Unprecedentedly high activity and selectivity for hydrogenation of nitroarenes with single atomic Co$_1$-N$_3$P$_1$ sites

Hongqiang Jin$^{1,2}$, Peipei Li$^{1,2}$, Peixin Cui$^3$, Jinan Shi$^{4,5}$, Wu Zhou$^{4,5}$, Xiaohu Yu$^6$, Weiguo Song$^{1,2}$ & Changyan Cao$^{1,2}$

Transition metal single atom catalysts (SACs) with M$_1$-N$_x$ coordination configuration have shown outstanding activity and selectivity for hydrogenation of nitroarenes. Modulating the atomic coordination structure has emerged as a promising strategy to further improve the catalytic performance. Herein, we report an atomic Co$_1$/NPC catalyst with unsymmetrical single Co$_1$-N$_3$P$_1$ sites that displays unprecedentedly high activity and chemoselectivity for hydrogenation of functionalized nitroarenes. Compared to the most popular Co$_1$-N$_4$ coordination, the electron density of Co atom in Co$_1$-N$_3$P$_1$ is increased, which is more favorable for H$_2$ dissociation as verified by kinetic isotope effect and density functional theory calculation results. In nitrobenzene hydrogenation reaction, the as-synthesized Co$_1$-N$_3$P$_1$ SAC exhibits a turnover frequency of 6560 h$^{-1}$, which is 60-fold higher than that of Co$_1$-N$_4$ SAC and one order of magnitude higher than the state-of-the-art M$_1$-N$_x$-C SACs in literatures. Furthermore, Co$_1$-N$_3$P$_1$ SAC shows superior selectivity (>99%) toward many substituted nitroarenes with co-existence of other sensitive reducible groups. This work is an excellent example of relationship between catalytic performance and the coordination environment of SACs, and offers a potential practical catalyst for aromatic amine synthesis by hydrogenation of nitroarenes.

1 Beijing National Laboratory for Molecular Sciences, CAS Research/Education Center for Excellence in Molecular Sciences, Laboratory of Molecular Nanostructures and Nanotechnology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. 2 School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China. 3 Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China. 4 School of Physical Sciences, CAS Key Laboratory of Vacuum Physics, University of Chinese Academy of Sciences, Beijing 100049, China. 5 CAS Center for Excellence in Topological Quantum Computation, University of Chinese Academy of Sciences, Beijing 100049, China. 6 Institute of Theoretical and Computational Chemistry, Shaanxi Key Laboratory of Catalysis, School of Chemical & Environment Sciences, Shaanxi University of Technology, Hanzhong 723000, China. **email: yuxiaohu@snut.edu.cn; cycao@iccas.ac.cn

NATURE COMMUNICATIONS | (2022) 13:723 | https://doi.org/10.1038/s41467-022-28367-9 | www.nature.com/naturecommunications

https://doi.org/10.1038/s41467-022-28367-9
Chemoselective hydrogenation of nitroarenes is a key reaction in the fine chemical industry and has wide applications in the synthesis of pigments and pharmaceuticals. Noble metal nanocatalysts (e.g., Pt, Au, and Pd) are usually used for this reaction. However, noble metal catalysts are costly and their high activities usually come with unsatisfactory selectivity against many substituted nitroarenes. Since Beller et al. reported highly selective traditional metal catalysts based on Co3O4@N/C and Fe3O4@N/C, it has sparked intensive research interest in this type of catalysts. Among them, transition metal single-atom catalysts (SACs) with M1-Nx-C (M = Fe, Co, Ni, x = 2–6) coordination configuration exhibited much better activities than their counterpart nanoparticles while maintaining high selectivity, owing to their maximum atom efficiency and particular electronic structure. Recently, Wang et al. found that the electron density of Ni single atoms increased with the decrease of Ni-N coordination numbers (CN), and the capability of Ni single-atom catalysts (SACs) with M1-Nx-C (M = Fe, Co, Ni, x = 2–6) coordination configuration exhibited much better activities than their counterpart nanoparticles while maintaining high selectivity, owing to their maximum atom efficiency and particular electronic structure. In most SACs, the central metal atoms were stabilized by coordination bonds with N, S, O, etc. atoms within support matrices. The electronic and geometric structures of central metal atoms can be adjusted by tailoring the coordination environment, which would change the absorption energy of reactants on metal atoms and thus influence the catalytic process. For SACs with M1-Nx-C sites, the symmetric electronic distribution may limit the activation of reactants, thereby leading to hampered catalytic kinetics and performance. Recent studies have found that introducing heteroatom P for an unsymmetrical N/P mixed-coordination can further modulate the electronic properties of center metal atoms. The unsymmetrical geometric structure can evoke the distortion of electronic density and alter the d-band center. For example, Yuan et al. prepared an N/P dual-coordinated Fe single-atom catalyst, which was more favorable for the adsorption of oxygen intermediates for ORR in fuel cell. Li et al. reported that a Fe-N3P1 single-atom nanozyme exhibited peroxidase-like catalytic activity, and the high activity was ascribed to the less positive charge on Fe atoms as P atoms are electron donors. Thus, we anticipated that constructing the unsymmetrical N/P dual-coordinated transition metal SACs would improve the catalytic performance for the hydrogenation of nitroarenes.

