrogenation. These findings are of significant importance in broadening the application of SACs, with the implication that SACs are able to achieve superior selectivity comparable to homogeneous catalysts and enzyme catalysts, for the catalysis of complex molecules.

![Diagram of catalytic performance of Pt1/N–C and Pt–NPs/N–C](https://example.com/diagram.png)
Methods

Catalyst Preparation. Take Pt/N-C as example. Under a nitrogen atmosphere, 100 mL stainless batch tank reactor was charged with a solution of PtP(T) (0.038 mmol), TPP (1.500 mmol), and anhydrous AlCl3 (24 mmol) in 30 mL of dichloromethane (PtP(T):TPP = 1:40, mol:mol). The reaction mixture was stirred at 80 °C for 24 h and then cooled to room temperature. The as-obtained precipitate was filtered and washed with methanol, dichloromethane, tetrahydrofuran, N,N-dimethylformamide, and acetone, respectively. Subsequently, the resulting powder was further purified by Soxhlet extractions for 24 h with methanol and dichloromethane, respectively. After dried at 80 °C in vacuum for 24 h, the polymer was placed in a tube furnace, heated to 600 °C for 3 h at the heating rate of 5 °C min⁻¹ under flowing nitrogen gas and then naturally cooled to room temperature to obtain Pt/N-C. Detailed preparation conditions for other samples were described in Supplementary Methods.

Characterization. EA and ICP-OES were performed on Vario EL cube instrument and PerkinElmer OPTIMA 8000DV, respectively. BET surface area measurements were performed on a Micromeritics ASAP2020M analyzer at liquid nitrogen temperature. Before the measurement, samples were evacuated at 200 °C for 6 h. Specific surface areas were calculated based on the BET equation. The Pt surface density was calculated by the equation: Pt surface density = [Pt loading] × N2/195.08 [true surface area], where N2 is the Avogadro’s number, and Pt loading and the surface area were obtained by the measurement of ICP-OES and BET, respectively. XRD patterns were obtained on a Bruker D8 Advanced diffractometer in the 2θ range 10°-80°. XPS measurements were performed on an ESCALab250 XPS system with Al Kα source and a charge neutralizer, and the binding energies were referenced to the contaminated C 1s (284.8 eV). TEM images and STEM images were obtained on FEI Tecnai G2 F30 operated at 300 kV. AC HAADF-STEM images were obtained on a JEM-ARM200F transmission electron microscopy operated at 200 kV, which incorporated with double spherical aberration correctors. X-ray absorption spectroscopy (XAS) measurements were conducted on BL14W beamline at the Shanghai Synchrotron Radiation Facility (SSRF) and 1W1B beamline at the Beijing Synchrotron Radiation Facility (BSRF). The sample of SACs were measured in fluorescence mode using Lytle detector or 32-element Ge solid state detector and the corresponding metal foils and metal oxides were used as reference samples and measured in the transmission mode. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained on Bruker Avance III 500 HD. High-resolution mass spectral (HRMS) data were obtained on Thermo Fisher Scientific Triddybrid Mass Spectrometer (Orbitrap Fusion Lumos).

Catalytic performance test. Catalytic hydrogenation reactions of various substrates, including 1-phenyl-1-propyne, 1-phenyl-1-pentyne, 5-decyn, 1-phenyl-1-propynylbenzene, and 1-(1-dec-1-yn-1-yl)-3-ethylbenzene, were carried out in 10 mL stainless autoclave. Take hydrogenation of 1-phenyl-1-propynylbenzene on Pt1/N-C as example. The typical reaction conditions were 0.5 mmol 1-phenyl-1-propynylbenzene, 20 mg Pt1/N-C catalyst (0.04 wt%), Pt1-nitro-4-ethylbenzene = 1:1200, mol: mol), 2.0 mL methanol as solvent, 1.0 MPa H₂ and 50 °C. After cooled and filtered, the reaction products were analyzed by GC (Shimadzu GCMS-QP2010 Ultra). Selectivities were reported on a carbon basis, 2. Yan, H. et al. Atomic engineering of high-density isolated Co atoms on graphene with proximal-atom controlled reaction selectivity. Nat. Commun. 9, 11927 (2018).

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Author contributions

X.H., Q.H. and Y.D. equally contributed to this work. X.H. developed the concept, designed these experiments, and analyzed experimental data. Q.H., H.C. and Y.Z. contributed to catalyst synthesis and catalytic experiments. Y.D., M.P., S.Y., M.Z. and D.M. performed the EXAFS measurements and analyzed the data. B.G. collected and analyzed the AC HAADF-STEM data. X.H., Q.H., D.X. and D.M. wrote the paper. D.M. and H.J. directed the project. All authors discussed the results and commented on the paper.

Additional information

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