The design of cheap, non-toxic, and earth-abundant transition metal catalysts for selective hydrogenation of alkynes remains a challenge in both industry and academia. Here, we report a new atomically dispersed copper (Cu) catalyst supported on a defective nanodiamond-graphene (ND@G), which exhibits excellent catalytic performance for the selective conversion of acetylene to ethylene, i.e., with high conversion (95%), high selectivity (98%), and good stability (for more than 60 h). The unique structural feature of the Cu atoms anchored over graphene through Cu-C bonds ensures the effective activation of acetylene and easy desorption of ethylene, which is the key for the outstanding activity and selectivity of the catalyst.
S\textsuperscript{electively hydrogenating remnant acetylene in the raw olefin streams to ethylene while avoiding the over-hydrogenation to undesired ethane is a key industrial reaction to manufacture polymer-grade raw materials for the production of polyethylene\textsuperscript{1–3}. The most commonly used industrial catalyst for the reaction is based on supported Pd nanoparticles (NPs) modified by Ag additives\textsuperscript{4}. Although the Pd-Ag catalyst prevents the usage of toxic promoters such as lead or sulfur (Lindlar catalyst)\textsuperscript{5}, the extremely high cost of Pd leaves ample room for improving the cost-effectiveness in catalyst design. In an effort to develop environment-friendly and cost-effective catalysts, various approaches have been pursued, including (i) reducing the amount of noble metals by “site-isolation” strategy or engineering a minimal ensemble\textsuperscript{6–11} and (ii) developing non-noble metals/metal oxides catalysts\textsuperscript{12–18}.

The key to the first strategy is to prepare atomically dispersed metal catalysts, a burgeoning class of catalytic materials, in which isolated metal atoms were anchored on the solid supports\textsuperscript{7,19}. Metal catalysts, a burgeoning class of catalytic materials, in which non-noble metals\textsuperscript{30}.

Yet, a small quantity of Pd proportion, suggesting that Cu, as an inexpensive and non-toxic catalyst, based catalysts have been developed and evaluated for the reaction. which is an important advance in non-noble metal catalysts for species was active for acetylene hydrogenation at up to 150 °C, employed to further investigate the distinct structure of Cu species deposited on ND@G (Fig. 3a). In contrast, for Cu\textsubscript{0}/ND@G, the Cu species was dominated by Cu clusters, together with a small amount of atomically dispersed Cu (see Fig. 1e, f). In good agreement with the results of TEM, Cu dispersion state observed by N\textsubscript{2}O titration (99.8% for Cu\textsubscript{0}/ND@G and 85.2% for Cu\textsubscript{0}/ND@G, see Supplementary Table 1) further confirmed that the two catalysts, sharing the same Cu loading, have different atomic dispersion states.

The X-ray adsorption fine structure (XAFS) measurement was performed to further investigate the distinct structure of Cu species. Clearly, the near-edge feature of Cu\textsubscript{0}/ND@G or Cu\textsubscript{0}/ND@G samples was in between that of Cu foil and CuO (Fig. 2a), indicating that the Cu species were partially positively charged (Cu\textsuperscript{0+}, 0 < \delta < 2). Fourier-transformed \(k^2\)-weighted extended X-ray absorption fine structure (EXAFS) in R space was performed to elucidate the coordination environments of Cu atoms anchored on ND@G. For Cu\textsubscript{0}/ND@G, the only distinct scattering was observed at 1.5 Å that corresponds to the first coordination shell of Cu-C or Cu-O. This evidences the single atom Cu on ND@G through Cu-C bonding, which is further verified by the appearance of Cu-C peak at 283 eV in C 1s XPS spectrum after Cu was loaded on ND@G (Fig. 3a)\textsuperscript{32}. In contrast, for Cu\textsubscript{0}/ND@G, besides the scattering of Cu-C at 1.5 Å, a major peak at 2.2 Å that ascribed to Cu-Cu scattering could be observed, indicating the formation of Cu clusters. A wavelet transformation (WT) of Cu k-edge EXAFS oscillations also displayed the dispersion of Cu in both samples visually in both k and R spaces. Figure 2c, d are the WT contour plots of Cu\textsubscript{0}/ND@G and Cu\textsubscript{0}/ND@G that showed a Cu-C back-scattering contribution near 1.5 Å, indicating that both Cu\textsubscript{0} and Cu\textsubscript{0} were anchored on ND@G through the Cu-C bonding. However, as shown in Fig. 2d, another peak at 2.2 Å in Cu\textsubscript{0}/ND@G, which is associated with the Cu-Cu scattering, further verified the dispersion state of Cu clusters.

