Nanocarbon-Edge-Anchored High-Density Pt Atoms for 3-nitrostyrene Hydrogenation: Strong Metal-Carbon Interaction

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HIGHLIGHTS

- A strategy is proposed to anchor metal atoms to edge carbon atoms of graphene sheets
- Formation of Pt1-C bond tunes performance of Pt1/h-NC single-atom catalyst (SAC)
- Pt1/h-NC SAC is 20 times more active than the best catalyst for 3-nitrostyrene hydrogenation
- Electronic SMSI can be effectively used to tune catalytic properties of SACs

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Nanocarbon-Edge-Anchored High-Density Pt Atoms for 3-nitrostyrene Hydrogenation: Strong Metal-Carbon Interaction

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SUMMARY
Strong metal-support interaction (SMSI) has been widely used to improve catalytic performance and to identify reaction mechanisms. We report that single Pt atoms anchored onto hollow nanocarbon (h-NC) edges possess strong metal-carbon interaction, which significantly modifies the catalytic behavior of the anchored Pt atoms for selective hydrogenation reactions. The strong Pt-C bonding not only stabilizes single Pt atoms but also modifies their electronic structure, tunes their adsorption properties, and enhances activation of reactants. The fabricated Pt1/h-NC single-atom catalysts (SACs) demonstrated excellent activity for hydrogenation of 3-nitrostyrene to 3-vinylaniline with a turnover number >31,000/h, 20 times higher than that of the best catalyst for such selective hydrogenation reactions reported in the literature. The strategy to strongly anchor Pt atoms by edge carbon atoms of h-NCs is general and can be extended to construct strongly anchored metal atoms, via SMSI, onto surfaces of various types of support materials to develop robust SACs.

INTRODUCTION
Supported metal catalysts with metal particles finely dispersed on high-surface-area support materials are vital for many industrially important catalytic reactions. The surface physicochemical properties of the supports play a crucial role in modifying the catalytic behaviors of supported metal species via the strong metal-support interaction (SMSI) (Lee et al., 2015; Tang et al., 2016a, 2016b; Vannice, 1979; Matsubu et al., 2017). The classical SMSI phenomenon was discovered on titania-supported Pt-group metals of which high temperature reduction significantly influenced the adsorption properties of small molecules such as H2 and CO (Tauster et al., 1978). It has been reported that pretreatment and reaction conditions induce the SMSI as well in oxides supported Au (for CO oxidation) (Liu et al., 2012) and Rh (for CO2 reduction by H2) catalysts (Matsubu et al., 2017), which are termed oxidative and adsorbate-mediated SMSI. Recent reports demonstrated that carbides (Dong et al., 2018), phosphates (Tang et al., 2016a, 2016b), and layered double hydroxides (Wang et al., 2017) supported Au catalysts exhibited the SMSI effects for water-gas shift, CO oxidation, and ethanol dehydrogenation reactions, respectively. The SMSI has been widely exploited to improve catalyst stability (Lee et al., 2015; Tang et al., 2016a, 2016b), identify reaction mechanisms (Matsubu et al., 2017; Bonanni et al., 2012), and enhance activity (Vannice, 1979; Sonstrom et al., 2011). It is highly desired to extend the applications of SMSI concept to broader catalyst systems, beyond metal particles, to tune catalytic properties for desirable performance.

Carbon-based catalysts have been widely used in liquid phase hydrogenation reactions because of their high chemical stability, high total surface area, and unique electronic properties (Su et al., 2017). It has been reported that the interaction between metal species and carbon surfaces can be significantly strengthened by engineering defects of, introducing functional groups to, and/or incorporating heteroatoms in carbon structures (Charlier, 2002; Lordi et al., 2001; Ebbsen and Takada, 1995). For example, single metal atoms that are anchored onto heteroatom-doped (e.g., N, O) carbon materials exhibited excellent catalytic performance for various catalytic transformations, such as methane activation (Cui et al., 2018), selective hydrogenation (Yan et al., 2015), hydrogen evolution (Fei et al., 2015; Liu et al., 2018), and oxygen reduction (Zitolo et al., 2015; Li et al., 2018). The uniformity of isolated active sites and the strong interaction between individual metal atoms and support surfaces facilitate the tuning of both selectivity and activity (Qiao et al., 2011; Liu, 2017a, 2017b; Gates et al., 2017; Wang et al., 2018; Chen et al., 2018). However, the structure of high-surface-area activated carbon supports can become...
extremely complex and consequently poses formidable challenges for correlating the metal-carbon interaction with the observed catalytic properties.

In this work, we fabricated hollow nanocarbons (h-NCs) that possess high-number density of surface edge/defect sites, high total surface area, and highly accessible mesopores. We anchored ~1.0 wt.% single Pt atoms to the edge/defect sites of the h-NCs to synthesize h-NC supported Pt1 single-atom catalysts (SACs), denoted as 1.0 wt.% Pt1/h-NC. The selective hydrogenation of 3-nitrostyrene to functionalized anilines, which are industrially key intermediates for fine chemicals (Downing et al., 1997; Corma and Serna, 2006), was chosen to probe how the SMSI between carbon and single metal atoms affects the catalytic performance of the fabricated Pt1/h-NC SAC for liquid phase catalytic reactions. Our comprehensive characterization results indicate that the strong interaction between Pt atoms and carbon edge/defect sites modulates the electronic structure of the anchored single Pt atoms and thus their reactivity. The 1.0 wt.% Pt1/h-NC demonstrates excellent activity for hydrogenation of 3-nitrostyrene to 3-vinylaniline with a turnover number (TON) > 31,000/h, more than 20 times higher than that of the best catalyst for such selective hydrogenation reactions reported in the literature (Wei et al., 2014).