In this work, we report an N/P dual-coordinated Co SAC (denoted as Co1/NPC) with Co1-N3P1 coordination structure and investigate its catalytic performance for chemoselective hydrogenation of nitroarenes. The single atomic feature and coordination structure of the Co1-N3P1 site are characterized through aberration-corrected high angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM), atomic-resolution electron energy-loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectrum (XAS). In nitrobenzene hydrogenation reaction, the Co1-N3P1 SAC exhibits a turnover frequency of 6560 h−1, which is 60 times higher than that of Co1-N4 SAC and 10 times higher than the state-of-the-art M1-Nx-C SACs in literatures. Furthermore, Co1-N3P1 SAC shows superior selectivity (>99%) toward many substituted nitroarenes with the coexistence of other sensitive reducible groups. The unprecedentedly high activity of Co1-N3P1 SAC can be ascribed to the upshift d-band center of Co single atoms, which is more favorable for H2 dissociation as verified by the kinetic isotope effect and density functional theory calculation results. This is an excellent example of such an unsymmetrical N/P dual-coordinated structure of metal SACs in hydrogenation.

Results

Structural characterization. Supplementary Fig. 1 illustrates the synthesis procedures for preparing N/P dual-coordinated Co SAC (denoted as Co1/NPC) via a two-step process. First, tannic acid, (2-Aminoethyl)phosphonic acid (AePA), and cobalt ion precursors were co-adsorbed on the surface of graphitic carbon nitride (g-C3N4) nanosheets; then the resultant powder was subjected to pyrolysis under flowing Ar gas at 900 °C to obtain Co1/NPC, where the AePA was absent and the introduced-P species served as the anchors for anchoring Co atoms (Supplementary Fig. 2). For comparison, N-coordinated Co SAC (denoted as Co1/NC) was also prepared via the same procedure without the addition of AePA. As exhibited in Raman spectra, the carbon matrices in both Co1/NPC and Co1/NC were disordered with a large number of defects (Supplementary Fig. 3). Only two broad peaks at ~24.3° and 42.6° could be observed from their X-ray diffraction (XRD) patterns (Supplementary Fig. 4), corresponding to (002) and (101) planes of carbon, suggesting highly dispersed states of Co species in both of two samples. Further increasing the pyrolysis temperature of Co1/NPC to 1000 °C led to the formation of CoP nanoparticles (Supplementary Figs. 4, 5). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that both catalysts retain a two-dimensional layered structure and no obvious nanoparticles are observed (Supplementary Figs. 6, 7). Energy-dispersive spectroscopy (EDS) mappings reveal Co elements are distributed uniformly over the entire samples (Supplementary Figs. 8, 9). Additionally, Co single-atom feature in Co1/NPC and Co1/NC is directly observed by AC HAADF-STEM, as reflected by the highly dispersed bright dots due to the heavy Z-contrast (Fig. 1a and Supplementary Fig. 10). The Co loading in Co1/NPC was ~0.45 wt% as determined by the inductively coupled plasma mass spectroscopy (ICP-MS) analysis (Supplementary Table 1). The porosity features of Co1/NC and Co1/NPC were investigated using nitrogen physisorption measurements. Both catalysts displayed characteristics of IV-type N2 adsorption-desorption isotherms, suggesting the existence of mesopores, which would be beneficial for the exposure of active sites and mass transportation (Supplementary Fig. 11). The calculated BET-specific surface area of Co1/NC and Co1/NPC were 512 and 471 m2 g−1, respectively.

