



# Enhancing the activity of Pd ensembles on graphene by manipulating coordination environment

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Atomic dispersion of metal catalysts on a substrate accounts for the increased atomic efficiency of single-atom catalysts (SACs) in various catalytic schemes compared to the nanoparticle counterparts. However, lacking neighboring metal sites has been shown to deteriorate the catalytic performance of SACs in a few industrially important reactions, such as dehalogenation, CO oxidation, and hydrogenation. Metal ensemble catalysts ( $M_n$ ), an extended concept to SACs, have emerged as a promising alternative to overcome such limitation. Inspired by the fact that the performance of fully isolated SACs can be enhanced by tailoring their coordination environment (CE), we here evaluate whether the CE of  $M_n$  can also be manipulated in order to enhance their catalytic activity. We synthesized a set of Pd ensembles ( $Pd_n$ ) on doped graphene supports ( $Pd_n/X$ -graphene where  $X = O, S, B$ , and  $N$ ). We found that introducing  $S$  and  $N$  onto oxidized graphene modifies the first shell of  $Pd_n$  converting  $Pd-O$  to  $Pd-S$  and  $Pd-N$ , respectively. We further found that the  $B$  dopant significantly affected the electronic structure of  $Pd_n$  by serving as an electron donor in the second shell. We examined the performance of  $Pd_n/X$ -graphene toward selective reductive catalysis, such as bromate reduction, brominated organic hydrogenation, and aqueous-phase  $CO_2$  reduction. We observed that  $Pd_n/N$ -graphene exhibited superior performance by lowering the activation energy of the rate-limiting step, i.e.,  $H_2$  dissociation into atomic hydrogen. The results collectively suggest controlling the CE of SACs in an ensemble configuration is a viable strategy to optimize and enhance their catalytic performance.

single-atom catalyst | metal ensembles | coordination environment

Single-atom catalysts (SACs), also referred to as atomically dispersed catalysts, have emerged as a promising material design option for various catalytic processes and as an alternative to conventional nanoscale catalysts. They are considered particularly attractive for noble metals since the atomic efficiency can be maximized and the material cost can be significantly reduced (1). SACs are typically strongly bound to a substrate material through interfacial bonds to prevent potential migration on the substrate surface. Otherwise, they tend to aggregate and form nanoparticles due to their high surface free energy (2, 3). Although such atomic dispersion is the core idea of SAC architecture, completely isolating each SAC from other SACs might not be universally desirable. In fact, the distant isolation of SACs to completely eliminate the interaction with other catalytic centers has been reported to have adverse effects on many important catalytic schemes, such as CO oxidation (4, 5), hydrogenation (6, 7), and hydrocarbon oxidation (8, 9). (Fig. 1)

Recent studies present an intriguing strategy to overcome these challenges by placing single-atom catalytic sites close to each other in a small cluster form (8, 10). Such extended single-atom architecture has been referred to as metal ensembles (9), neighboring SACs (11, 12), or fully exposed clusters (13). What distinguishes this structure, called herein as an ensemble with a notation of  $M_n$ , from fully isolated SACs ( $M_1$ ) is the additional bonding/nonbonding interaction between neighboring metal atoms (14, 15). Metals in an ensemble structure otherwise resemble isolated SACs in their coordination environment (CE), i.e., dominant existence of substrate atom bonding to metals (4, 16). In this configuration, neighboring metal atoms provide contiguous positions as active sites, enabling functions that are inefficient with completely isolated SACs (17). For example, simultaneous adsorption of reactants and intermediates on nearby SAC sites (18) can accelerate catalysis without the catalyst poisoning that is prevalent with fully isolated SACs (16, 19).

It is noteworthy that CE can be a deciding factor for the catalytic performance of isolated  $M_1$  sites (20). For example,  $Cu_1-S_1N_3$  exhibits much higher activity toward oxygen reduction than  $Cu_1-N_4$  (21);  $Fe_1-N_2S_2$  is more efficient toward  $CO_2$  reduction than  $Fe_1-N_2$  (22);  $Fe_1-N_4$  exhibits superior activity toward benzene oxidation compared to  $Fe_1-N_3C_1$  and  $Fe_1-N_2C_2$  (23); and  $Pt_1-O_4$  displays much improved activity over  $Pt_1-O_6$

## Significance

Substrate-anchored, single-atom catalysts (SACs) have emerged as a promising alternative to conventional nanocatalysts for various catalytic processes. The catalytic performance of SACs can be controlled by various synthetic strategies, including the manipulation of substrate atoms surrounding metal sites. This study examines whether the coordination environment (CE) of the palladium metal ensemble, a newly identified small-clustered structure with CE resembling that of SAC, can also be tuned by doping nonmetal elements onto the substrate. The results demonstrate that such CE manipulation could decrease the activation energy of the rate-limiting step and achieve efficient  $H_2$  dissociation for several important reductive catalytic schemes, establishing a new strategy to effectively engineer metal ensemble catalysts.