RESULTS

Synthesis of h-NCs, Pt1/h-NC SACs, and Control Catalysts

The h-NCs were synthesized via a catalytic decomposition and reductive evaporation process by using ZnO nanowires as catalyst/template and ethanol as feedstock (see details in Transparent Methods). The residual Zn content in the synthesized h-NCs is non-detectable (<1 ppb measured by inductively coupled plasma mass spectrometry [ICP-MS]). The fabricated h-NCs possess high total surface area (1,100 m²/g), a tube-like morphology with inner diameters ranging from 20 to 100 nm, and lengths ranging from 1 to 20 μm (Figures 1A and S1). The wall thicknesses of the h-NCs range 2–5 nm. In addition to the large mesopores of the interior regions of the hollow tubes, the h-NCs also possess numerous small mesopores (~3.2 nm, Figure S2) on their sidewalls. Aberration-corrected scanning transmission electron microscopy (ac-STEM) images clearly revealed numerous hyper-cross-linked graphene sheets with sizes ranging from 0.5 to 3.1 nm, representing highly disordered and defective graphene-like structures (Figures 1B and S3).

A strong electrostatic adsorption method (Qiao et al., 2015) was used to disperse Pt atoms onto the h-NCs with a nominal loading of 1.0 wt.% Pt (actual loading of 0.93 wt.% by ICP-MS). High-angle annular dark-field (HAADF) imaging technique, indispensable for characterizing metal atoms in SACs (Liu, 2017a, 2017b), was used to examine the spatial distribution of Pt atoms, clusters, and/or particles. The synthesized 1.0 wt.% Pt1/h-NC contained only isolated Pt single atoms without the presence of any Pt particles/clusters (Figures 1C and S4) in the h-NCs. By analyzing numerous ac-STEM images (Figure S4) obtained from different regions, we unambiguously concluded that the as-synthesized Pt1/h-NC catalysts contained only isolated Pt atoms uniformly dispersed onto the surfaces of the mesoporous h-NCs. The Pt atoms preferentially decorated the edges of the hyper-cross-linked nanoscale graphene sheets (Figures 1B and 1D).

A control catalyst, consisting of 1.0 wt.% Pt nanoparticles (actual loading of 0.84 wt.% by ICP-MS) with an average size of 2.3 ± 0.1 nm dispersed onto the h-NCs (Figure S5), was synthesized and denoted as 1.0 wt.% nano-Pt/h-NC. We also synthesized another control catalyst by using the carbon black Vulcan XC-72 powders. Since the BET surface area of the XC-72 (254 m²/g) is ~4 times lower than that of our homemade h-NCs (1,100 m²/g), we loaded only ~0.25 wt.% of Pt (actual loading of 0.15 wt.% by ICP-MS) so that the normalized number density of surface Pt atoms is approximately the same for both the Pt/h-NC and Pt/XC-72 catalysts. The STEM images (Figure S6) show that the 0.25 wt.% Pt1/XC-72 catalyst mainly contained atomically dispersed Pt atoms.

Catalytic Performance and Stability of the Fabricated Pt1/h-NC SACs

Hydrogenation of 3-nitrostyrene is used to probe the catalytic properties of the synthesized catalysts. As shown in Table 1 and Figure S7, the 1.0 wt.% Pt1/h-NC SAC is highly active with a selectivity of ~78% toward 3-vinylaniline even under very mild reaction conditions (5 bar H2 at 40°C). The 3-ethylaniline is the only detectable by-product. For comparison, the literature reports a selectivity of <3% (toward 3-vinylaniline) on un-modified Pt/C catalysts (Corma and Serna, 2004). The TON for 3-vinylaniline was calculated to be 31,157/h (see details on kinetic data measurements in Transparent Methods), more than 20 times higher than that of the best catalyst (0.08 wt.% Pt1/FeOx) reported in the literature (Wei et al., 2014). Under the
same reaction conditions, the 1.0 wt.% nano-Pt/h-NC yielded a dramatically decreased selectivity toward 3-vinylaniline: the products consisted of ~47% 3-vinylaniline and ~53% 3-ethylaniline, and the TON for producing 3-vinylaniline was ~2,018/h, about 15 times smaller than that of the 1.0 wt.% Pt/h-NC SAC. Furthermore, the presence of single Pt atoms in the 1.0 wt.% nano-Pt/h-NC catalyst (Figure S5) might have contributed to the activity and selectivity of the 1.0 wt.% nano-Pt/h-NC catalyst, suggesting that the true TON and selectivity toward 3-vinylaniline on the Pt nanoparticles may be much smaller than those of the measured values. These catalytic testing results unambiguously demonstrate that the h-NC supported single Pt atoms are much more active and selective toward 3-vinylaniline. Our experimental results clearly show that the h-NC supported Pt nanoparticles produce dominantly 3-ethylaniline (~53%), whereas the graphene-edge-anchored Pt single atoms yield dominantly 3-vinylaniline (~78%). The large differences in product selectivity manifest the intrinsically different catalytic properties of strongly anchored Pt single atoms from those of the supported Pt nanoparticles.