XPS was used to study the valence states of Cu in two catalysts (Fig. 3b). For Cu\textsubscript{0}/ND@G, the Cu 2p\textsubscript{3/2} peak appeared at 933.7 eV, situated between Cu\textsuperscript{0}/Cu\textsuperscript{2+} (932.4 eV) and Cu\textsuperscript{2+} (934.6 eV)\textsuperscript{33,34}, which is consistent with the XANES results (Fig. 2a and Supplementary Fig. 6). The results imply that the Cu species in Cu\textsubscript{0}/ND@G interact strongly with the substrate. Through Cu-C bonds, an elevated chemical valence of single atom Cu species due
to charge transferred from Cu atoms to substrate could be observed, which was absent on Cu\textsubscript{n}/ND@G due to the similar properties between Cu clusters and bulk Cu.

Quantitative chemical configuration analysis of Cu\textsubscript{1}/ND@G and Cu\textsubscript{n}/ND@G were carried out through the least-squared EXAFS fitting. The R-space fitting results are shown in Fig. 2e and Supplementary Fig. 9, and the corresponding structure parameters are listed in Supplementary Table 2. The coordination number of the center Cu atom with surrounding C atoms on Cu\textsubscript{1}/ND@G was 3.1, and the mean bond length of Cu-C was 1.94 Å. Based on these results, the proposed local atomic structure of Cu was constructed as that in Fig. 2f. The isolated Cu atom was anchored over the defective sites of graphene through bonding with three C atoms.

Acetylene hydrogenation performance over Cu\textsubscript{1}/ND@G and Cu\textsubscript{n}/ND@G. Selective hydrogenation of acetylene was carried out using Cu\textsubscript{1}/ND@G and Cu\textsubscript{n}/ND@G, respectively, to gain insight into the impact of the atomic structure and spatial arrangement of Cu over the catalytic performance. The conversion and selectivity as a function of temperature over these two catalysts are shown in Fig. 4a. For aggregated Cu species in Cu\textsubscript{n}/ND@G, the conversion was still <20% even at 200 °C. Significantly, Cu\textsubscript{1}/ND@G manifested robust catalytic activity and remarkably high selectivity toward ethylene (see Fig. 4a). The conversion of acetylene reached 95% at 200 °C, with ethylene selectivity of 98%. We further compared the intrinsic activity of two catalysts, as shown in Fig. 4b. Cu\textsubscript{1}/ND@G showed a high TOF of 0.0017 s\textsuperscript{-1} (4.25 times higher than that of Cu\textsubscript{n}/ND@G) and a high ethylene yield.
of 93.1%, showing competitive advantages over former results [<90%] (see Supplementary Table 3 and Supplementary Fig. 10). Apparent activation energies ($E_a$) of the Cu1/ND@G and Cun/ND@G catalysts were 41.9 and 54.3 kJ/mol, respectively (see Fig. 4c), suggesting the superiority of atomically dispersed Cu catalysts. The stability of Cu1/ND@G catalyst was found to be excellent. As shown in Fig. 4d, the conversion and selectivity at 200 °C over Cu1/ND@G remained steady at 95% and 98%, respectively, for at least 60 h under reaction conditions. The atomic structure of the Cu1/ND@G catalyst was well maintained (see Supplementary Figs. 7–9 and Supplementary Tables 1 and 2) during the stability test. Meanwhile, under the reaction conditions where the conversion is high enough to meet the industrialization requirement (see Supplementary Fig. 11), Cu1/ND@G remained stable for at least 30 h.