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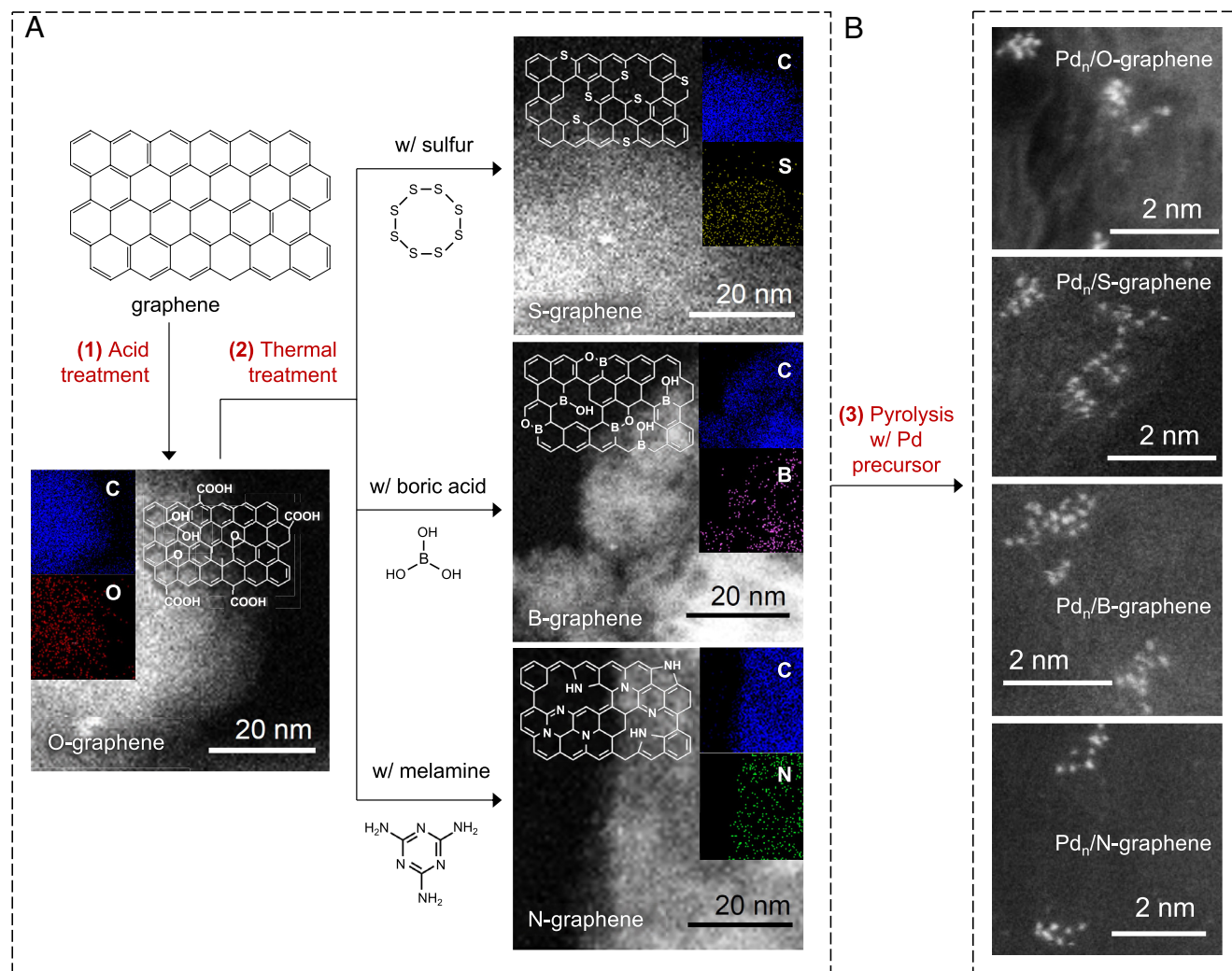
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**Fig. 1.** Schematic illustration of the step-by-step synthesis procedure for Pd<sub>n</sub>/X-graphene (X indicates O, S, B, or N): (A) nonmetals doping and EELS mapping of O-graphene, S-graphene, B-graphene, and N-graphene; (B) AC-HAADF-STEM images of Pd<sub>n</sub>/O-graphene, Pd<sub>n</sub>/S-graphene, Pd<sub>n</sub>/B-graphene, and Pd<sub>n</sub>/N-graphene.

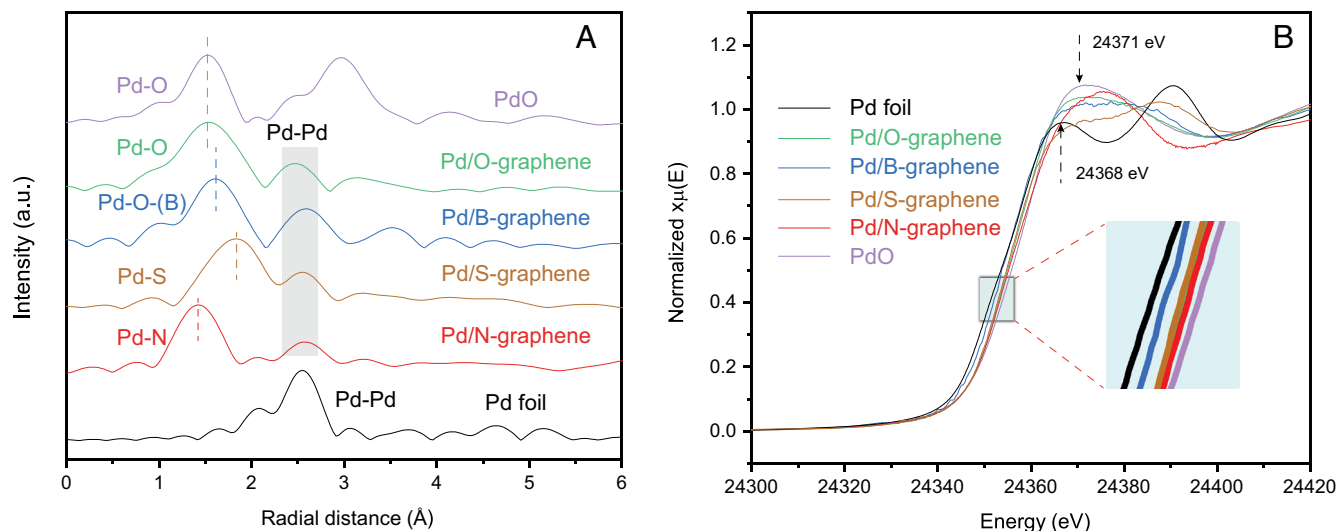
for CO oxidation (20). These examples of enhancing performances of M<sub>1</sub> by CE manipulation hint that CE of M<sub>n</sub> can also be tailored to enhance catalytic performance. However, there is no study yet exploring the CE effect on M<sub>n</sub>, likely due to the difficulty of synthesizing M<sub>n</sub> with controlled CE (i.e., different substrate atoms binding to M<sub>n</sub>). If the atomicity becomes too high, M<sub>n</sub> may aggregate into nanoparticles. If the atomicity gets too low, M<sub>n</sub> may lose the characteristic interaction between neighboring metal atoms and instead function as M<sub>1</sub>. (Fig. 2)