XPS was then applied to reveal the chemical structures of both Co SACs. In N 1s spectra, besides pyridinic N, pyrrolic N, graphitic N, and oxidized N species, a peak at 399.1 eV corresponding to Co-N can be distinguished, indicating the existence of N coordination environment with Co single atoms in both catalysts (Fig. 1b and Supplementary Fig. 12). Note that from P 2p spectra in Fig. 1c, an obvious peak at ~129.3 eV corresponding to Co-P bond was presented in Co1/NPC, which can also be observed in the comparison CoP NPs/C (Supplementary Fig. 13); while it is absent in Co1/NC sample. These results suggest that the atomically dispersed Co atoms possess N/P dual-coordinated configuration in Co1/NPC, while only N-coordinated configuration in Co1/NC.

To further determine the coordination environment of Co single atoms, X-ray absorption fine structure (XAFS) measurements were conducted. Figure 1d shows the Co K-edge X-ray absorption near-edge structure (XANES) curves of Co1/NC and Co1/NPC, with Co foil, CoO, and cobalt phthalocyanine (CoPc) as reference samples. It can be seen that the absorption threshold positions for Co1/NC and Co1/NPC are located between Co foil and CoO, suggesting that the valence states of Co species are between 0 and +2 in both two catalysts. Moreover, the Co K-edge position and white line of Co1/NPC are lower than that of Co1/NC (inset of Fig. 1d), which indicates that Co atoms in Co1/NPC possess more negative charges than Co1/NC. Such difference could be attributed to the less electron transfer from Co to P.
The Fourier-transformed $k^3$-weight EXAFS (FT-EXAFS) spectra demonstrated that both Co$_1$/NC and Co$_1$/NPC only exhibited a prominent peak at 1.38 Å (without phase shift), no Co-Co peaks at 2.17 Å or larger bond distances were detected, confirming atomically dispersed Co species in Co$_1$/NC and Co$_1$/NPC (Supplementary Figs. 14, 15). The coordination configuration of Co moieties was further surveyed using quantitative least-squares fitting analysis. The EXAFS spectrum of Co$_1$/NPC was investigated by utilizing Co-N and Co-P backscattering pathways. The best-fitting analysis displays that the main peak at 1.38 Å could be satisfactorily interpreted as Co-N first-shell coordination with CN $= 3.2 \pm 0.1$ and the shoulder peak at 1.77 Å originated from Co-P contribution with CN $= 0.9 \pm 0.1$ (Fig. 1e and Supplementary Table 2), suggesting the possible Co$_1$N$_3$P$_1$ configuration in Co$_1$/NPC. For comparison, fitting of Co$_1$/NC resulted in an average of about four N atoms with a distance of 1.37 Å (Supplementary Fig. 14 and Supplementary Table 2). In order to better confirm the proposed configurations, the theoretical XANES spectrum were simulated based on the Co$_1$N$_3$P$_1$ model as well as Co$_1$N$_4$, which presented a good agreement with the experimental data, indicating the rationality of the two structures (Fig. 1f and Supplementary Fig. 16).

Besides, we performed atomic-resolution electron energy-loss spectroscopy (EELS) analysis at a relatively low beam current to minimize electron-beam perturbations to provide strong evidence of Co$_1$N$_3$P$_1$ structure (Fig. 2a, b). The extracted Co L-edge EELS spectrum from Fig. 2d presents a clear Co signal (Fig. 2g), providing direct evidence for the presence of atomically dispersed Co species. Moreover, the existence of N, P dual-coordination vicinal to Co site is revealed by identifying the surrounding heteroatoms. From the N, P, and overlap maps (Fig. 2e, f, c), three N atoms (green) and one P atom (red) exist around the Co site. Atomic-scale N K-edge and P L-edge EELS spectra collected at the corresponding positions from Fig. 2e, f are further demonstrated by the N and P signals (Fig. 2h, i). This forcefully confirms the Co$_1$N$_3$P$_1$ configuration in Co$_1$/NPC sample. Moreover, the formation energy of the Co$_1$N$_3$P$_1$ structure in the Co$_1$/NPC sample was estimated to be about $-0.864$ eV by DFT calculation, indicating the high stability of the proposed configuration (Supplementary Fig. 17). These results revealed that the Co single sites in Co$_1$/NPC were stabilized with N/P dual-coordinated structure, forming an unsymmetrical Co$_1$N$_3$P$_1$ geometric configuration (as depicted in Fig. 1f), which is different from the Co site in Co$_1$/NC with traditional in-plane Co$_1$N$_4$ configuration.