For the atomically dispersed 0.25 wt.% Pt/XC-72 control catalyst, the selectivity toward 3-vinylaniline was measured to be ~41% and the corresponding TON was 1,225/h, ~25 times lower than that on the 1.0 wt.% Pt/h-NC SAC. The significant changes in both the TON and selectivity implies that the catalytic property of the 1.0 wt.% Pt/h-NC SAC is intrinsically different from that of the atomically dispersed 0.25 wt.% Pt/XC-72. As clearly shown in Table 1, the TON for 3-vinylaniline on the 1.0 wt.% Pt/h-NC SAC is at least one order of magnitude higher than that on all other catalysts. Control experiments conducted on pure h-NC and XC-72 supports only, under the same reaction conditions, did not exhibit any detectable products.
For the used 1.0 wt.% Pt1/h-NC SAC, most of the single Pt atoms (99%) were still isolated and only very few small aggregates of loosely connected Pt atoms (0.4 nm) were detected (Figure S8). These atomically dispersed aggregates do not seem to form Pt-Pt bond since the distances among these Pt atoms are much larger than that of crystalline Pt clusters (Yang et al., 2015). The fact that the Pt single atoms remained isolated after the catalytic reaction suggests that the isolated single Pt atoms were strongly anchored onto the edge/defect sites of the h-NCs. Moreover, atomic resolution HAADF-STEM images show that the individual Pt atoms primarily decorated the edges/steps of nanoscale pieces of graphene sheets (indicated by the green dash lines in Figures 1Da and S4) present in the h-NCs. These edge carbon atoms strongly interact with the individual single Pt atoms as suggested by density functional theory (DFT) calculations (Wei et al., 2017a). Since the XC-72 carbon support is highly graphitic and does not possess many strong anchoring edge/defect sites, the originally atomically dispersed Pt atoms sintered into Pt nanoparticles/clusters with an average size of 1.1 ± 0.1 nm after one cycle of selective hydrogenation of 3-nitrostyrene (Figure S9). These results suggest that, although the Pt was atomically dispersed in the fresh Pt/XC-72 catalyst, these Pt atoms did not strongly interact with the XC-72 carbon and thus sintered during the hydrogenation reaction. The XC-72 carbon and the h-NCs are structurally very different, resulting in different degrees of Pt-carbon interactions and consequently the differences in catalytic performance.

Characterization of the Edge Site Defects in the Fabricated Pt1/h-NC SACs

To understand why the synthesized h-NCs strongly anchored Pt single atoms, Raman spectroscopy, capable of providing the density of defects of carbon materials (Ferrari and Robertson, 2000; Sadezky et al., 2005), was used to evaluate the properties of the carbon supports. By using the empirical formula models (Cançado et al., 2006; Tuinstra and Koenig, 1970), the defect density of h-NCs was estimated to be about five times higher than that of the XC-72 carbon (Figure S10 and Table S1), which suggests that the synthesized h-NCs consist of numerous defects (edge sites) as evidenced in STEM images. After Pt single atoms were deposited on the h-NCs, the defect density decreased by ~17% (Table S1). Based on the STEM images (Figures 1D and S8) as well as the spectroscopy data we propose that the drop of the estimated defect density by Raman spectroscopy is caused by the strong anchoring of Pt atoms to the edge/defect sites of the nanoscale graphene sheets. DFT calculations suggested that single Pt atoms can directly bond with graphene edges with a binding energy as high as 7.46 eV (Wei et al., 2017a). After Pt single atoms were deposited on the XC-72 carbon, the defect density slightly decreased by ~6%, suggesting that the XC-72 carbon cannot strongly anchor the atomically dispersed Pt atoms, which

| Sample                  | T/C | Time/min | Conv (%) | Sel (%) | TON* | Reference               |
|-------------------------|-----|----------|----------|---------|------|-------------------------|
| 1.0 wt.% Pt1/h-NC SAC   | 40  | 10       | 97.1     | 77.8    | 31,157 | This work*              |
| 1.0 wt.% nano-Pt/h-NC   | 40  | 10       | 93.8     | 47.1    | 2,018  | This work*              |
| Pure h-NCs              | 40  | 60       | 0        | 0       | 0     | This work*              |
| 0.25 wt.% Pt/XC-72      | 40  | 10       | 9.7      | 41.3    | 1,225  | This work*              |
| Pure XC-72              | 40  | 60       | 0        | 0       | 0     | This work*              |
| 0.08 wt.% Pt1/FeOx     | 40  | 50       | 96.5     | 98.6    | 1,493  | Wei et al., 2014        |
| 0.2 wt.% Pt/TiO2        | 40  | 390      |          | 93.1    | 56    | Serna et al., 2009     |
| 0.01 wt.% Pt/TiO2       | 85  | 360      |          | 48.4    | 1,449  | Serna et al., 2009     |
| 1.4 wt.% Pt/ZnO         | 75  | /        |          | 97      | 1,560  | Berguerand et al., 2015 |
| Commercial Pt/C         | 75  | /        |          | 0       | 0     | Berguerand et al., 2015 |

Table 1. Chemoselective Hydrogenation of 3-Nitrostyrene on Pt/h-NC Catalysts Compared with Most Active Catalysts Reported in the Literature

*The amount of the produced 3-vinylaniline molecules per active site per hour. The turnover number (TON) value was measured by keeping the substrate conversion below 25% by tuning the molecular ratio of Pt atoms to 3-nitrostyrene molecules.
*Reaction conditions: H2 pressure = 5 bar; Pt/substrate = 0.078%; 8 mL reaction mixture: 0.5 mmol 3-nitrostyrene, ethanol as solvent, O-xylene as internal standard.
*The Pt loading of the commercial Pt/C catalyst is 1.0 wt.% (Berguerand et al., 2015).
corroborates the STEM results that the atomically dispersed Pt atoms sintered to particles (~1.1 nm) after the hydrogenation reaction.