In this study, we prepared a series of Pd ensemble catalysts (Pd<sub>n</sub>) with varying CE by anchoring Pd onto a graphene substrate doped with heteroatoms, such as O, S, B, and N. We selected graphene as the substrate considering a couple of advantageous features: i) high specific surface area (theoretically, 2,600 m<sup>2</sup> g<sup>-1</sup>) (24), ensuring uniform distribution of Pd<sub>n</sub> and favoring reactant adsorption during catalysis, and ii) facile modification with oxygen-containing groups which can be reductively removed to generate substitutional doping sites (25, 26). We then evaluated the performance of Pd<sub>n</sub> for H<sub>2</sub> dissociation into atomic H (H\*), a highly active species for many essential reductive reactions, e.g., selective hydrogenation (27, 28), dehalogenation (29), and reduction of CO<sub>2</sub> (30) and NO<sub>3</sub><sup>-</sup> (31). Our results suggest that these nonmetal dopants can effectively modulate the CE of Pd<sub>n</sub> and affect the catalytic performance. We discuss the key role of CE in determining the catalytic performance of Pd<sub>n</sub> based on detailed X-ray

analysis, reaction kinetics evaluation, and density functional theory (DFT) calculations.

## Results and Discussion

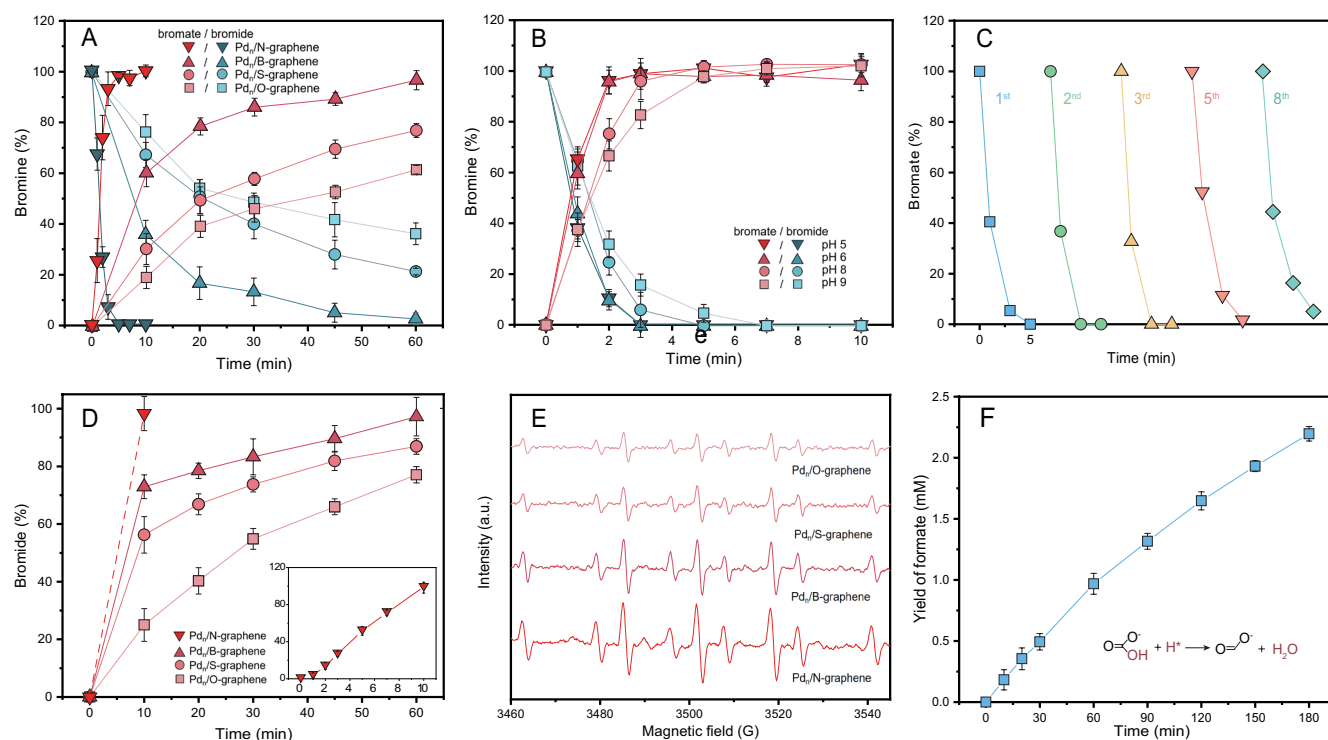
**Synthesis and Structural Characterization of Pd<sub>n</sub>/X-Graphene Catalysts.** We synthesized a set of X-graphene catalysts (X = O, S, B, and N) loaded with Pd following a two-step synthesis method. The first step involved substitutional doping of nonmetals onto a graphene substrate. We prepared O-graphene by acid treatment of graphene to introduce oxygen functionalities. X-ray photoelectron spectroscopy (XPS, *SI Appendix*, Fig. S1) suggests the presence of epoxy and hydroxyl groups on the basal plane and carboxyl and carbonyl groups on the edge of O-graphene (32). We then prepared S-, B-, and N-graphene by thermally treating O-graphene under a reducing atmosphere to remove O-containing groups and substituting S, B, and N using their respective precursors (sulfur, boric acid, and melamine). For S-graphene, we observed only S 2p<sub>3/2</sub>/2p<sub>1/2</sub> doublets (164.1/165.3 eV) in the XPS spectrum (*SI Appendix*, Fig. S2), which can be assigned to C-bound thiophene-like sulfur (C–S–C) (33, 34). The absence of oxidized sulfur species [SO<sub>x</sub>, 167.9 eV (33)] confirmed that oxygen was effectively removed from O-graphene. For N-graphene, peaks at 398.3, 399.4, and 401.1 eV in N 1s XPS spectrum (*SI Appendix*, Fig. S3) can be attributed to pyridinic, pyrrolic, and graphitic N