**Catalytic performance.** To evaluate the catalytic performances of the as-prepared Co SACs for the hydrogenation of nitroarenes, nitrobenzene is first chosen as a probe molecule. The reaction kinetics with Co$_1$/NC and Co$_1$/NPC were obtained at 110 °C with 3 MPa H$_2$ in a Teflon-lined stainless steel autoclave. As shown in Fig. 3a, Co$_1$/NPC exhibits significantly higher activity than that of Co$_1$/NC. Nitrobenzene was completely converted with >99% amine selectivity in 210 min with Co$_1$/NPC, while less than 20% conversion was observed with Co$_1$/NC under the same reaction condition. In addition, no conversion was observed with NC and NPC supports, suggesting that atomic Co site was active species in both Co$_1$/NC and Co$_1$/NPC catalysts (Supplementary Fig. 18). The reaction rate (k) for hydrogenation of nitrobenzene over Co$_1$/NPC could reach as high as 35.9 mol mol$^{-1}$ min$^{-1}$, which is ten times higher than that with Co$_1$/NC (3.1 mol mol$^{-1}$ min$^{-1}$).

The turnover frequency value (TOF) (based on the substrate conversion at about 20%) of Co$_1$/NPC is calculated to be 6560 h$^{-1}$, which is over 60 times higher than that with Co$_1$/NC (108 h$^{-1}$) (Fig. 3b). Besides nitrobenzene, Co$_1$/NPC also exhibited superior high activity and excellent selectivity (>99.7%) for hydrogenation of 3-nitrostyrene with TOF of 4499 h$^{-1}$. The impressive activity of Co$_1$/NPC is ten times higher than the state-of-the-art M$_1$-N$_x$-C SACs in
Such excellent catalytic performance of Co1/NPC sample inspired us to carry out the reaction under milder conditions (e.g., 40 °C, 1 bar H2). A high nitrobenzene conversion of 97.2% was achieved within 5 h (Supplementary Fig. 19). To further compare the catalytic performance between Co1/NC and Co1/NPC, the apparent activation energies of these two catalysts were measured (Supplementary Fig. 20 and Supplementary Table 4). As shown in Fig. 3d, the calculated activation energy of Co1/NPC catalyst is about 21.8 kJ mol\(^{-1}\), which is much lower than that of Co1/NC (51.3 kJ mol\(^{-1}\)).

In order to clarify the intrinsic higher activity of Co1-N3P1, the electronic properties of the central metal sites over Co1/NC and Co1/NPC are examined by electron-density isosurface and partial density of states from DFT calculations. Different charge distributions of the two models are observed (Fig. 3e). Compare to the Co1-N4 configuration, the symmetric electron structure is broken by introducing heteroatom P in Co1-N3P1. The Bader charge of the Co1-N3P1 site is estimated to be +0.81 e, while the Co1-N4 site is +0.97 e, indicating the Co atom in the Co1-N3P1 site carries more charge since the P element in the Co1/NPC transfers 2.308 e to support, which is consistent with the XAFS results. Moreover, the Co d-band center of Co1/NPC is up-shifted, much closer to the Fermi level (Fig. 3f). As a result, the antibonding states of Co atoms and adsorbed H\(_2\) species are more occupied, then such change enhances the capabilities of H\(_2\) dissociation\(^{6,44}\). Thus, Co1/NPC catalyst with Co1-N3P1 configuration exhibits much higher activity than that of Co1/NC with Co1-N4 configuration.

Catalytic hydrogenation mechanism. Such a large activity difference between Co1/NC and Co1/NPC implies that the hydrogenation activity is closely correlated with local coordination structure, which influences the electronic structure of Co single atoms. In order to elucidate the reaction mechanisms on both catalysts, we carried out a kinetic isotope effect (KIE) study to examine the H\(_2\) dissociation step. Using D\(_2\) for nitrobenzene hydrogenation, the reaction rate was slowed down by a factor of 3.25 for Co1/NC (Fig. 4a). For comparison, a larger KIE (k\(_H\)/k\(_D\) = 5.54) was observed on Co1/NPC catalyst (Fig. 4b). These results suggest that H\(_2\) dissociation undergoes heterolytic cleavage on both Co1/NC and Co1/NPC\(^{45-47}\).