The Electronic Structure of the Fabricated Pt₁/h-NC SACs

The X-ray photoelectron spectroscopy (XPS) C1s spectrum of the 1.0 wt.% Pt₁/h-NC SAC shows that, in addition to the carbon sp² (284.7 eV) and sp³ (285.2 eV) peaks, there is a new component located at 284.3 eV (Figure S11A), attributable to a Pt-C bond originating from a strong covalent interaction between Pt atoms and the under-coordinated carbon atoms of the h-NCs (Rajasekaran et al., 2012; Ng et al., 2010). XPS spectra (Figure 2) suggest that the 1.0 wt.% Pt₁/h-NC SAC contains only ~10% of Pt²⁺ species, whereas ~90% of the Pt species possess a binding energy of 71.8 eV, higher than that of the metallic Pt species (71.3 eV) but lower than that of the Pt²⁺ species (72.6 eV). We denote these Pt species as Pt⁺⁺ (0<δ<2). The occurrence of the Pt⁺⁺ (71.8 eV) species can be attributed to the formation of Pt-C bonds with electron transfer from the Pt single atoms to the carbon support (Alderucci et al., 1995; Axnanda et al., 2015). The presence of the Pt²⁺ species may result from the oxidation by the oxygen-containing groups present on the surfaces of the h-NCs as evidenced by the O 1s spectrum (Figure S11B), which shows three components assignable to the Pt-OH (532.1 eV, 60%), Pt-H₂O (533.1 eV, 37%), and Pt-O species (530.0 eV, 3%) (Alderucci et al., 1995). The STEM images, Raman spectra, and XPS data all support the conclusion that the Pt single atoms decorated the edges of the cross-linked nanoscale graphene sheets in the h-NCs (Figures 1D and S4) and directly bonded with the edge carbon atoms to form strong Pt-C bonds (Rajasekaran et al., 2012; Ng et al., 2010), probably arising from the hybridization of Pt 5d and the abundant C 2p orbitals of the edge carbon atoms (Tang et al., 2011).

The Pt 4f XPS spectrum of the 1.0 wt.% nano-Pt/h-NC (Figure 2) exhibits mostly metallic Pt species (71.3 eV, 61%), an appreciable amount of Pt⁺⁺ (72.6 eV, 30%) and a minor amount of Pt⁺⁺⁺ (71.8 eV, 9%). The XPS C1s spectrum of the 1.0 wt.% nano-Pt/h-NC (Figure S11A) shows that, in addition to the carbon sp² (284.7 eV) and sp³ (285.2 eV) peaks, there is also a very weak peak at 284.3 eV, suggesting the formation of a minor amount of Pt-C bond, which may originate from the interaction of the edge atoms of the Pt nanoparticles with the carbon support (Rajasekaran et al., 2012; Ng et al., 2010). The Pt 4f XPS spectrum of the 0.25 wt.% Pt₁/XC-72 catalyst could not be quantitatively analyzed because of the signal-to-noise problem (Yang et al., 2011).
Effects of Strong Pt-Carbon Interaction on Catalytic Performance

The geometric and electronic properties of active metal species play a crucial role in determining the adsorption behavior of functional groups and the dissociation behavior of H2 (Armbrüster et al., 2012; Blaser et al., 2009; Wei et al., 2014, 2017b; Lou et al., 2018). Pt metals show excellent catalytic capability of H2 dissociation with a reaction barrier as low as 0 and 0.067 eV on Pt (001) and Pt (111) surfaces, respectively (Pasteur et al., 1997; Olsen et al., 1999). The strength of the Pt-H bonds is too high (even close to H-H in H2) to be efficient and chemoselective for catalytic reactions (Ludwig et al., 2006; Corma et al., 2008). For selective hydrogenation of nitro groups, a catalyst that possesses facile activation of H2 and weak adsorption strength of the dissociated H atoms can exhibit optimal efficiency in balancing activity and selectivity for the targeted products (Lucci et al., 2015a, 2015b; Kny kou et al., 2012). For the Pt1/h-NC SAC system, the metal-carbon interaction results in electron transfer from the Pt atoms to the carbon support and they most probably maintain their valence state under the hydrogenation reaction conditions. The electron depletion of the edge-carbon-anchored Pt atoms induces downshift of the d-band center of the Pt species (0 < δ < 2) and consequently reduces, when compared with the metallic Pt species, the binding strength of the dissociatively adsorbed hydrogen atoms (Armbrüster et al., 2012; Namba et al., 2018). Such a change of the d-band center of the single Pt species facilitates the activation of H2 and thus provides more activated and weakly bound hydrogen species to accelerate the catalytic reaction. Under hydrogenation reaction conditions, the nanometer-sized Pt oxide species can be easily reduced to the metallic state and sintered to Pt particles (Huizenga et al., 1984; Duan et al., 2018), which will strongly bind the adsorbed H species, resulting in the lack of weakly bound hydrogen species for catalytic reactions. Furthermore, the H2 dissociation over Pt1/h-NCs may follow the heterolytic dissociation procedure to yield H+ and H atoms on the Pt-carbon interface, which may significantly enhance the catalytic activity of hydrogenation reactions as reported in the literature (Liu et al., 2016; Wang et al., 2016; Dhiman and Polshettiwar, 2018). The spillover effects of the activated H species over the carbon support cannot be ruled out. The influence of such spillover H species on the observed activity and selectivity on hydrogenation reactions is not clear and needs to be further investigated. Based on our characterization and catalytic testing data, we propose that the strong Pt-carbon interaction in the Pt1/h-NCs significantly modifies the electronic structure of the carbon-edge-anchored single Pt atoms and correspondingly their catalytic properties for H2 activation. The enhanced electronic SMSI makes the 1.0 wt.% Pt1/h-NC SAC a much more highly active catalyst than that of the atomically dispersed 0.25 wt.% Pt1/XC-72 and 1.0 wt.% nano-Pt/h-NC catalysts for 3-nitrostyrene hydrogenation.