**Fig. 2.** (A) The normalized Pd  $k^3$ -weighted FT-EXAFS of Pd foil, PdO, and Pd<sub>n</sub>/X-graphene samples; (B) XANES measurements of different Pd<sub>n</sub>/X-graphene samples and standards at the Pd K-edge.

species, respectively (35), while an oxidized N peak at 403.3 eV (36) was not observed. In contrast, the B 1s spectrum of B-graphene exhibited a peak at 191.2 eV (*SI Appendix, Fig. S4*) for the O-containing BC<sub>2</sub>O structure (25). Considering the absence of oxygen in S- and N-graphenes which underwent the same reductive treatment, O in B-graphene likely originated from the boric acid precursor. Electron energy loss spectroscopy (EELS) mapping (Fig. 1A) demonstrates the even distribution of nonmetal dopants on all these graphene substrates. (Fig. 3)

The second step involved H<sub>2</sub>PdCl<sub>4</sub> precursor physisorption onto these substrates and subsequent pyrolysis under a N<sub>2</sub> atmosphere. Raman spectra (*SI Appendix, Fig. S5*) suggest a high concentration of defects on these graphene substrates with the  $I_D/I_G$  ratio ranging from 1.09 to 1.11 [ $I_D$  represents disordered sp<sup>3</sup> C at ~1,350 cm<sup>-1</sup>;  $I_G$  represents lattice sp<sup>2</sup> C at ~1,580 cm<sup>-1</sup> (37, 38)] which serve as trapping sites to stabilize Pd. Pyrolysis conditions were optimized to obtain Pd<sub>n</sub> morphology since too low of a temperature can lead to residual Cl (*SI Appendix, Fig. S6*) and



**Fig. 3.** (A) Kinetic plots of BrO<sub>3</sub><sup>-</sup> reduction and Br<sup>-</sup> generation with Pd<sub>n</sub>/O-graphene, Pd<sub>n</sub>/S-graphene, Pd<sub>n</sub>/B-graphene, and Pd<sub>n</sub>/N-graphene. (B) BrO<sub>3</sub><sup>-</sup> reduction with Pd<sub>n</sub>/O-graphene catalyst under various pH conditions. (C) BrO<sub>3</sub><sup>-</sup> reduction with Pd<sub>n</sub>/N-graphene catalyst after repetitive cycling. (D) De bromination of TBBPA with Pd<sub>n</sub>/O-graphene, Pd<sub>n</sub>/S-graphene, Pd<sub>n</sub>/B-graphene, and Pd<sub>n</sub>/N-graphene catalysts; the *Inset* is a kinetic plot using Pd<sub>n</sub>/N-graphene within 10 min. (E) EPR spectra with Pd<sub>n</sub>/O-graphene, Pd<sub>n</sub>/S-graphene, Pd<sub>n</sub>/B-graphene, and Pd<sub>n</sub>/N-graphene, using DMPO as the probe to identify the existence of H<sup>•</sup>. (F) Formate yield during the hydrogenation of HCO<sub>3</sub><sup>-</sup> with Pd<sub>n</sub>/N-graphene. Experimental conditions: catalysts (0.5 g L<sup>-1</sup>), TBBPA/BrO<sub>3</sub><sup>-</sup> (50 ppm) or HCO<sub>3</sub><sup>-</sup> (0.5 M), H<sub>2</sub> (1 atm), room temperature (25 °C).



