INTRODUCTION
Precise control over a catalyst’s spatial and electronic configurations is of considerable importance in structure-specified synthesis of both organic molecules (1–3) and nanomaterials (4–7). Structurally ordered intermetallic compounds with definite composition and unique geometric and electronic effects have been extensively studied for this purpose (8–14). For example, the active site location concept using structurally ordered intermetallic compounds as well-defined catalysts has shown great success in selective heterogeneous catalysis (semi-hydrogenation and isomerization) (15) and electrocatalysis (16–22). In addition, relying on the structural template of a solid intermetallic catalyst with unique atomic arrangements and lower crystalline symmetry (23), single-walled carbon nanotubes with single chirality were realized through a specific “recognition” between catalyst and nanotube (5). One fundamental issue on intermetallic catalysts is the relation between their atomic structures and active sites (24).

The strong metal-support interaction (SMSI) has long been a hot topic in heterogeneous catalysis, which presents geometric, electronic, and compositional effects that can be used to control the catalyst structure and property (25–31). For the alloying of intermetallic nanocrystals, it is well accepted that a foreign metal is introduced into the pristine lattice of an element, and then one element is well isolated and surrounded by a foreign element accompanied by the formation of ordered structure under certain thermodynamic conditions (32). When the migration/diffusion of metal on a support is associated with SMSI, the nucleation of intermetallic compounds will be greatly influenced. For example, it was predicted by theoretical calculations that carbon has a larger affinity (i.e., carbon-metal adhesion) to the strong carbide formatting elements (e.g., Mo and W) than noble metals (33–36). Therefore, it is possible to control the nucleation of the intermetallic nanocrystals by manipulating the metal-support interaction and metal atom diffusion rate.

On the other hand, the kinetically controlled metal diffusion results in various types of defects in mono- and bimetallic nanocrystals, such as stacking faults, phase boundaries, and grain boundaries (37, 38). The interfaces generated from these defects commonly promote the catalytic activity by regulating the specific adsorption, desorption, and activation of molecules (39–43). To date, synthesis of intermetallic nanocrystals with controlled interface structure remains challenging, partially because of the complex growth and ordering processes (44–50). Regardless of the alluring performance, it is essential to elucidate the microscopic origin mechanisms of interface in intermetallic nanocrystals and its structure-function relationship.

Here, inspired by the SMSI, we report a strategy of synthesizing intermetallic Pt2Mo with twin structure by controlling the dynamic diffusion of metal species on carbon support and the alloying rate. The state-of-the-art in situ scanning transmission electron microscope (STEM) combined with x-ray diffraction (XRD) enables us to reveal the nucleation and growth kinetics of intermetallic Pt2Mo directly and conclusively. The twinned Pt2Mo/C catalyst exhibits superior aryamine yields and CO resistance for the selective hydrogenation of nitroarenes. These synthetic strategy and performance are also proven to be valid in other twinned intermetallic Pt2W/C catalyst. The mechanisms of CO resistance are unveiled by density functional theory (DFT) calculations and aberration-corrected environmental TEM (ETEM).

RESULTS
Synthesis and characterization of twinned intermetallic Pt2Mo nanocrystals
The polyoxometalate K2[H4PtMo6O24] supported on mesoporous carbon (BP-2000; specific surface area, 1434 m²/g) is used as a precursor to prepare intermetallic Pt2Mo in H2 at 1000°C (denoted as
Pt$_2$Mo/C (see Materials and Methods), which is a feasible way to fabricate uniform intermetallic nanocrystals, because the precursor is nanoscale, and two metal elements are already well mixed in molecule. The XRD pattern of the as-prepared Pt-Mo/C presents diffraction peaks corresponding to the (011), (110), (101), (002), (130), etc., planes of intermetallic Pt$_2$Mo with space group *Immm* (Fig. 1A). However, this XRD pattern is distinct from that of standard Pt$_2$Mo recorded in Joint Committee on Powder Diffraction Standards (JCPDS, no. 65-9665), in that several diffraction peaks are clearly split (inset in Fig. 1A and fig. S1), which is consistent with previous reports that the presence of twins has a significant influence on XRD pattern (39). The sharp protruding XRD peaks of Pt$_2$Mo imply the presence of some large nanoparticles. The low-magnified high-angle annular dark-field STEM (HAADF-STEM) image shows that the size of most Pt$_2$Mo nanoparticles is well dispersed on mesoporous carbon with uniform size of 3 to 5 nm but accompanied a few large particles (Fig. 1B and figs. S2 and S7J). The STEM energy-dispersive x-ray (EDX) elemental maps of an individual particle show that both Pt and Mo elements uniformly distributed in a nanoparticle, where the region marked by white dashed circles indicates that the nanocrystal skin does not segregate (Fig. 1C). An atomic Pt/Mo ratio of 1.9 is calculated from an individual nanocrystal based on EDX (fig. S3), which is in good agreement with the intermetallic Pt$_2$Mo stoichiometry of 2. Note that the ratio of Mo to Pt (6:1) is high enough in precursor, which benefits the formation of intermetallic Pt$_2$Mo without free Pt.