**DFT calculations.** To better understand the nature of the superior acetylene hydrogenation activity of Cu1/ND@G, the reaction process was studied by DFT. The details of the computational simulation methods can be found in the “Methods” section. Cu1 supported over graphene layer (Cu1@Gr) was used to model the Cu1/ND@G catalyst, while a Cun cluster on ND@G to model the Cun/ND@G catalyst. The computational details are summarized in Supplementary Information, including all of the possible binding modes of different adsorbates on the catalytic

---

**Fig. 2** Synchrotron XAFS measurements of Cu1/ND@G and Cun/ND@G catalysts. a Cu k-edge XANES profiles for Cu1/ND@G, Cun/ND@G, Cu foil, and CuO. b Cu k-edge EXAFS spectra in $R$ space for Cu1/ND@G, Cun/ND@G, Cu foil, and CuO. c WT analysis of Cu1/ND@G. d WT analysis of Cun/ND@G. e EXAFS fitting curve for Cu1/ND@G. f The optimized Cu-C3 structure; color code: Cu (orange), C (gray)
surfaces. The energy profiles (including the entropy contribution) for the catalysis of Cu$_1$/ND@G are shown in Fig. 5. On Cu$_1$/ND@G, the adsorption energy of acetylene on Cu atoms is $-1.19$ eV (see Supplementary Table 4). Then the molecular hydrogen undergoes dissociative adsorption. This step is exothermic by 0.36 eV with an energy barrier of 1.36 eV (from B to C), which is the rate determining step (RDS) for acetylene hydrogenation. On the Cu$_{13}$ cluster catalyst, the barrier of RDS is 1.50 eV (see Supplementary Fig. 14), implying that the cluster catalyst is less active than the Cu$_1$ catalyst (see Supplementary Fig. 16). More importantly, the transition-state energy of ethylene hydrogenation on Cu$_1$/ND@G (TS2, 1.27 eV) is above the energy of gas-phase ethylene (1.08 eV), suggesting that ethylene favors desorption over further hydrogenation in the following step. In another word, the high selectivity of acetylene hydrogenation here is due to the priority of ethylene desorption at the atomically dispersed Cu sites of Cu$_1$/ND@G. This calculated result is consistent with the observed difference in catalytic performance between Cu$_1$/ND@G and Cu$_{13}$/ND@G.

**Discussion**

In summary, we synthesized an atomically dispersed Cu$_1$/ND@G catalyst for acetylene semihydrogenation reaction. It exhibited remarkably outstanding acetylene conversion (~95%), ethylene selectivity (~98%), and stability (>60 h), exceeding the Cu-cluster catalyst with the same Cu loading. The unique bonding structure and electronic property of Cu atoms on Cu$_1$/ND@G facilitate the acetylene activation and ethylene desorption, which clearly elucidates the importance of isolated Cu atoms in catalysts for high-
performance acetylene semi-hydrogenation. Our results and conclusions pave the way for rational design of promising non-noble catalysts for hydrogenation processes.

**Methods**

**Materials.** ND powders were purchased from Beijing Grish Hitech Co., Ltd, China. Copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) was the analytical reagent and purchased from Sinopharm Chemical Reagent Co., Ltd, China. Deionized (DI) water with the specific resistance of 18.25 MΩ cm was used in all our experiments.