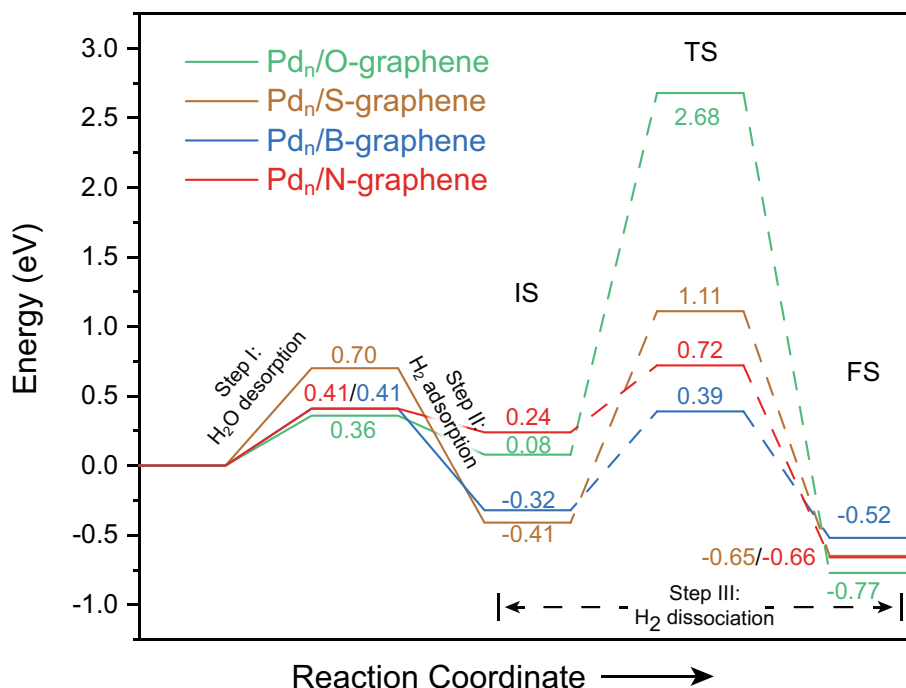
insufficient reduction of Pd precursor (39), while too high of a temperature can lead to the redistribution into Pd<sub>1</sub> (40). In addition, a gentle heating rate (2 °C/min) was applied to avoid too rapid precursor reduction and consequential Pd nanoparticle growth (41).

Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) images (Fig. 1 B and *SI Appendix*, Fig. S7) provided visual confirmation of the ensemble configuration of Pd at atomic scale (referred to as Pd<sub>n</sub>/X-graphene hereafter) and the absence of Pd nanoparticles. Fourier-transformed extended X-ray absorption fine structure spectroscopy (FT-EXAFS) analysis further confirmed that Pd<sub>n</sub>/X-graphene appeared drastically different compared to metallic Pd (Pd foil), which showed only one dominant Pd–Pd peak at 2.61 Å (Fig. 2A). The FT-EXAFS spectra of Pd<sub>n</sub>/O-graphene featured one distinct peak at 1.52 Å in the first shell, which matched well with Pd–O peak in the PdO reference. The slight peak shift of Pd–O to 1.59 Å in Pd<sub>n</sub>/B-graphene likely resulted from the influence of B, which causes an asymmetrical expansion of the first shell (42). In the Pd<sub>n</sub>/S-graphene catalyst, the main peak at a much higher radial distance (1.82 Å) was attributed to the Pd–S shell (43). Finally, the peak at 1.45 Å in Pd<sub>n</sub>/N-graphene was assigned to the Pd–N coordination (44). Pd–Pd peaks shifted slightly among different Pd<sub>n</sub>/X-graphene samples (gray box in Fig. 2A), which is likely associated with the specific CE offered by different nonmetal dopants (Fig. 4).

We observed that the Pd K-edge absorption energy in the X-ray absorption near-edge spectroscopy (XANES) spectra (Fig. 2B) was in the order: metallic Pd < Pd<sub>n</sub>/B-graphene < Pd<sub>n</sub>/O-graphene ≈ Pd<sub>n</sub>/S-graphene ≈ Pd<sub>n</sub>/N-graphene < PdO. This correlates with the oxidation state of the metal (45), where Pd in Pd<sub>n</sub>/B-graphene would be in a more reduced state compared to Pd in other Pd<sub>n</sub>/X-graphenes. Consistently, we observed that the first peak of the XANES derivative was positioned at 24,351 eV for Pd<sub>n</sub>/B-graphene, which is at lower energy than 24,352 eV for Pd<sub>n</sub>/O-, Pd<sub>n</sub>/S-, and Pd<sub>n</sub>/N-graphenes (*SI Appendix*, Fig. S8). This result

corroborates a recent work that reported the increased oxidation state of metal centers induced by electron-withdrawing F doping on Pd-hosting substrate, even when F does not directly bind to Pd (46). The results so far collectively suggest that i) doping S or N replaces Pd–O coordination in the first shell of Pd<sub>n</sub> by Pd–S or Pd–N coordination and ii) doping B into graphene retains Pd–O coordination in the Pd<sub>n</sub> but with lower Pd oxidation state.

We postulate that Pd ensembles exist in more than one configuration and have a distribution of atomicity (e.g., few to several single-atom Pd centers). We therefore evaluated the average CE of Pd in ensembles based on structural parameters obtained from fitting EXAFS and XPS results (*SI Appendix*, Figs. S9 and S10) (47). For example, the average CN of Pd–Pd shell in all Pd<sub>n</sub>/X-graphenes is ~3 (*SI Appendix*, Table S1), indicating that each Pd atom binds, on average, to 3 other Pd atoms within each Pd<sub>n</sub>. We therefore propose tetrahedron-structured Pd<sub>4</sub> as a dominant Pd<sub>n</sub> form (48) among other possible structures (e.g., inverted tetrahedron or tetrahedron aligned to X-graphene layer along the edge/facet) based on best fitting of EXAFS data. Although different dopants would affect the metal-support interaction, (49, 50), we found that the surface energy of the Pd atom and the resultant thermodynamic driving force to aggregate were not significantly influenced, as evidenced by the average nuclearity of Pd<sub>4</sub> in all Pd<sub>n</sub>/X-graphenes. We then employed DFT calculations to estimate the Gibbs energy of formation among all possible structures to construct the most probable structure for each Pd<sub>n</sub>/X-graphene as shown in *SI Appendix*, Table S2. For Pd<sub>n</sub>/O-graphene, Pd would be anchored via C–O–Pd (51). For Pd<sub>n</sub>/B-graphene, we predict that Pd also binds with O (C<sub>2</sub>–B–O–Pd) covalently. This covalent bond will likely have a partial ionic bond character due to the much higher electronegativity of O (3.44) than B (2.04) and C (2.55) in BC<sub>2</sub>O moiety. For Pd<sub>n</sub>/S-graphene, we propose C<sub>2</sub>–S–Pd structure, since S atom in C<sub>2</sub>–S has been demonstrated to be able to form an additional bond with a metal atom (52). For Pd<sub>n</sub>/N-graphene, we propose Pd coordinates with pyrrolic N (i.e., C<sub>2</sub>–N–Pd), not graphitic nor pyridinic N. We considered that