The as-prepared intermetallic Pt$_2$Mo/C with twin structures was revealed by aberration-corrected TEM and HAADF-STEM. Typically, the single- and multiple-twin interfaces are readily visible in intermetallic Pt$_2$Mo (Fig. 1, D and E). More results are shown in fig. S4. The observed superlattice spacing of 4.1 Å in HAADF-STEM image is unique for intermetallic Pt$_2$Mo (020) plane, and periodic oscillation of intensity is attributed to the Z-contrast difference between Mo and Pt in an ordered lattice (Fig. 1D). Because Pt (Z = 78) and Mo (Z = 42) differ greatly in atomic number, Pt atoms appear much brighter than Mo atoms in an ordered structure, demonstrating the well-defined intermetallic structure. The inverse fast Fourier transform (IFFT) of HAADF-STEM image is also in good accordance with the STEM simulation of Pt$_2$Mo [T11] (Fig. 1H). The atomic structure

![Fig. 1. Characterizations of intermetallic twinned Pt$_2$Mo nanocrystals. (A) XRD pattern of Pt$_2$Mo/C catalyst. The standard Pt$_2$Mo card (JCPDS, no. 65-9665) is used as reference. Inset: Unit cell of Pt$_2$Mo (ICSD 105070), space group: *Immm*, a = 2.76 Å, b = 8.30 Å, c = 3.94 Å and zoomed-in XRD peaks. (B) Low-magnified HAADF-STEM image of Pt$_2$Mo/C. (C) STEM-EDX elemental maps of Pt and Mo and overlay of the Pt and Mo EDX maps. (D and E) Typical aberration-corrected HAADF-STEM (D) and HRTEM (E) images of twinned Pt$_2$Mo nanocrystals. The twin boundary is marked by a dashed line. (F and G) FFT (F) and superimposed HRTEM image and twinned Pt$_2$Mo atomic model (G) derived from the region marked in (E). (H) Atom-resolved IFFT image and STEM simulation. a.u., arbitrary units.](image-url)
shows a symmetrical lattice arrangement mirrored by the twin boundary. The FFT pattern at the boundary shows two sets of diffraction pattern, in which the (130) and (101) spots are mirrored with (130) and (101) separated by (031) twin plane, suggesting a typical twin boundary pattern (Fig. 1, E and F). The twin structure of Pt₂Mo is superimposed on a high-resolution TEM (HRTEM) image (Fig. 1G). All above results demonstrate that twinned intermetallic Pt₂Mo nanocrystals with small size are formed on mesoporous carbon support.

**Dynamic nucleation of twinned intermetallic Pt₂Mo nanocrystals**

To elucidate the nucleation mechanism of twinned Pt₂Mo nanocrystals, we compared the differences in nucleating Pt₂Mo on carbon and non-carbonous (MgO) supports, which was prepared under the same conditions. The evolution of Pt-Mo upon annealing at 600° to 1000°C in H₂ was revealed by ex situ and in situ STEM, EDX mapping, and XRD.