**Preparation of ND@G.** ND@G was prepared by annealing ND powders at 1100 °C (heating rate 5 °C min⁻¹) for 4 h under flowing Ar gas (100 mL min⁻¹) and then naturally cooled to room temperature. The as-prepared products were further purified by hydrochloric acid for 24 h and then washed with DI water. Finally, the ND@G nanocarbon support was obtained after drying in vacuum at 60 °C for 24 h.

**Preparation of Cu/ND@G and Cu₅/ND@G.** Typically, 200 mg ND@G was dispersed into 30 mL DI water in a 100 mL round-bottom flask, and the mixture was ultrasonically treated for 30 min to obtain a homogeneous suspension. Then the pH value of ND@G support suspension was adjusted to about 11 by dropping 1.08 eV as internal standard. XPS were carried out on ESCALAB 250 instrument with Al Kα X-rays (1489.6 eV, 150 W, 50.0 eV pass energy) and the C 1s peak at 284.6 eV as internal standard. XRD patterns were collected by using an X-ray diffractometer (Bruker Smart APEX II) using a Cu Kα source at a scan rate of 2° min⁻¹. N₂ physisorption were measured at –196 °C using a Micrometrics ASAP-2020 instrument. The porosity of samples was obtained through Brunauer–Emmett–Teller analysis with the pore volume measured at a 0.99, and the pore size distribution was analyzed by BJH method from desorption curve. Ten 0.04 eV ML⁻¹. The as-prepared products were analyzed by GC (Agilent 7890 A) equipped with a flame ionization detector and a HP-PLOT AL/S (HP-plot 19091 P-S15, Agilent, 50 m × 0.32 mm × 8 μm) capillary column with He as the carrier gas.

Acetylene conversion and selectivity to ethylene were calculated as the following:

\[
\text{Conversion} = \frac{C_2H_2 \text{ (feed)} - C_2H_2 \text{ (after)}}{C_2H_2 \text{ (feed)}} \times 100\%
\]

\[
\text{Selectivity} = \left(1 - \frac{C_2H_2 \text{ (after)} + 2C_2H_2 \text{ (feed) - C_2H_2 \text{ (after)}}}{C_2H_2 \text{ (feed)}} \right) \times 100\%
\]

**Computational simulations of the catalytic mechanisms by Cu/ND@G and Cu₅/ND@G.** All of the catalytic structures were obtained by the geometry optimizations using the plane-wave-based DFT method implemented in the Vienna Ab Initio Simulation Package (VASP). We describe the electron–ion interaction using the projector augmented wave method (PAW). The generalized gradient approximation and the Perdew–Burke–Ernzerhof functional (GGA) describes the exchange and correlation energies for all systems. All the calculations take spin polarization into consideration. The plane-wave expansion of the wave functions adopted an energy cutoff of 400 eV. The Monkhorst–Pack k-point was set to 3 × 3 × 1 in the reciprocal lattice. The convergence criteria for electronic self-consistent interactions is 10⁻². The geometries of bulk and surface were optimized by the conjugate gradient algorithm until the maximum force on any ion was <0.03 eV Å⁻¹, where all the atoms in the catalyst and adsorbate were fully relaxed. The most stable configurations of the reactant and intermediates on Cu₅/Gr were determined by using the climbing image nudged elastic band method (CI-NEB), and vibrational frequencies were analyzed to ensure the transition state with only one imaginary frequency.

**Discussion**

**Catalytic performance tests.** The selective hydrogenation activity of the catalysts was conducted in a quartz-bed flow reactor for acetylene hydrogenation with 200 mg catalysts. A gas mixture of 1 vol% C₂H₂, 10 vol% H₂, and 20 vol% C₂H₆ with He balance (flow rate = 10 mL min⁻¹, GHSV = 3000 mL g⁻¹ h⁻¹) was introduced, followed by ascending temperature testing. Gas chromatograph (GC) injections were done at each temperature after stabilization for 30 min. The reactants and products were analyzed by GC (Agilent 7890 A) equipped with a flame ionization detector and a HP-PLOT AL/S (HP-plot 19091 P-S15, Agilent, 50 m × 0.32 mm × 8 μm) capillary column with He as the carrier gas.