**Fig. 4.** DFT calculated minimum energy paths for H\* formation on various Pd<sub>n</sub> moieties with the engineered CE. IS stands for initial state, TS for transition state, and FS for final state. All theoretical models involved in the reaction process are presented in *SI Appendix*, Figs. S21–S24.

i) graphitic N in coordinative saturation has been experimentally and theoretically demonstrated to be unable to bind with Pd (53), and ii) pyridinic N is in a much lower concentration than pyrrolic N (*SI Appendix, Fig. S3*) and has been demonstrated to be less favorable as N coordination species (54).

**Relationship between CE and Catalytic Performance.** We investigated the performance of Pd<sub>n</sub>/X-graphenes for catalytic reduction involving H<sub>2</sub> dissociation and H\* generation. We selected bromate (BrO<sub>3</sub><sup>-</sup>) as a representative target for reductive decontamination, considering its prevalent occurrence as a disinfection byproduct and serious public health threat as a Group 2B carcinogen (55, 56). We observed a near-complete bromine mass balance throughout the reaction (stoichiometric generation of Br<sup>-</sup> from the destruction of BrO<sub>3</sub><sup>-</sup>) (*SI Appendix, Figs. S11 and S12*). This indicates that all BrO<sub>3</sub><sup>-</sup> was selectively reduced to Br<sup>-</sup> by Pd<sub>n</sub>/X-graphene catalysts, without the accumulation of intermediates such as BrO<sub>2</sub><sup>-</sup> and BrO<sup>-</sup> which could form depending on the reduction pathways (57).

However, the kinetics of BrO<sub>3</sub><sup>-</sup> depended on the type of heteroatoms that affect CE of Pd in Pd<sub>n</sub>; the kinetics were in the order of Pd<sub>n</sub>/O-graphene < Pd<sub>n</sub>/S-graphene < Pd<sub>n</sub>/B-graphene < Pd<sub>n</sub>/N-graphene (Fig. 3A). The Pd<sub>n</sub>/N-graphene exhibited the fastest kinetics, with over 95% BrO<sub>3</sub><sup>-</sup> reduction within 3 min (*SI Appendix, Fig. S13*). We additionally compared the turnover frequency (TOF, per Pd atom basis) to those of other reported catalysts (summarized in *SI Appendix, Tables S3 and S4 and Figs. S14 and S15*) and found that Pd<sub>n</sub>/N-graphene exhibited the highest TOF (up to 11.2 min<sup>-1</sup>) under neutral pH condition. Due to the low activity of conventional Pd-based catalysts toward H\* generation, acidic conditions are typically required to enhance BrO<sub>3</sub><sup>-</sup> adsorption onto the positively charged surface and thereby improve the H\* utilization efficiency (58, 59). The superior activity of Pd<sub>n</sub>/N-graphene rendered a broad pH-adaptability (Fig. 3B), wherein the electrostatic adsorption between BrO<sub>3</sub><sup>-</sup> and catalyst was no longer necessary. EXAFS results demonstrate that all Pd<sub>n</sub>/X-graphene catalysts retained their original property even after being stored in H<sub>2</sub>-saturated solution for 1 wk (*SI Appendix, Fig. S16*). We filtered the suspension after the storage and confirmed no Pd leaching [i.e., Pd in the permeate was below the detection limit of inductively coupled plasma mass spectrometry (ICP-MS) analysis]. The catalysts recovered by the filter maintained the original bromate reduction capability, confirming the dominant role of heterogeneous catalysis without the involvement of dissolved Pd species (*SI Appendix, Fig. S17*). Finally, the activity of Pd<sub>n</sub>/N-graphene was maintained over eight cycles of repetitive use (Fig. 3C).

Electron paramagnetic resonance (EPR) spectra obtained using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the probe (Fig. 3D) showed a series of nine characteristic peaks for all Pd<sub>n</sub>/X-graphene samples, which indicate the occurrence of H\* (60). Although the relative intensities of the DMPO/H\* adducts cannot provide a quantitative correlation, a stronger intensity can generally be interpreted as a higher concentration of H\*. Relative intensities of the H\* signal are in the order of Pd<sub>n</sub>/O-graphene < Pd<sub>n</sub>/S-graphene < Pd<sub>n</sub>/B-graphene < Pd<sub>n</sub>/N-graphene, which matches well with the increasing reaction kinetics. We consequently infer that the highest activity of Pd<sub>n</sub>/N-graphene results from the most efficient H\* generation. Considering that Pd atoms in Pd<sub>n</sub>/O-graphene, Pd<sub>n</sub>/S-graphene, and Pd<sub>n</sub>/N-graphene are all similar in oxidation state (Fig. 2B), size (with an atomicity of ~4), and structure (*SI Appendix, Tables S1 and S2*), we postulate that the difference in H<sub>2</sub> dissociation activity is mostly influenced by the Pd–X coordination environment. Such influence of support

on the catalytic activity of metal sites has also been observed when Ir clusters were loaded on different substrates such as MgO and γ-Al<sub>2</sub>O<sub>3</sub> (61).