Figure 2A depicts the temperature-sequential evolution of Pt-Mo on mesoporous carbon by STEM-EDX elemental mapping. At 600°C, ultrasmall Mo and Pt species were well dispersed on carbon. This was followed by the preferential aggregation of Pt species into small nanoparticles (2 to 3 nm) when increasing the temperature to 800°C, whereas Mo species still retain atomic dispersion. Subsequently, Mo migrated and diffused into Pt nucleus to form intermetallic Pt₂Mo at 1000°C, evidenced by EDX maps that Pt and Mo are uniformly distributed in nanoparticles. The XRD results are consistent with the STEM-EDX observation that Pt species was preferentially reduced to metallic Pt nanoparticles at 800°C, and then Mo diffused and alloyed with Pt nucleus to form ordered Pt₂Mo at 1000°C (fig. S5A). In randomly selected regions under STEM/TEM based on 100 well-defined Pt₂Mo nanoparticles, there are 44% Pt₂Mo nanoparticles on carbon support exhibiting twin structure (Fig. 2E).

Figure 2B shows the evolution of Pt-Mo on MgO support at 600° to 1000°C. Differently, Mo already alloyed with Pt as a solid solution with randomly distributed Mo and Pt atoms at a lower temperature of 600°C, demonstrated by EDX maps and XRD (fig. S5B). Then, the Pt-Mo solid solution nanoparticles grew larger at 800° to 1000°C and transformed to ordered Pt₂Mo at 1000°C (Fig. 2B and fig. S5B). In addition, Mo particle phase visible in XRD pattern appeared at 1000°C (fig. S5B), indicating that Mo atoms are more easily aggregated to particles on MgO than on carbon support due to the weaker Mo-MgO interaction than Mo-C. We analyzed from considerable TEM images that 95% intermetallic Pt₂Mo on MgO are untwinned (denoted as untwinned Pt₂Mo/MgO) (Fig. 2E and fig. S6). The twin structure of Pt₂Mo/C is further demonstrated by synchrotron x-ray absorption spectroscopy (XAS). In x-ray absorption near-edge structure spectroscopy (XANES) region, the pre-edge peak at 11,548 eV obviously appeared for twinned Pt₂Mo/C but very weak for untwinned Pt₂Mo/MgO and Pt (Fig. 2F), which is attributed to the symmetry breaking (51) of twin defect structure. The XAS result agrees with TEM observation. The nucleation rate of Pt-Mo nanocrystals is plotted as a function of the mean size of nanoparticles versus reduction temperature (Fig. 2G). The particle size is statistically measured from HAADF-STEM images (fig. S7). It shows that the nucleation/alloying rate of Pt₂Mo on carbon is slower than that
on MgO at 600° to 1000°C, as schematically illustrated in Fig. 2 (C and D). This difference implies that Mo mobility on carbon is much smaller than on MgO, attributed to the stronger Mo-C interaction than Mo-MgO. We found that Pt$_2$Mo forming on other oxide support (Al$_2$O$_3$) also exhibits an un-twinned structure (figs. S8 and S9).

To directly reveal the diffusion-controlled nucleation of twinned Pt$_2$Mo, we performed in situ aberration-corrected dark-field STEM to track the diffusion of Mo species at atomic scale. The time-sequenced HAADF-STEM images show that Mo single atoms migrated slowly on carbon and incorporated tardily into Pt or PtMo$_x$ nucleus at 1000°C (Fig. 3, A to C, labeled by circles). The complete process is shown in fig. S10. At the early nucleation stage, a large proportion of defected PtMo$_x$ nucleus with poorly crystalized structure appeared mainly (figs. S7D and S11) because Mo atoms diffused slowly into Pt nucleus on carbon. Therefore, the insufficient Mo