It is generally accepted that heterolytic cleavage of H\(_2\) on metal single atoms occurs to form metal-H\(_{\delta^-}\) and heteroatom-H\(_{\delta^+}\)\(^{45,48}\). Therefore, DFT calculations were further performed to understand the H\(_2\) heterolytic cleavage on Co1/NC and Co1/NPC, respectively. As shown in Supplementary Fig. 21, the H\(_2\) molecule is adsorbed on the Co atom of Co1/NPC with adsorption energy of −0.08 eV, and the bond length of H\(_2\) is 0.814 Å, which is much longer than free molecular H\(_2\) (0.752 Å) in the gas phase. While H\(_2\) molecule is adsorbed on Co atom of Co1/NC with adsorption energy of 0.033 eV, and the bond length of H\(_2\) is 0.783 Å. The much longer H-H bond length of adsorbed molecule H\(_2\) indicates that Co1/NPC has a higher activation ability for H\(_2\) dissociation than Co1/NC. Subsequently, one of the H atoms moves to a nearby heteroatom (N and P) to yield heteroatom-H\(_{\delta^+}\), leaving another H atom on Co atom as Co-H\(_{\delta^-}\). Direct dissociation of H\(_2\)
on both Co1/NPC and Co1/NC in the absence of water, the transition state is almost the same (~1.21 eV), the only difference is that the dissociation of H2 on Co1/NPC is exothermic by 0.20 eV, while on Co1/NC is endothermic by 1.11 eV, suggesting such dissociation manner on Co1-N4 site is thermodynamically unfavorable (Supplementary Fig. 22). The above difference in the DFT calculations confirms that Co1-N3P1 exhibits much higher catalytic activity for heterolytic cleavage of H2.

Ding et al.18 reported that the protic solvents play a dominant role in the case of Co-N-C-catalyzed hydrogenation of nitroaranes, where the solvent-mediated H-shuttling mechanism is crucial in the reaction pathway. Compared to the intrinsic hydrogen transfer, the protic solvent-mediated one usually possesses a lower activation barrier, leading to an enhancement of hydrogenation activity in the presence of water or alcohol49. Indeed, both Co1/NC and Co1/NPC show the best activities under ethanol/water solvent and significantly decreased activities in an aprotic solvent such as toluene, acetonitrile, THF, and n-hexane (Supplementary Fig. 23). Further DFT calculations suggest that the activation energy barriers with water-mediated H-shuttling mechanism for the heterolytic cleavage of H2 are lower by about 0.16 and 0.01 eV than that through direct dissociation on Co1-N3P1 and Co1-N4 sites, respectively (Fig. 4c, d). Both kinetic and thermodynamic results suggest that the dissociative activation of H2 with help of H2O is more favorable to Co1/NPC catalyst.

According to the previous reports, the hydrogenation reduction of nitrobenzene to aniline follows the Haber mechanism7, namely,

\[ \text{PhNO}_2^* \rightarrow \text{PhNOOH}^* \rightarrow \text{PhNO}^* \rightarrow \text{PhNOH}^* \rightarrow \text{PhNHOH}^* \rightarrow \text{PhNH}^* \rightarrow \text{PhNH}_2^* \]

Based on the above results and reported mechanism in literature, the reaction pathway for hydrogenation of nitrobenzene over Co1-N3P1 catalyst is further proposed by virtue of DFT calculations, as shown in Fig. 5 and Supplementary Fig. 24. One H2 molecule first goes through heterolytic cleavage with the assistance of the H2O-mediated H-shuttling mechanism to form Co-Hδ- and P-Hδ+ at Co1-N3P1 sites, which can serve as the initial state for the hydrogenation process (Fig. 5a and Supplementary Fig. 25). Then, the target nitrobenzene molecule was adsorbed on the Co1-N3P1 site with a free energy of −0.78 eV (Fig. 5b, I). Subsequently, the activated H atom on Co-Hδ- and the O atom of PhNO2 are combined to produce PhNOOH intermediate, which is later reduced to PhNO intermediate by the H atom transfer from P-Hδ+ (II). Notably, the PhNO intermediate can be detected during the reaction process (Supplementary Fig. 26). After that, another H2 molecule is dissociated to form an activated H atom, which attacks the oxygen atom of PhNO and reduces it to PhNHOH (III, IV). It is worth noting that...
noting that the adsorption energies of intermediates PhNO and PhNHOH on the Co$_1$-N$_3$P$_1$ site are more favorable than Ph-NO$_2$, ensuring the reaction progress of the targeted substrate (Supplementary Fig. 27). In the next step, the third H$_2$ molecule participates in and the formed H atom interacts with PhNHOH to generate the final PhNH$_2$ product (V, FS). It can be seen the whole process is highly endothermic, confirming the possibility of the proposed reaction path.