DISCUSSION

The selective hydrogenation of the C=C bonds is considered to be highly sensitive to the size of the Pt ensembles (Wei et al., 2014; Corma et al., 2008; Lucci et al., 2015a, 2015b). On the other hand, the selectivity for nitro groups is independent of the size of the Pt particles (Corma et al., 2008; Peng et al., 2018). It has been reported that Pt single atoms especially prefer the adsorption of nitro groups to the C=C groups (Wei et al., 2014; Peng et al., 2018). The dissociated H species may spillover via carbon support to the nitro groups that are activated by single Pt atoms to complete the catalytic reaction cycle (Wei et al., 2014). Hence, the strong Pt-C interaction in the 1.0 wt.% Pt1/h-NC SAC not only enhances H2 activation to provide more activated and weakly bound hydrogen species but also provides stable single sites that inhibit the C=C activation and simultaneously enhances the nitro group activation. The strong electronic Pt-carbon interaction not only enhances anchoring of single Pt atoms to the edge carbon atoms of the h-NCs but also significantly modifies their catalytic properties for selective hydrogenation. As a result of the strong Pt-carbon interaction the Pt atoms transfer electrons to carbon support to form Pt species, which are proposed to be the active sites for facilely dissociating H2 and preferential adsorption of the specific sites of the reactant molecules. The fabricated Pt1/h-NC SACs exhibited excellent catalytic performance for selective hydrogenation of 3-nitrostyrene to 3-vinylaniline because of the covalent bonding of Pt1 to the edge carbon atoms of the nanoscale graphene pieces in the synthesized h-NCs.
Although further improvement in designing the carbon structure to tune the Pt-carbon interaction may result in further improved selectivity, our research work clearly demonstrated the power in utilizing the electronic SMSI in SACs to significantly enhance the activity for desired reaction products. The strategy utilized in this work is general and can be broadened to construct different catalytic systems, especially SACs, for a plethora of catalytic reactions, including liquid- and gas-phase transformation of important molecules.

**Limitations of Study**

Our research on electronic strong metal-carbon interaction in SACs has extended the SMSI concept to broader catalyst systems for tuning catalytic properties of strongly anchored single metal atoms. A combined density functional theory and Monte Carlo approach for quantifying the metal-carbon interactions at the reaction temperatures can provide an in-depth understanding on the electronic strong metal-carbon interaction in SACs and may provide guidance for designing better catalysts for liquid-phase transformation of important molecules. The reaction mechanisms of selective 3-nitrostyrene hydrogenation, the spillover effects of the activated H species, and the role of the highly defective carbon structures in the adsorption of reactant molecules need to be further investigated. Although the study of these important questions on the fundamental understanding of selective hydrogenation of important complex molecules is beyond the scope of this current work, such fundamental studies can provide guidance on effectively utilizing the strong metal-carbon interaction to design robust SACs with desired catalytic performance.

**METHODS**

All methods can be found in the accompanying Transparent Methods supplemental file.

**SUPPLEMENTAL INFORMATION**

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.02.016.

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**AUTHOR CONTRIBUTIONS**

J.L. designed and conceived the experiments, acquired the STEM images and analyzed the experimental data, and reviewed and edited this manuscript. Y.L. designed, synthesized, and tested the catalysts; conducted the spectroscopy experiments; and analyzed the data and drafted the manuscript. H.W. synthesized the hollow nanocarbons.

**DECLARATION OF INTERESTS**

The authors declare no competing interests.

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Supplemental Information

Nanocarbon-Edge-Anchored High-Density Pt Atoms for 3-nitrostyrene Hydrogenation: Strong Metal-Carbon Interaction

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SUPPLEMENTAL INFORMATION

Nanocarbon-Edge-Anchored High-Density Single Pt Atoms for Selective Hydrogenation of 3-nitrostyrene: Strong Metal-Carbon Interaction

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Table S1 Summary of the defect density and crystallite size of the synthesized Pt SACs and nano-Pt catalysts.

Transparent Methods

Supplemental References
Figure S1 SEM images (a-c) and aberration-corrected HAADF-STEM image (d) of h-NCs show the general morphology and the wall thicknesses of the synthesized hollow nanocarbon tubes, Related to Figure 1.
Figure S2 Pore size distribution of the synthesized h-NCs, Related to Figure 1.

The average size of the pores on the wall of the h-NCs was estimated to be 3.2 nm.
Figure S3 Aberration-corrected STEM images of h-NCs and the size distributions of the corresponding nanoscale graphene sheets (a-c), Related to Figure 1.