![Fig. 3. In situ HAADF-STEM characterization of Mo diffusion on carbon and MgO supports at 1000°C. (A to C) Random diffusion of Mo atoms and tiny clusters on mesoporous carbon. The circles are meant to help with observation of mobile Mo atoms. (D to F) Coalescence of Mo clusters along the MgO lattice. The parallel lines are meant to help with observation of the alignment of Mo nanocrystals with the same lattice spacing. (G and H) Ex situ HAADF-STEM image of as-formed Pt$_2$Mo nanocrystals orientated along MgO, FFTs of MgO, and four Pt$_2$Mo nanocrystals labeled in (G). The rhombic frameworks in FFTs are meant to help with observation of the same orientation of nanocrystal. (I) A mismatch model of (022) MgO||(132)Pt$_2$Mo. (J) Size distribution of mobile Mo on carbon and MgO supports.](image-url)
supply will lead to the uneven growth of Pt₂Mo nanocrystals and thus emerging twin interfaces. By contrast, Mo easily migrated and coalesced on MgO as the cluster/particle state rather than the single-atom state at 1000°C due to the weak Mo-MgO interaction (Fig. 3, D to F). The sufficient Mo supply enabled the fast and uniform alloying of Pt to form single-crystal Pt₂Mo. Figure 3 summarizes the size distribution of mobile Mo species on carbon and MgO supports, showing the obvious difference in size. The growth kinetics of twinned intermetallic nanocrystals is similar to that of the wet-chemical nucleation of twinned nanocrystals observed by in situ liquid cell TEM (52). In addition, we also found that nanocrystals are well aligned along the lattice of the single-crystal surface of MgO with similar lattice spacing (Fig. 3, D to F, labeled by parallel lines). Figure 3 (G and H) shows the ex situ HAADF-STEM images and FFTs of the as-nucleated Pt₂Mo on MgO, where there exists a lattice mismatch (022)ₓMgO//(132)ₓPt₂Mo between MgO and Pt₂Mo nanocrystals (Fig. 3I). More evidence showing the mismatch structure is shown in fig. S12. Therefore, orientation and coalescence of Pt₂Mo were guided by the lattice of MgO, thus resulting in single-crystal Pt₂Mo. However, Mo species randomly coalesced to PtMoₓ on carbon without lattice match, and consequently, the twin boundary was more likely to form in Pt₂Mo/C.

We further noticed that the difference in specific surface area of mesoporous carbon (1434 m²/g) and MgO (50 m²/g) supports may also influence the averaged interparticle distance, particle diffusion, and size (53). To exclude the effect of support specific surface area, we compared the intermetallic Pt₂Mo and Pt-M (M = Co, Fe, and Cu) on the same mesoporous carbon prepared under the same conditions. Previous computational studies have predicted that the metal-carbon interaction scales somewhat with the carbophilicity of the metal, which is in the order of W/Mo > Fe/Co/Ni > Cu (35, 54). We did not find the twinned intermetallic nanocrystals when using weaker carbon interaction elements Fe, Co, and Cu to alloy with Pt on mesoporous carbon (figs. S13 to S15). In addition, the size of twinned Pt₂Mo/C is smaller than that of untwinned Pt-M (M = Co, Fe, and Cu) (fig. S16). These comparative results between different metals again demonstrate that the strong Mo-C interaction results in sluggish Mo migration on carbon and in slow diffusion of Mo into Pt nucleus. The mechanism is further proved valid using another strong carbon interaction element, W, to prepare the intermetallic Pt₂W/C with the same method, in which the twin boundary is also frequently observed in intermetallic Pt₂W nanocrystals (fig. S17).

Selective hydrogenation of nitroarenes over twinned intermetallic catalysts

Hydrogenation of nitrobenzene derivatives to anilines is highly demanded for the production of high-value intermediates (55). We demonstrated the applicability of twinned intermetallic catalysts for the selective hydrogenation of 4-nitrostyrene (Fig. 4A), which is the most demanding reaction among a variety of substituted nitroarenes, because the C=O group in this molecule is highly reactive toward reduction over Pt-based catalyst.

Figure 4B illustrates the catalytic performance of Pt-Mo/C catalysts prepared at 600° to 1000°C. The twinned Pt₂Mo/C catalyst formed at 1000°C exhibits higher 4-nitrostyrene conversion (99.9%) and selective production of 4-vinylaniline (95.7%) than when Pt-Mo catalysts prepared at lower temperature (600° and 800°C) were used in otherwise identical reactions. Essentially undiminished results are achieved during eight reaction cycles using the catalyst recovered