**Substrate exploration and catalytic stability.** A broad scope of substituted nitroarenes was tested to examine the chemoselectivity in nitroarene hydrogenation (Fig. 6). Co$_1$/NPC shows impressive chemoselectivity toward the substituted nitroarenes in the presence of other sensitive reducible groups, such as alkenyl (99.7%, 2b), halogen (>98.9%, 2c–f), ketones (>99%, 2g, h), nitrile groups (>99%, 2i), etc. Notably, Co$_1$/NPC also exhibits high activity and selectivity toward heterocyclic nitro-compounds (>99%, 2n–q). The superior high selectivity to corresponding anilines is ascribed to the unique character of metal SACs, where there is only one single metal atom for adsorption and activation of substrates.

Furthermore, Co$_1$/NPC exhibited tolerable stability. As shown in Supplementary Fig. 28, a slight decrease of activity is observed after five cycles with Co$_1$/NPC, which can be ascribed to the loss of some catalysts and active Co species during the recycling experiments (Supplementary Table 1). The AC HAADF-STEM image and Co K-edge EXAFS spectrum of spent Co$_1$/NPC indicate that the atomically dispersed Co species is well preserved after five cycles (Supplementary Fig. 29). All these results demonstrate that the Co$_1$/NPC catalyst with unsymmetrical Co$_1$-N$_3$P$_1$ configuration possesses unprecedented high activity, high selectivity, and good stability to a wide scope of substrates for hydrogenation of nitroarenes.

**Discussion**

In summary, we produced an atomically dispersed Co$_1$/NPC catalyst with an unsymmetrically Co$_1$-N$_3$P$_1$ coordination structure. Due to the increased electron density and upshift d-band center of Co atoms in Co$_1$-N$_3$P$_1$, H$_2$ dissociation was proved to be more favorable, resulting in much enhanced catalytic activity. In nitrobenzene hydrogenation reaction, the as-prepared Co$_1$-N$_3$P$_1$ SAC exhibited a 60-fold higher TOF value (6560 h$^{-1}$) than that of Co$_1$-N$_3$C SAC and more than tenfold higher than the state-of-the-art M$_1$-N$_x$-C SACs in literature. In addition, Co$_1$-N$_3$P$_1$ SAC also displayed superior selectivity (>99%) towards the substituted nitroarenes with the co-existence of other sensitive reducible groups. This work provides new insight into rationally modulating the coordination structure of central metal atoms for boosting the catalytic performance of SACs in heterogeneous catalysis.

**Methods**

**Synthesis of Co$_1$/NPC and Co$_1$/NC**. In a typical procedure, Co(NO$_3$)$_2$·6H$_2$O (6.5 mg), tannic acid (TA, 500 mg), and (2-Aminoethyl) phosphonic acid (AePA, 126 mg) were dissolved into 30 mL DI water at 100 °C (marked as solution A). g-C$_3$N$_4$ nanosheets (1 g) were dispersed well in 100 mL DI water with ultrasound (marked as solution B). Then, solution A was added dropwise into solution B with a strong stirring at 100 °C until the mixed system was forced to yield a slurry. Subsequently, the obtained powder after freeze-dried was pyrolyzed at 900 °C without further treatment, denoted as Co$_1$/NPC.

The synthesis process for Co$_1$/NC is the same as that of Co$_1$/NPC except without the addition AePA.

**Characterizations**. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500R diffractometer with Cu K$_a$ radiation ($\lambda$ = 1.5418 Å) at 40 kV and 200 mA. The morphologies and microstructures of the samples were measured on the transmission electron microscopy (TEM) (JEM-2100F, JEOL, Japan) and the scanning electron microscopy (SEM) (HITACHI S-4800, Japan). Element mapping was characterized on TEM equipped with Oxford detection. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG
In all cases, complete conversions of nitroarenes were observed. The proposed reduction factor $S_{02}$ was set to the best-fit value of 0.87 determined from fitting the data of cobalt foil by fixing coordination numbers as the known crystallographic value. In order to fit the curves in the R-range of 1.0–2.0 Å, we considered Co-N and Co-P paths as the central-peripheral. For each path, the structural parameters, like coordination number (CN), interatomic distance (R), Debye–Wallker weights, and inner potential correction ($ΔE_{p}$) were opened to be varied.