The synthesized h-NCs are composed of stacking of hyper-cross-linked graphene sheets, resulting in highly disordered structure, high surface area and tube-type morphology. The hyper-cross-linked graphene sheets exhibit high number density edge sites (Figure S3a-S3c). The lateral sizes of the graphene sheets range from 0.5 nm to 3.1 nm with an average length of 1.2 ± 0.2 nm. The histograms were obtained by measuring the identifiable lengths of the graphene sheets in the corresponding bright-field STEM images.
Figure S4 Low-magnification and high-magnification aberration-corrected HAADF/STEM images of fresh 1.0 wt.% Pt/h-NC SAC (a-f); schematic diagram for single Pt atoms anchored on the edges of graphene sheets of h-NCs (g), Related to Figure 1.

As clearly shown in Figure S4 (a), low-magnification HAADF-STEM image confirms the absence of any Pt particles or clusters in the fresh 1.0 wt.% Pt/h-NC SAC. The high-magnification HAADF-STEM images (Figure S4 (b-f)) confirm that the Pt atoms are atomically dispersed on the surfaces of the h-HC support. By examining numerous low/high magnification HAADF-STEM images (Figure S4 (a-f)) obtained from different regions of the synthesized h-NCs, we unambiguously concluded that the fresh 1.0 wt.% Pt/h-NC SAC contains only isolated Pt atoms without the presence of any Pt particles or clusters. Moreover, Pt atoms are mainly decorated on the edges of those hyper-cross-linked graphene sheets. A small amount of single Pt atoms may have trapped between the layers of the graphene sheets (Yan et al., 2015; Tang et al., 2016). However, since the sizes of the graphene sheets are so small and there are almost no observable close stacking of parallel graphene sheets in the synthesized h-NCs the Pt atoms should not be stably trapped between layers of graphene. Figure S4 (g) is the schematic diagram to illustrate the anchoring of single Pt atoms onto the edges of nanoscale graphene sheets in the synthesized h-NCs.
Figure S5 Low-magnification and high-magnification aberration-corrected HAADF/STEM images of 1.0 wt.% nano-Pt/h-NC, Related to Figure 1. The average particle size is 2.3 ± 0.1 nm.

Pt particles of 1.0 wt.% nano-Pt/h-NCs are distributed on the surfaces of the h-NCs (Figure S5 a-b) and the average size of the Pt particles was measured to be 2.3 ± 0.1 nm. From the high-magnification image (c), we can see the presence of some single Pt atoms in the 1.0 wt.% nano-Pt/h-NC catalyst. The presence of these anchored Pt single atoms may make appreciable contribution to the experimentally measured activity and selectivity for 3-nitrostyrene hydrogenation over the 1.0 wt.% nano-Pt/h-NC catalyst.
Figure S6 Low-magnification and high-magnification aberration-corrected HAADF/STEM images of an as-synthesized atomically dispersed 0.25 wt.% Pt/XC-72 catalyst, Related to Figure 1.

Figure S6 (a) and numerous other low-magnification HAADF-STEM images confirm the absence of any Pt particles or clusters in the fresh 0.25 wt.% Pt/XC-72 catalyst. The high-magnification HAADF-STEM images (Figure S6 (b-f)) confirm that the Pt atoms are atomically dispersed on the surfaces of the XC-72 support. By examining numerous low/high magnification HAADF-STEM images (Figure S6 (a-f)) obtained from different regions, we unambiguously concluded that the as-prepared 0.25 wt.% Pt/XC-72 contains only isolated Pt atoms and atomically dispersed small Pt clusters of a few Pt atoms without the presence of Pt particles.
Figure S7 Time-dependent conversion and selectivity of 1.0 wt.% Pt/h-NC SAC, 1.0 wt.% nano-Pt/h-NC and 0.25 wt.% Pt/XC-72 for selective hydrogenation of 3-nitrostyrene, Related to Table 1.

With the increase of reaction time, the catalytic conversion of 3-nitrostyrene over 1.0 wt.% Pt/h-NC SAC, 1.0 wt.% nano-Pt/h-NC and 0.25 wt.% Pt/XC-72 gradually increases but the selectivity toward the 3-vinylaniline gradually decreases. Further hydrogenation of the produced 3-vinylaniline to 3-ethylaniline is possible but the formation of small Pt clusters or particles with reaction time also decreases the selectivity toward 3-vinylaniline. Promoters to either boost the activity or selectivity may need to be developed to increase the yield of the final product.
Figure S8 Low-magnification and high-magnification aberration-corrected HAADF/STEM images of used 1.0 wt.% Pt/h-NC SAC, Related to Figure 1. The 1.0 wt.% Pt/h-NC SAC was used for 30 min at a reaction temperature of 40 °C.

As clearly shown in Figure S8 (a-b), low-magnification HAADF-STEM images did not show Pt particles in the used 1.0 wt.% Pt/h-NC SAC. Only the presence of very few Pt clusters (around 0.4-0.5 nm) are observable (Figure S8 b). The high-magnification HAADF-STEM images (Figure S8 (c-f)) confirm that the used catalyst consists primarily of isolated single Pt atoms uniformly dispersed on the surfaces of the h-NCs.