![Fig. 4. Selective hydrogenation of 4-nitrostyrene. (A) Reaction route. (B) Performance of Pt-Mo/C catalyst prepared at 600° to 1000°C. (C) Reusability of twinned Pt₂Mo/C catalyst tested at a medium conversion. (D and E) Time course plots for the conversion (D) and selectivity (E) over twinned Pt₂Mo/C and untwinned Pt₂Mo/C, Pt₂Mo/MgO, and Pt₂Mo/Al₂O₃ catalysts.](image-url)
after each run of evaluation (Fig. 4C). The twinned Pt₆Mo/C catalyst, after an eight-cycle test, retained the uniform size of 3 to 5 nm, homogeneous elemental distribution, and twin structure confirmed by STEM and EDX (fig. S18), indicating no obvious elemental segregation or leaching during the catalytic process. To reveal the effect of twin boundary of Pt₆Mo, we compared the catalytic performance of twinned Pt₆Mo/C and untwinned Pt₆Mo/oxide (MgO and Al₂O₃) catalysts prepared at 1000°C tested under the same conditions. It was obviously found that twinned Pt₆Mo/C exhibits lower activity for converting substrate but higher selectivity toward 4-vinylaniline (95.7%) than untwinned Pt₆Mo/oxide (17 to 18%) (Fig. 4, D and E). The possible reason is that lower activity of twinned Pt₆Mo/C inhibits the fast overhydrogenation of 4-nitrostyrene to 4-ethylnitrobenzene and 4-ethylaniline. In addition, to reveal the effect of support, we also used untwinned Pt₆Mo catalysts supported on the same mesoporous carbon (BP-2000) (denoted as untwinned Pt₆Mo/C) for comparison. The untwinned intermetallic Pt₆Mo/C was synthesized by annealing Pt-Mo random solid solution nanoparticles prepared through a wet-chemical approach (see Materials and Methods and fig. S19, A to D). It was found that untwinned Pt₆Mo/C exhibited similar activity but lower selectivity than twinned Pt₆Mo/C catalyst (Fig. 4, D and E), implying that twin interface may be a key factor for the high selectivity. The twinned Pt₆Mo/C catalyst also maintains a high 4-vinylaniline selectivity (94.7%), and few overhydrogenated products were found when prolonging the reaction time to 300 min (Fig. 4E), indicating that the twinned Pt₆Mo is only active in the hydrogenation of N=O bond rather than C=O bond.

We noticed that there exists a size difference between Pt₆Mo/C (BP-2000) (mean, 3.7 ± 0.9 nm) and Pt₆Mo/MgO (mean, 6.0 ± 3.1 nm). To exclude the effect of the size difference, we used another mesoporous carbon support (EC-600J) with a specific surface area (1345 m²/g) smaller than that of mesoporous carbon (BP-2000, 1434 m²/g) to prepare twinned Pt₆Mo nanocrystals with the same method. The twinned Pt₆Mo/C (EC-2000) exhibits a similar size (mean, 6.0 ± 2.3 nm) to those of untwinned Pt₆Mo/MgO, which shows a similar conversion but a significantly higher selectivity in comparison with untwinned Pt₆Mo/MgO catalyst tested under the same conditions (fig. S20). All above results indicate that the improved hydrogenation selectivity is induced by the twin structure of Pt₆Mo with regulated active sites at interface rather than particle size or catalyst-support interface effect.

**CO-resistant hydrogenation**

In the industrial hydrogenation process, ultrahigh purity of H₂ (99.99%) is required to prevent the poisoning of the Pt-based catalyst by the accumulated trace amount of CO impurity in the gas feed. Therefore, developing a CO-resistant catalyst using crude H₂ is not only of significant scientific importance but also economically appealing.

The Pt/C catalyst was found to be highly active but poorly selective toward 4-vinylaniline under pure H₂ (Table 1, entry 1). However, when 0.1%-CO/H₂ was adopted, the Pt/C catalyst was completely poisoned without activity (Table 1, entry 2). By contrast, comparing the performance with and without CO, twinned Pt₆Mo/C catalyst was active, with the retention of 99.9% 4-nitrostyrene conversion and 99.9% 4-vinylaniline selectivity (Table 1, entries 3 and 4). The present catalyst was also proven to be generally applicable for all nitroarene derivatives containing various reducible groups at different substituted positions in benzene (Fig. 5), with conversion of ≥99.9% and aniline selectivity of ≥96.4%. Even under 0.1%-CO/H₂ condition, no obvious decrease in activity or selectivity was observed (Table 1, entries 5 to 14). For another twinned Pt₆W/C catalyst, it also had high conversion (95.7 to 99.9%) and aniline selectivity (94.4 to 99.9%) for hydrogenation of all nitroarene derivatives under 0.1%-CO/H₂ condition (Table 1, entries 15 to 20). However, the performance of untwinned Pt₆Mo/C decreases notably as 0.1%-CO/H₂ was introduced (Table 1, entries 21 and 22), in comparison with twinned Pt₆Mo/C. All other untwinned Pt₆Mo/oxides and untwinned Pt-Cu/Fe/Cu/C also show poor CO resistance (Table 1, entries 23 and 24, and table S1). These results again demonstrate that the improved hydrogenation performance and CO resistance are induced by the twin structure of Pt₆Mo rather than the catalyst-support interface effect.