**Fig. 5 Reaction mechanism of the nitrobenzene reduction.** a. The proposed reaction pathway for the hydrogenation of nitrobenzene to aniline at Co-P interface site. b. Energy profile of hydrogenation of nitrobenzene over Co/NPC site.

**DFT calculations.** All the spin-polarized first-principles calculations have used the code VASP21,22. Valence electrons of O(2s, 2p), N(2s, 2p), H(1s), C(2s, 2p), P(3s, 3p), and Co(3d, 4s) were treated on a basis of plane waves explicitly23, while the core electrons were described with the projector-augmented wave method24. Spin-polarized calculations were carried out at the level of the generalized gradient approximation (GGA) adopting the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional25. A kinetic energy cutoff of 400 eV was used for all calculations. The truncation criteria for the electronic and ion-loops were 10−3 eV and 10−2 eV/Å, respectively. Long-range dispersion was included according to the D3 method introduced by Grimme26. The vacuum layer was set to 20 Å to avoid interaction from adjacent cells. All the transition states were determined by using the climbing image nudged elastic band (CINEB) method27,28. The calculated energies were characterized via frequency analysis to ensure a single imaginary frequency in the desired reaction direction. The pure graphene is modeled according to the D3 method introduced by Grimme54. The vacuum layer was set to 20 Å to avoid interaction from adjacent cells. All the transition states were determined by using the climbing image nudged elastic band (CINEB) method27,28. The calculated energies were characterized via frequency analysis to ensure a single imaginary frequency in the desired reaction direction. The pure graphene is modeled by a $\Gamma \times \Gamma$ supercell with 49 carbon atoms, and the Co-N$_x$P$_y$-Gr model is modeled by a (7 × 7) supercell with 49 carbon atoms and the Co-N$_x$P$_y$-Gr model. The Co-bulk model is modeled by a (7 × 7) supercell with 49 carbon atoms.