In order to quantify the amount of the small Pt clusters present in the used 1.0 wt.% Pt/h-NC SAC, we conducted a statistical analysis of the number of Pt single atoms and small clusters (Figure S8 c) and the result is shown in Figure S8 g. We estimated that ~99% of the Pt in the used 1.0 wt.% Pt/h-NC SAC remained as isolated single Pt atoms after the hydrogenation reaction. Only ~1% of the Pt single atoms in the fresh catalyst sintered to atomically dispersed, loosely connected Pt clusters without the formation of Pt-Pt bonding (Yang et al., 2015). These results suggest that all the Pt atoms were still atomically dispersed after the catalytic hydrogenation reaction. Such stable SACs assure that the measured catalytic activity and kinetic data originated from the anchored single Pt atoms rather than from Pt clusters/particles.

By examining numerous low/high magnification HAADF-STEM images (Figure S8 (a-f)) obtained from different regions, we unambiguously concluded that the used 1.0 wt.% Pt/h-NC SAC still predominately consists of isolated Pt atoms (99%). However, after three cycles, many of the Pt atoms aggregated to form Pt clusters.
Figure S9 Pt particle size distributions and HAADF/STEM images of the used 0.25 wt.% Pt/ XC-72, Related to Figure 1. The 0.25 wt.% Pt/ XC-72 was used for 30 min at a reaction temperature of 40 °C.

As clearly shown in Figure S9 (a-c), the HAADF-STEM images confirm the sintering of the atomically dispersed 0.25 wt.% Pt/ XC-72 into Pt clusters/particles during the hydrogenation reaction. The sintered Pt particles are uniformly distributed on the surfaces of the XC-72 carbon powders. Statistical analyses of the sintered Pt particles of the used 0.25 wt.% Pt/ XC-72 catalyst yielded an average size of 1.1 ± 0.1 nm.
Figure S10 Raman spectra of carbon and carbon supported Pt catalysts, Related to Figure 2. Pure h-NCs, 1.0 wt.% nano-Pt/h-NC and 1.0 wt.% Pt/h-NC SAC (a); Pure XC-72 and 0.25 wt.% Pt/XC-72 (b).

Raman spectroscopy, capable of providing useful information on the density of defects of carbon materials based on the ratio of D1 to G band intensities (I_D/I_G) (Ferrari et al., 2000; Sadezky et al., 2005), was used to evaluate the carbon supports. As shown in Figure S10 (a-b), the peaks at 1190 cm\(^{-1}\), 1345 cm\(^{-1}\), and 1508 cm\(^{-1}\) can be assigned to the D4, D1 and D3 band and the peak at 1591 cm\(^{-1}\) can be assigned to the G band (Gopinadhan et al., 2013; Chernyak et al., 2017). The D1-band is associated with the defects within the carbon atom plane and the G-band originates from the sp\(^2\)-bonded carbon atoms (Wang et al., 2016). The presence of the D3 band can be attributed to the presence of stacking faults, changes in the interlayer spacing, and the mixed breathing and asymmetric stretching vibrational modes of sp\(^2\)-carbons near defects (Maldonado et al., 2006; Smith et al., 2016). The broad component of D4 can be assigned to amorphous impurities in graphite materials (Prawer et al., 2000). The ratio between D1 and G band intensities (I_D/I_G) can be used to quantify the degree of disorder and the presence of sp\(^3\)-hybridized carbon atoms within the structure. The pure h-NCs support exhibits a high I_D/I_G ratio (1.1), suggesting the presence of high-density defects in the synthesized h-NCs (Wang et al., 2016; Wen et al., 2015). The ratio between D1 and G band intensities (I_D/I_G) of pure XC-72 is 0.85, which is in line with the previously reported data (0.84) (Peng et al., 2017). The ratio between D1 and G band intensities (I_D/I_G) of the 0.25 wt.% Pt/XC-72 is ~0.84.

The I_D/I_G values for the h-NCs and XC-72 carbon are calculated to be 1.1 and 0.85 respectively, suggesting high density of edge/defect sites present in the h-NCs (Sadezky et al., 2005). From analyses of atomic resolution STEM images and Raman spectra we can confidently conclude that the synthesized h-NCs consist of numerous nanoscale graphene sheets with large number of edge sites. Prior to characterizing the carbon defects in the control carbon supports the pure carbon powders were pretreated/exposed to the identical condition that was used for synthesizing Pt single atom catalysts. Therefore, the effect of the chemical processes of adding the Pt single atoms onto the carbon supports on the Raman spectroscopy measurement was significantly minimized.