Acetylene conversion and selectivity to ethylene were calculated as the following:

\[
\text{Conversion} = \frac{C_2H_2 \text{ (feed)} - C_2H_2 \text{ (after)}}{C_2H_2 \text{ (feed)}} \times 100\%
\]

\[
\text{Selectivity} = \left(1 - \frac{C_2H_2 \text{ (after)} + 2C_2H_2 \text{ (feed) - C_2H_2 \text{ (after)}}}{C_2H_2 \text{ (feed)}} \right) \times 100\%
\]
9. Lin, R. et al. Design of single gold atoms on nitrogen-doped carbon for molecular recognition in alkylene semi-hydrogenation. Angew. Chem. Int. Ed. 131, S14-S19 (2019).

10. Wei, S. et al. Direct observation of noble metal nanoparticles transforming to thermally stable single atoms. Nat. Nanotechnol. 13, 856-861 (2018).

11. Huang, X. et al. Enhancing both selectivity and coking-resistance of a single-atom Pd/CN4 catalyst for acetylene hydrogenation. Nano Res. 10, 1302-1312 (2017).

12. Vilé, G., Bridier, B., Wichert, J. & Pérez-Ramírez, J. Ceria in hydrogenation catalysis: high selectivity in the conversion of alkynes to olefins. Angew. Chem. Int. Ed. 51, 8620-8623 (2012).

13. Vilé, G., Colussi, S., Kruemeich, F., Trouvarelli, A. & Pérez-Ramírez, J. Opposite face sensitivity of CeO2 in hydrogenation and oxidation catalysis. Angew. Chem. Int. Ed. 53, 12068-12072 (2014).

14. Werner, K. et al. Toward an understanding of selective alkylene hydrogenation on ceria: on the impact of O vacancies on H2 interaction with CeO2(111). J. Am. Chem. Soc. 139, 17608-17616 (2017).

15. Cao, T. et al. An in situ DRIFTS methodic study of CeO2-catalyzed acetylene semihydrogenation reaction. Phys. Chem. Chem. Phys. 20, 9659-9670 (2018).

16. Padole, M. C. et al. Adsorption of C2H2 gases over CeO2-based catalysts: synergistic of cationic sites and anionic vacancies. Phys. Chem. Chem. Phys. 19, 14148-14159 (2017).

17. Tejeda-Serrano, M. et al. Synthesis of supported planar iron oxide nanoparticles and their chemo- and stereoselectivity for hydrogenation of alkynes. ACS Catal. 7, 3721-3729 (2017).

18. Tejeda-Serrano, M. et al. Isolated Fe(III)-O sites catalyze the hydrogenation of acetylene in ethylene flows under front-end industrial conditions. J. Am. Chem. Soc. 140, 8827-8832 (2018).

19. Lin, L. et al. Low-temperature hydrogen production from water and methanol using Pts2/Mo2C catalyst. Nature 554, 80-83 (2017).

20. Li, T. et al. Maximizing the number of interfacial sites in single-atom catalysts for the highly selective, solvent-free oxidation of primary alcohol. Angew. Chem. Int. Ed. 57, 7795-7799 (2018).

21. Qiao, B. et al. Single-atom catalysis of CO oxidation using Pt1/FeOx. Nat. Chem. 3, 634-641 (2011).

22. Lee, B.-H. et al. Reversible and cooperative photoactivation of single-atom Cu/TiO2 photocatalysts. Nat. Mater. 18, 620-626 (2019).

23. Derita, L. et al. Structural evolution of atomically dispersed Pt catalysts dictates reactivity. Nat. Mater. 18, 746-751 (2019).

24. Lin, L. et al. A highly CO-tolerant atomically dispersed Pt catalyst for chemoselective hydrogenation. Nat. Nanotechnol. 14, 354-361 (2019).