**DISCUSSION**

It is generally accepted that the CO poisoning is attributed to the strong chemisorption of CO on Pt and, consequently, blockage of the hydrogen adsorption and dissociation sites (55–57). In our results, the CO poisoning occurred in all untwinned Pt–based intermetallic catalysts. However, twinned Pt₆Mo/C catalyst still exhibits excellent CO-resistant property and selectivity. Therefore, it is reasonable to assume that the twin boundary of Pt₆Mo may not only act as active sites for hydrogenation but also weaken the adsorption of CO.

**CO resistance mechanism on twinned catalyst**

To further understand the insights into the effect of twin boundary on weakening the CO adsorption, we performed DFT calculations to explore the CO adsorption on intermetallic Pt₆Mo surface. Figure 6 (A and B) depicts the representative of several different configurations of CO adsorption on untwinned and twinned Pt₆Mo (101) surface, including linear (adatom Pt), bridge (adatoms Pt-Pt and Pt-Mo), and hollow (adatoms Pt-Mo-Pt) sites. Other configurations are shown in figs. S21 and S22 and tables S2 to S4. To elucidate the bonding nature of CO involved in the associative mechanism, we investigated the densities of states (DOSs) of CO adsorption on a typical low-index (101) plane of Pt₆Mo. We calculated the projected DOS of the 5d states of Pt at adsorption site and the 2p states of CO (fig. S23). For CO adsorption on untwinned Pt₆Mo (101), there is a large overlap between Pt 5d states and CO 2p states (Fig. 6C). The 2p* orbital of CO molecule originally far upon the Fermi level spreads out across the Fermi level after adsorption, revealing the strong interaction between Pt site and CO. This can be attributable to the electron “acceptance-donating” mechanism (58) that the unoccupied Pt 5d orbitals accept the electrons from CO 5σ and 1π orbitals, and the Pt sites back-donate their occupied d electrons into CO 2π* orbital, thus weakening the C≡O bond. However, for CO adsorption on twinned Pt₆Mo (101), the overlap between Pt 5d and CO 2p near the Fermi level decreases (Fig. 6D). The characteristic peaks of the original 1σ, 5σ, and 2π* orbitals of free CO emerge, indicating the weak interaction between Pt and CO.

We further calculated the adsorption energies of CO at different sites of twinned Pt₆Mo (101), which are found to be −1.19 to −1.29 eV and are larger than those on untwinned (101) surface (−1.86 to −1.91 eV) (Fig. 6E), indicating more resistance to CO adsorption on twinned Pt₆Mo. Other Pt₆Mo planes such as (031) also exhibit similar tendency that the twinned surface shows larger CO
adsorption energies than the untwinned surface (figs. S24 and S25 and tables S5 and S6), indicating the general resistance to CO on various twinned surfaces. In addition, it was observed that resistance to CO adsorption occurs not only on the twin boundary but also on the local region around the twin boundary of Pt$_2$Mo with the higher CO adsorption energies (Fig. 6, B and E, labeled by i, iii, and iv).

The computational results are further demonstrated by in situ ETEM under CO environment. To avoid any possible effect from the long electron exposure–induced structural changes, the beam is on only when capturing TEM images. We performed the aberration-corrected ETEM and found that obvious structure evolution after exposing in CO occurred in the untwinned Pt$_2$Mo catalyst (Fig. 6F), suggesting the strong binding of CO-induced reconstruction. This observation is in line with previous reports that the CO molecules caused the facets of a noble metal nanocrystal to reconstruct due to the strong CO chemisorption (59, 60). However, the multiple-twin Pt$_2$Mo nanocrystal illustrated no apparent change in surface lattice spacing and preserved the morphology upon exposure to CO (Fig. 6G), which is attributable to the weak adsorption of CO. More ETEM images shown in fig. S26 depict the similar results of twinned and untwinned Pt$_2$Mo nanocrystals under CO.