To expand the potential applications to other environmentally relevant catalytic schemes, we additionally examined the reductive debromination of tetrabromobisphenol A (TBBPA), one of the most widely used brominated flame retardants. TBBPA is a potent endocrine disrupter and a widespread water pollutant (62, 63). The optimized Pd<sub>n</sub>/N-graphene also exhibited fast kinetics, achieving around 100% TBBPA debromination within 10 min of catalysis (Fig. 3E and *SI Appendix, Figs. S18*). As another example, we evaluated the reduction of bicarbonate (HCO<sub>3</sub><sup>-</sup>) (Fig. 3F) (64), where H\* has been identified as the main reductant (65). Pd<sub>n</sub>/N-graphene efficiently converted HCO<sub>3</sub><sup>-</sup> into value-added formate (HCO<sub>2</sub><sup>-</sup>) with a TOF of 45 h<sup>-1</sup> (*SI Appendix, Fig. S19*), which is much higher than TOFs by previously reported catalysts (*SI Appendix, Table S5 and Fig. S20*). Such Pd-catalyzed HCO<sub>3</sub><sup>-</sup> reduction has demonstrated 100% selectivity without the generation of any other products (e.g., CH<sub>4</sub>, CO, methanol, or acetate) (66, 67), avoiding a downstream process for product separation.

**Reaction Mechanisms.** We performed DFT calculations to examine how Pd<sub>n</sub> with different CEs differently interact with H<sub>2</sub> and form H\*. The lowest-energy pathways for the overall H\* generation process for different Pd<sub>n</sub>/X-graphenes are shown in (Fig. 4). After the endothermic H<sub>2</sub>O desorption from Pd atom in Pd<sub>n</sub>, H<sub>2</sub> adsorbs onto this Pd site. The H–H bond of adsorbed H<sub>2</sub> (initial state, IS) is stretched from 0.74 Å of the H<sub>2</sub> molecule due to its σ-bonding to 4d orbitals of Pd atoms (48). The DFT results (*SI Appendix, Figs. S21 to S24 and Table S6*) suggest that the length of H–H bonds in the IS varies from 0.82 to 0.90 Å depending on X in Pd<sub>n</sub>/X-graphene. In addition, the distance between Pd (from 1.68 to 1.86 Å) and H as well as the orientation of H<sub>2</sub> on Pd<sub>n</sub> are also different.

The final state (FS), defined as two fully-separated H\* atoms adsorbed onto Pd<sub>n</sub>, also depends on the identity of X in Pd<sub>n</sub>/X-graphene (*SI Appendix, Figs. S21 to S24*). A Bader analysis (*SI Appendix, Table S7*) demonstrates that both H\* atoms in FS states are negatively charged, resulting from homolytic H<sub>2</sub> dissociation (68). In Pd<sub>n</sub>/O-graphene, one H\* diffuses to the center of the triangle facet by binding to three Pd atoms, and the other H\* diffuses to the middle of the Pd–Pd edge by binding to two Pd atoms. In Pd<sub>n</sub>/B-graphene, two H\* atoms bind to the same Pd atom. Though two separated H\* atoms diffuse to two Pd–Pd edges in both Pd<sub>n</sub>/S-graphene and Pd<sub>n</sub>/N-graphene, the location of the Pd–Pd edge is different due to the specific Pd<sub>n</sub> configuration affected by the dopant species. The activation energy from IS to transition state (TS), as estimated by simulating and scanning possible states, varies significantly depending on the catalysts: Pd<sub>n</sub>/N-graphene (0.48 eV) < Pd<sub>n</sub>/B-graphene (0.71 eV) < Pd<sub>n</sub>/S-graphene (1.52 eV) < Pd<sub>n</sub>/O-graphene (2.60 eV). The sequence of activation energy offers a rational interpretation for the experimentally observed variations in reaction kinetics (i.e., Pd<sub>n</sub>/N-graphene > Pd<sub>n</sub>/B-graphene > Pd<sub>n</sub>/S-graphene > Pd<sub>n</sub>/O-graphene). In order to experimentally confirm H<sub>2</sub> dissociation as the rate-limiting step, we evaluated the kinetic isotope effect (KIE) using D<sub>2</sub> as an alternative hydrogen source. As shown in *SI Appendix, Fig. S25*, D<sub>2</sub> substitution led to a primary KIE (k<sub>H</sub>/k<sub>D</sub>) of 1.74, since the lower zero-point energy of D<sub>2</sub> resulted in a higher activation energy of D<sub>2</sub> dissociation.

We would like to note that the above activation energies can only be used to qualitatively compare the activities of Pd<sub>n</sub>/X-graphenes. It is difficult to build a quantitative relationship between calculated energy barriers and observed kinetics (69) since representative DFT

models cannot fully capture the inherent complexity of real metal ensembles (47, 70). We propose that further research should focus on improving synthetic strategies, for example, by optimizing non-metal dopants or using organic ligands, in order to synthesize  $M_n$  with uniform atomicity and thereby alleviate the gap between the theoretical predictions and experimental observations.