**Fig. 6 Substrate scope of hydrogenation over the Co/NPC catalyst.** Reaction conditions: 1 mmol nitroarenes; 10 mL EtOH; 5 mg catalyst; 110 °C; 3 MPa H$_2$; EtOH/H$_2$O, v-v = 4:1, 10 mL; H$_2$. 2 MPa; Temperature, 120 °C. In all cases, complete conversions of nitroarenes were observed.
3. Lang, R. et al. Single-atom catalysts based on the metal-oxide interaction.
4. Wei, H. et al. FeOx-supported platinum single-atom and pseudo-single-atom
5. Zhang, L. L., Zhou, M. X., Wang, A. Q. & Zhang, T. Selective hydrogenation
over supported metal catalysts from nanoparticles to single atoms. Chem. Rev. 120, 683–733 (2020).
6. Lan, T. et al. Single-atom catalysts based on the metal–oxide interaction. Chem. Rev. 120, 11986–12043 (2020).
7. Yan, H. et al. Atomic engineering of high-density isolated Co atoms on graphene with proximal-atom controlled reaction selectivity. Nat. Commun. 9, 3197 (2018).
8. Wei, H. et al. FeOx-supported platinum single-atom and pseudo-single-atom catalysts for chemoselective hydrogenation of functionalized nanorattles. Nat. Commun. 5, 6634 (2014).
9. Ye, T.-N. et al. Stable single platinum atoms trapped in sub-nanometer cavities in 12CaO·7Al2O3 for chemoselective hydrogenation of nanorattles. Nat. Commun. 11, 1020 (2020).
10. Zhang, S. et al. High catalytic activity and chemoselectivity of sub-nanometric Pd clusters on porous nanorods of CeO2 for hydrogenation of nitroarenes. J. Am. Chem. Soc. 138, 2629–2637 (2016).
11. Boronat, M. et al. A molecular mechanism for the chemoselective hydrogenation of substituted nitroaromatics with nanoparticles of gold on TiO2 catalysts: a cooperative effect between gold and the support. J. Am. Chem. Soc. 129, 16230–16237 (2007).
12. Serna, P. & Corma, A. Transferring nano metal nonselective particulates into chemoselective catalysts for hydrogenation of substituted nitrobenzenes. ACS Catal. 5, 7114–7121 (2015).
13. Wang, Y.-F. et al. Single-atom catalysts: a new frontier in heterogeneous catalysis. Acc. Chem. Res. 46, 1740–1748 (2013).
14. Fu, T. et al. Acid-resistant catalysis without use of noble metals: carbon nitride with underlying nickel. ACS Catal. 4, 2536–2543 (2014).
15. Westerhausen, F. A. et al. Heterogenized cobalt oxide catalysts for nitroarene reduction by pyrolysis of molecularly defined complexes. Nat. Chem. 5, 537–543 (2013).
16. Wang, Y. et al. Chemoselective hydrogenation of nitroaromatics at the nanoscale iridium(III)-OH-platinum interface. Angew. Chem. Int. Ed. 59, 12736–12740 (2020).
17. Li, H. et al. Cobalt single atoms anchored on N-doped ultrathin carbon nanosheets for selective transfer hydrogenation of nitroaromatics. Sci. China Mater. 62, 1306–1314 (2019).
18. Zhang, L. et al. Atomically dispersed Co catalyst for efficient hydrodeoxygenation of lignin-derived species and hydrogenation of nitroaromatics. ACS Catal. 10, 8672–8682 (2020).
19. Zhou, H. et al. High performance of a cobalt-nitrogen complex for the reduction and reductive coupling of nitro compounds into amines and their derivatives. Sci. Adv. 3, NO. e1601945 (2017).
20. Liu, W. et al. Single-atom dispersed Co–N–C catalyst: structure identification and performance for hydrogenative coupling of nitroaromatics. Chem. Sci. 7, 5758–5764 (2016).
21. Li, M. et al. Origin of the activity of Co–N–C catalysts for chemoselective hydrogenation of nitroaromatics. ACS Catal. 11, 3026–3039 (2021).
22. Zhou, D. et al. Tuning the coordination environment of single-atom catalyst M–N–C towards selective hydrogenation of functionalized nitroaromatics. Nano Res. 11, 1–9 (2021).
23. Wan, J. et al. In situ phosphatizing of triphenylphosphine encapsulated within metal-organic frameworks to design atomic Co1–P1–N3 interfacial structure for chemoselective hydrogenation of nitroaromatics. Angew. Chem. Int. Ed. 59, 14639–14646 (2020).
24. Long, X. et al. Graphitic phosphorus coordinated single Fe atoms for hydrogenreative transformations. Nat. Commun. 11, 4074 (2020).
25. Yuan, K. et al. Boosting oxygen reduction of single iron active sites via geometric and electronic engineering: nitrogen and phosphorus dual coordination. J. Am. Chem. Soc. 142, 2404–2421 (2020).
26. Ren, Y. et al. Unraveling the coordination structure-performance relationship in Pt3FeO4 single-atom catalyst. Nat. Commun. 10, 4500 (2019).
Acknowledgements
We thank the National Key R&D Program of China (Grant No. 2018YFA0703503 and 2018YFA0208504, C.C. and W.S.), the National Natural Science Foundation of China (NSFC 21932006, W.S.), the Youth Innovation Promotion Association of CAS (2017049, C.C.), Beijing Outstanding Young Scientist Program (BJJWZYJH01201914430039, W.Z.) and National Science Basic Research Program of Shaanxi (No. S2020-3C-WT-0001, X.Y.) for financial support. We thank the beamline 1W1B station in Beijing Synchrotron Radiation Facility (BSRF) and Dr. Lirong Zheng for help in XAFS characterization.

Author contributions
H.J., C.C., and W.S. were responsible for most of the investigations, methodology development, data collection/analysis, and writing the original manuscript. P.L. assisted with the experiments analysis. X.Y. conducted the DFT calculations. P.C. helped to analyze the XAFS results. J.S. and W.Z. helped to conduct the atomic-resolution EELS. C.C. and W.S. were responsible for the funding and resources acquisition, supervising the project, revising, and editing the manuscript.

Competing interests
The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-28367-9.

Correspondence and requests for materials should be addressed to Xiaohu Yu or Changyan Cao.

Peer review information Nature Communications thanks Chun Zhang, Jianglan Shui and the other, anonymous, reviewers 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.