In summary, the intermetallic twinned Pt$_2$Mo nanocrystals with a small size of 3 to 5 nm supported on mesoporous carbon were synthesized by using polyoxometalate as a precursor. The strong binding of CO-induced reconstruction. This observation is in line with previous reports that the CO molecules caused the facets of a noble metal nanocrystal to reconstruct due to the strong CO chemisorption (59, 60). However, the multiple-twin Pt$_2$Mo nanocrystal illustrated no apparent change in surface lattice spacing and preserved the morphology upon exposure to CO (Fig. 6G), which is attributable to the weak adsorption of CO. More ETEM images shown in fig. S26 depict the similar results of twinned and untwinned Pt$_2$Mo nanocrystals under CO.

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Mo-C interaction leads to the sluggish migration of Mo and slow diffusion into Pt nucleus, thereby resulting in the uneven growth of Pt 2 Mo and emerging twin boundary, while weak Mo-MgO interaction and MgO lattice template lead to the fast coalescence of Pt 2 Mo along the MgO lattice to form single crystals. This nucleation process of intermetallic nanocrystals was revealed by in situ STEM and EDX elemental mapping at 600°C to 1000°C. The twinned Pt 2 Mo/C catalyst shows a markedly high activity and selectivity in hydrogenating all types of nitroarenes as well as excellent CO resistance, compared to untwinned Pt–based intermetallic catalysts. The synthetic strategy and CO resistance performance are also proven to be valid in twinned Pt 2 W/C catalyst when using the other strong carbon interaction element W. Combined use of in situ ETEM and DFT calculations demonstrates that the local regions around the Pt 2 Mo twin boundary weaken the CO adsorption and act as active sites for hydrogenation.

**MATERIALS AND METHODS**

**Preparation of twinned intermetallic Pt-Mo and Pt-W nanocrystals**

The K 2[H 6 PtMo 6 O 24] was synthesized according to the previous literature (more detail in the Supplementary Materials) (61). The synthesis of Pt 2 Mo/C by thermal annealing approach was conducted in a tube furnace. Typically, 20 mg of K 2[H 6 PtMo 6 O 24] and 100 mg of mesoporous carbon (Black Pearls 2000, BP-2000, produced by Cabot Corporation; specific surface area, 1434 m 2/g) were mixed in 50 ml of deionized water, which was then stirred for 2 hours to obtain a black suspension and dried by rotary evaporator. Then, the powder was transferred to a quartz boat and annealed in a tube furnace. Before annealing, the furnace was purged with Ar (200 ml/min) for 5 minutes to remove air. The furnace was heated from room temperature to 200°C and maintained for 1 hour and then heated to 1000°C for another 4 hours at a rate of 10°C/min under 10% H 2/Ar (200 ml/min). The Pt 2 Mo/C was obtained after cooling down to room temperature and washed by deionized water and ethanol to remove K 2 O. Another mesoporous carbon support, EC-600J, with a specific surface area of 1345 m 2/g was also used to prepare the
Pt₂Mo with the same methods. The twinned intermetallic Pt₂W was synthesized with the same method by using K₂[H₄PtW₆O₂₄] as precursor.

Preparation of untwinned intermetallic Pt₂Mo and other Pt-based nanocrystals
The conditions in preparing untwinned intermetallic Pt₂Mo on MgO and Al₂O₃ supports are the same as those used in preparing twinned Pt₂Mo/C. For the synthesis of Pt₂Mo random solid solution alloy through a wet-chemical approach, 50 mg of carbon support (BP-2000), 3.2 mg of K₂PtCl₆, and 10.9 mg of K₂MoO₄ were dispersed in 30 ml of deionized water and kept stirring for 4 hours to obtain a uniform suspension. Then, 50 mg of NaBH₄ was added as a reductant to reduce the precursors. The as-obtained precipitation was separated by centrifugation and washed by deionized water, followed by drying in oven at 60°C. Then, it was annealed in a tube furnace at 1000°C for 4 hours under 10% H₂/Ar (200 ml/min) to form untwinned intermetallic Pt₂Mo/C.

The synthesis of Pt-M/C (M = Co, Fe, and Cu) alloys was conducted in a similar way to Pt₂Mo/C. Typically, 6.4 mg of K₂PtCl₆, 1.2 mg of FeCl₃, and 100 mg of mesoporous carbon were mixed in 50 ml of deionized water, which was then stirred for 2 hours to obtain a black suspension and dried by a rotary evaporator. Then, the powder was annealed at 1000°C under H₂ to form Pt-M/C. The synthesis of Pt/C was similar to that of Pt₂Mo/C by using 5.8 mg of K₃Pt(OH)₆ as a precursor and 100 mg of mesoporous carbon (BP-2000).