25. Chen, Z. et al. A heterogeneous single-atom palladium catalyst surpassing homogeneous systems for Suzuki coupling. Nat. Nanotechnol. 13, 702-707 (2018).

26. Qiao, B. et al. Highly efficient catalysis of preferential oxidation of CO in H2-rich stream by gold single-atom catalysts. ACS Catal. 5, 6249-6254 (2015).

27. Lin, J. et al. Remarkable performance of Ir/FeOx single-atom catalyst in water gas shift reaction. J. Am. Chem. Soc. 135, 15314-15317 (2013).

28. Cao, L. et al. Atomically dispersed iron hydroxide anchored on Pt for preferential oxidation of CO in H2. Nature 565, 631-635 (2019).

29. Riley, C. et al. Design of effective catalysts for selective alkynes hydrogenation by doping of ceria with a single-atom promoter. J. Am. Chem. Soc. 140, 12964-12973 (2018).

30. Kyriakou, G. et al. Isolated metal atom geometries as a strategy for selective heterogeneous hydrogenations. Science 335, 1209-1212 (2012).

31. Pei, G. X. et al. Performance of Cu-alloyed Pd single-atom catalyst for semihydrogenation of acetylene under simulated front-end conditions. ACS Catal. 7, 1491-1500 (2017).

32. Jasson, U. et al. Design of carbide-based nanocomposite thin films by selective alloying. Surf. Coat. Technol. 206, 583-590 (2011).

33. Qu, Y. et al. Direc transformation of bulk copper into copper single sites via emitting and trapping of atoms. Nat. Catal. 1, 781-786 (2018).

34. Gong, J. et al. Synthesis of ethanol via syngas on Cu/SiO2 catalysts with balanced Cu2O-Cu+ sites. J. Am. Chem. Soc. 134, 13922-13925 (2012).

35. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab inito total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169-11186 (1996).

36. Kresse, G. & Furthmüller, J. Efficency of ab-inito total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 6, 15-50 (1996).

37. Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953-17979 (1994).

38. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758-1775 (1999).

39. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865-3868 (1996).

40. Perdew, J. P. & Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. Phys. Rev. B 45, 13244-13249 (1992).

41. Graeme, H., Uberuaga, B. P. & Hannes, J. A clipping image nged elastic band method for finding saddle points and minimum energy paths. J. Chem. Phys. 113, 9901-9904 (2000).

Acknowledgements
This work was supported by the Ministry of Science and Technology (2016YFA0204100, 2017YFB0602200), the National Natural Science Foundation of China (91845201, 21575254, 91545110, 21725301, 91645115, 21932002 and 21730003), the Joint Fund of National Natural Science Foundation of China (U1732667), the Youth Innovation Promotion Association, and Chinese Academy of Science (CAS). N.W. hereby acknowledges the funding support from the Research Grants Council of Hong Kong (Project Nos. C0621-14E and 16306818). The XAS experiments were conducted in Shanghai Synchrotron Radiation Facility (SSRF).

Author contributions
H.L. and D.M. conceived the research. F.H. conducted material synthesis and carried out the catalytic performance test. Y.D., Z.J. and M.P. conducted the X-ray absorption fine structure spectroscopic measurements and analyzed the data. M.P. and J.X. conducted the X-ray photoelectron spectroscopy. Y.C. and X.W. performed the DFT calculations. X.C. and N.W. contributed to the aberration-corrected high-angle annular dark-field scanning transmission electron microscopy. Z.J. performed some of the experiments. The manuscript was primarily written by F.H., Y.D., H.L. and D.M. and revised by D.X. All authors contributed to discussions and manuscript review.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-019-12460-7.

Correspondence and requests for materials should be addressed to Z.J. or D.M.

Peer review information Nature Communications thanks Antonio Leyva-Pérez and the other anonymous reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s) 2019