## Conclusions

This study presents the precise control of the CE of Pd ensembles and the resulting enhancement of catalytic performance by O, S, B, and N doping of a graphene substrate. We observed that reconstructing the Pd–O coordination in the first shell of  $Pd_n$  into Pd–S/N through S/N doping significantly affects the catalytic performance. Even when Pd–O in the first shell remains unchanged after B doping, B substantially tunes the electronic structure of  $Pd_n$  centers as an electron donor in the second shell, leading to a much higher activity. Computational results reveal that the activation energy of  $H_2$  dissociation as the rate-limiting step highly depends on the CE of  $Pd_n$  and that the highest catalytic activity of  $Pd_n$ /N-graphene results from enhanced  $H_2$  dissociation. Our findings highlight the importance of CE manipulation for  $Pd_n$ , similar to isolated  $Pd_1$ , since the identity of substrate atom that binds to the metal affects the geometric/electronic structure of metal centers and thus determines the overall reaction kinetics. Our study calls for future efforts to establish a fundamental understanding of the CE effect on a wider range of  $M_n$  catalysts beyond  $Pd_n$  and additional strategies to tailor CE with the goal of fully exploiting the catalytic capability of SAC materials.

## Materials and Methods

**Materials.** All chemicals used in the experiments were of reagent grade or higher and were used as received without further purification. Tetrabromobisphenol A ( $C_{15}H_{12}Br_4O_2$ , TBBPA) and Bisphenol A ( $C_{15}H_{16}O_2$ , BPA) were obtained from J&K Scientific. Sodium bromate ( $NaBrO_3$ ), boric acid ( $H_3BO_3$ ), sulfur (S), melamine ( $C_3H_6N_6$ ), sodium bicarbonate ( $NaHCO_3$ ), sodium formate ( $NaCOOH$ ), sulfate acid ( $H_2SO_4$ ), and nitric acid ( $HNO_3$ ) are purchased from Sigma-Aldrich. Graphene nanoplatelet was obtained from Strem Chemicals. All aqueous solutions were prepared with ultrapure/deionized water obtained from a Milli-Q system.

**Catalyst Synthesis. O-graphene preparation.** First, 0.5 g graphene nanoplatelets was dispersed in 100 mL mixed acid solution ( $HNO_3:H_2SO_4 = 70:30$ ) in a round-bottom flask. This flask was subsequently connected to a reflux system under stirring and heated in an oil bath at 90 °C for 6 h. After cooling down to the room temperature, O-graphene was separated by centrifugation, washed with deionized water (until neutral pH), and dried in an oven at 80 °C.

**B-graphene, S-graphene, and N-graphene syntheses.** O-graphene was well-ground together with boric acid (sulfur or melamine, ten times the weight of O-graphene) and then heated at 800 °C for 2 h (4 h for boron) with a heating rate of 2 °C/min in a tube furnace under a  $H_2/Ar$  (5:95) atmosphere.

**Syntheses of  $Pd_n$  with various CE.** First, 80 mg O-graphene (B-graphene, S-graphene, or N-graphene) was dispersed into 40 mL deionized water under probe sonication for 0.5 h, followed by the addition of 375  $\mu$ L  $H_2PdCl_4$  (10 mM). The mixture was shaken at 300 rpm for 24 h and then dried at 80 °C in the oven.

The obtained powder was then well-ground and moved to a crucible, heated at 800 °C for 2 h with a heating rate of 2 °C/min in a tube furnace under a  $N_2$  atmosphere. The Pd loading amount was determined by ICP-MS: 0.45 wt%, 0.43 wt%, 0.47 wt%, 0.46 wt% for  $Pd_n$ /O-graphene,  $Pd_n$ /S-graphene,  $Pd_n$ /B-graphene, and  $Pd_n$ /N-graphene, respectively.

**Catalyst Characterization.** HAADF-STEM images were taken on a Titan Themis Z STEM (ThermoFisher Scientific) operated at 200 kV, coupled with a probe aberration-corrector to improve imaging spatial resolution to less than 1 Å. The X-ray absorption spectroscopy spectra at Pd K-edge were measured at Inner Shell Spectroscopy beamline of the National Synchrotron Light Source II at Brookhaven National Laboratory (60), using a Si (111) double-crystal monochromator and a passivated implanted planar silicon (PIPS) fluorescence detector at room temperature, with energy calibrated using Pd foil. The catalyst samples were pressed into pellets and sealed in Kapton films for XAFS measurements. XAFS data were analyzed using Athena and Artemis software for conversion of raw data to  $\mu(E)$  spectra, background subtraction and normalization, Fourier transformation and plotting, and fitting in k-space and R-space.

**Evaluation of Catalytic Performance.**  $BrO_3^-$  reduction, TBBPA debromination, and  $HCO_3^-$  reduction tests were conducted in a serum glass bottle sealed with rubber septa at room temperature (25 °C). The suspension containing 0.5 g/L catalyst and 50 ppm TBBPA (50 ppm  $BrO_3^-$  or 0.5 M  $HCO_3^-$ ) was sonicated for 15 min to ensure the dynamic adsorption/desorption equilibrium (SI Appendix, Figs. S26 and S27). Hydrogen gas was continuously sparged into the bottle at 5 mL/min throughout the whole reaction. Aliquots (250  $\mu$ L) were taken at defined time points from the sample solutions by a syringe and immediately filtered by a polyethersulfone filter. To evaluate the catalyst stability, catalysts were collected and washed with ethanol and water after each cycle and redispersed in 50 ppm  $BrO_3^-$  solution for recycling tests. All experiments were conducted in triplicates and the error bars in figures represent the SD from the mean value.

**Quantification of Reactants and Final Products.** Aliquots were filtered, and 200  $\mu$ L solution was diluted to 5 mL deionized water for ion chromatography (IC, Dionex LC20) tests, equipped with Dionex IonPac<sup>TM</sup> AG14A column.  $NaBrO_3$ ,  $NaBr$ ,  $NaHCO_3$ , and  $NaCOOH$  standard solutions were used to calibrate the peak area in relation to concentration.

**Data, Materials, and Software Availability.** Supporting figures and tables described within the manuscript are provided. All study data are included in the article and/or SI Appendix.

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