Characterizations of catalysts
HAADF-STEM was performed on an aberration-corrected STEM (FEI Titan Cubed Themis G2, 300 kV) equipped with Cs double-corrector DCOR and a high-brightness field-emission gun. TEM was performed on an aberration-corrected ETEM (FEI Titan G2 80-300, 300 kV). EDX mapping was carried out on a FEI Talos F200X electron microscope (200 kV) with a HAADF detector. XRD was performed on Rigaku SmartLab equipped with a Cu Ka radiation source, operated at 200 mA and 45 kV. X-ray photoelectron spectroscopy was performed on a Thermo K-Alpha+ X-ray photoelectron spectrometer with an Al Kα source. XAS was investigated at BL14W-1 beamline at Shanghai Synchrotron Radiation Facility, China. The nitrogen adsorption measurement was characterized by the ASAP 2020 System, and the surface area of the powder samples was calculated by the Brunauer–Emmett–Teller method (BET method).

In situ STEM and ETEM experiments
In situ STEM experiment was conducted on an aberration-corrected STEM (FEI Titan Cubed Themis G2, 300 kV) equipped with Cs double-corrector DCOR and a high-brightness field-emission gun. The Pt₂Mo/C already annealed at 1000°C in the furnace with H₂ was dispersed onto a heating chip mounted on a single-tile FEI MEMS holder, which was reheated to 1000°C in ETEM at a rate of 1°C/s at high vacuum. Then, HAADF-STEM images were acquired.

ETEM experiment was conducted on an aberration-corrected Titan G2 80-300 ETEM, operating at 300 kV in vacuum (~10⁻⁵ Pa). The as-prepared Pt₂Mo catalysts were dispersed onto TEM grids mounted on a single-tile FEI MEMS holder. Then, the catalysts were observed in situ under CO atmosphere (1% CO/N₂, 50 Pa). To minimize the electron irradiation damage, the electron dosage was rigidly controlled at 94 e⁻ Å⁻² s⁻¹.

Computational detail
The DFT calculations have been performed with the Vienna Ab-initio Simulation Package with Projector Augmented Wave (PAW) pseudopotential. Electronic exchange and correlation were treated within the generalized gradient approximation functional due to Perdew, Burke, and Ernzerhof. The calculations were conducted in a spin-polarized manner and have been performed within periodic boundary condition supercells. The free CO molecule was placed into a cubic box with dimensions of 8 Å by 8 Å by 8 Å with Gamma point sampling. Both untwinned and twinned Pt₂Mo (101) and (031) slabs used the supercells with dimensions of 17 Å by 20 Å by 27 Å and 16 Å by 14 Å by 29 Å consisting of four atomic layers including 192 atoms (128 Pt atoms and 64 Mo atoms) and 144 atoms (96 Pt atoms and 48 Mo atoms), respectively, which were separated by 20 Å of vacuum space to prevent interactions between periodic slabs. For Brillouin zone integration, the Gamma point with a 1 × 1 × 1 k-point grid was used in convergence test verification. Lattice constants of bulk Pt₂Mo were fully optimized until residual forces fell below 0.05 eV/Å. A kinetic energy cutoff of 400 eV was used for the plane-wave expansion, and for the slabs, the atomic positions of the two upper layers were fully relaxed until the residual atomic force and total energy were less than 0.05 eV/Å and 10⁻⁶ eV, respectively. The adsorption energy is calculated by the equation

\[ \Delta E_{\text{ads-CO}} = E_{\text{CO/Pt2Mo(101)}} - E_{\text{Pt2Mo(101)}} - E_{\text{CO}} \]

where \( E_{\text{CO/Pt2Mo(101)}} \) is the total energy of the Pt₂Mo (101) surface with one adsorbed CO molecule, \( E_{\text{Pt2Mo(101)}} \) is the total energy of the clean Pt₂Mo (101) surface, and \( E_{\text{CO}} \) is the total energy of an isolated gas-phase CO molecule. In the used sign convention, a more negative (smaller) \( \Delta E_{\text{ads-CO}} \) value indicates a stronger surface adsorption.
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