The experimentally measured I_D/I_G ratio of the 1.0 wt.% Pt/h-NC SAC decreased from 1.1 to 0.9. We propose that the drop in the I_D/I_G ratio is caused by the strong anchoring of Pt atoms to the edge/defect sites of graphene sheets, which are evidenced in the STEM images (Figure 1d and S8). For the XC-72 carbon, the I_D/I_G ratio slightly decreased by ~1%, suggesting that the atomically dispersed Pt atoms were not strongly affect the XC-72 carbon, which corroborates STEM results that Pt atoms sintered to particles (~ 1.1 nm) after the hydrogenation reaction. Since the density of the Pt particles in the 1.0 wt.% nano-Pt/h-NC is extremely low, the I_D/I_G ratio of 1.0 wt.% nano-Pt/h-NC is only decreased by 2%.
XPS spectra of the fresh 1.0 wt.% nano-Pt/h-NC catalyst and the pure h-NCs show only the carbon sp² (284.7 eV) and sp³ (285.2 eV) peaks. However, the XPS spectrum, obtained from the 1.0 wt.% Pt/h-NC SAC, shows, in addition to the carbon sp² (284.7 eV) and sp³ (285.2 eV) peaks, a new component located at 284.3 eV, assignable to a Pt-C bond originating from strong covalent interaction between Pt atoms and under-coordinated carbon atoms of the h-NCs (Rajasekaran et al., 2012; Ng et al., 2010). Our XPS data suggest that charge transfer occurred between the anchored Pt atoms and the edge carbon atoms in the h-NC mesoporous carbon. Such charge transfer results in oxidized Pt atoms, Ptδ⁺ (0 < δ < 2), which can have catalytic properties different from those of the zero valent Pt⁰. Similarly, the XPS C1s spectrum of the 1.0 wt.% nano-Pt/h-NC shows that in addition to the carbon sp² (284.7 eV) and sp³ (285.2 eV) peaks, there is also a weak peak at 284.3 eV, probably originating from the presence of a small amount of Pt-C bond in the 1.0 wt.% nano-Pt/h-NC catalyst.
The Pt 4f XPS spectrum of the 0.25 wt.% Pt\textsubscript{1}/XC-72 catalyst could not be quantitatively analyzed due to the signal-to-noise problem (Ref 32 and 43). But the obvious peak located in the range of 73.2 and 73.5 eV as shown in Figure S12 indicates the oxidation state of Pt atoms in 0.25 wt.% Pt\textsubscript{1}/XC-72 catalyst should be between +2 (72.6 eV) (Alderucci et al., 1995; Axnanda et al., 2015) and +4 (74.1 eV) (Peuckert et al., 1984; Ono et al., 2010).
Figure S13 XPS C 1s spectra of: 1.0 wt.% Pt/h-NC SAC, atomically dispersed 0.25 wt.% Pt/ XC-72 and pure XC-72, Related to Figure 2.

The C 1s XPS spectrum of the 0.25 wt.% Pt/ XC-72 is similar to that of the pure XC-72 carbon, mainly displaying sp² (284.7 eV) and sp³ (285.2 eV) components as shown in Figure S13. The absence of an obvious Pt-C peak in the 0.25 wt.% Pt/ XC-72 suggests that the interaction of the atomically dispersed Pt atoms with the graphitic carbon support is much weaker than that between the Pt single atoms and the h-NCs in the 1.0 wt.% nano-Pt/h-NC SAC.
| Sample         | La /nm<sup>a</sup> | Defect density<sup>b</sup> | Defect density<sup>c</sup> |
|---------------|-------------------|-----------------------------|----------------------------|
| h-NCs         | 6.6 (1.2<sup>d</sup>) | 2.27E+12 (6.94E+13<sup>e</sup>) | 7.21E+11 (2.21E+13<sup>e</sup>) |
| 1.0 wt.% Pt/h-NC SAC | 7.2              | 1.92E+12                   | 6.11E+11                   |
| 1.0 wt.% nano-Pt/h-NC | 6.7              | 2.21E+12                   | 7.04E+11                   |
| XC-72         | 14.2 (2.6<sup>d</sup>) | 4.96E+11 (1.48E+13<sup>e</sup>) | 1.58E+11 (4.71E+12<sup>e</sup>) |
| 1.0 wt.% Pt/XC-72 | 14.6            | 4.66E+11                   | 1.48E+11                   |

<sup>a</sup> The crystallite size (La) is estimated based on the La (nm)=560*(El<sup>4</sup>)*(I<sub>D</sub>/I<sub>G</sub>)<sup>-1</sup>, El is the excitation energy laser energy used in the Raman experiment in eV units and the integrated intensities (peak areas) of the D and G bands instead of the ratio of peak amplitudes is used (Cançado et al., 2006). And the estimated value is normally larger than that of actual one (Chen et al., 2009).

<sup>b</sup> The defect density (n<sub>a</sub>/cm<sup>-2</sup>) is calculated by the formula of n<sub>a</sub>=(1/La)<sup>2</sup> (Cançado et al., 2006).

<sup>c</sup> The defect density (n<sub>a</sub>/cm<sup>-2</sup>) is calculated by the formula of n<sub>a</sub>=10<sup>14</sup>/πLa<sup>2</sup> (Zhong et al., 2014; Cancado et al., 2011).

<sup>d</sup> The crystallite size is calculated based on the STEM images as shown in Figure S3 and Figure S6.

<sup>e</sup> The defect density is calculated based on crystallite size in the parenthese.

Based on the estimate from the published two empirical formula models (Cançado et al., 2006; Zhong et al., 2014; Cancado et al., 2011), it is clear that the defect density of the synthesized h-NCs is ~5 times higher than that of the XC-72 carbon. After Pt deposition, the defect density of the 1.0 wt.% Pt/h-NC SAC is significantly decreased in comparison to pure h-NCs. Since the density of the Pt particles in the 1.0 wt.% nano-Pt/h-NC is extremely low, the defect density is only decreased by 4% due to Pt deposition, in comparison to pure h-NCs.
Transparent Methods

Preparation of single atom catalysts

Single Pt atoms were dispersed onto, via an adsorption method (Qiao et al., 2015; Lou et al., 2017; Lou et al., 2017), the surfaces of commercial carbon black (Vulcan XC-72) and home-made hollow nanocarbons (h-NCs). The precursors of Pt were hexachloroplatinic acid (Sigma-Aldrich).

1) Preparation of h-NCs. The h-NCs were synthesized via catalytic reforming/decomposition of ethanol on the surfaces of the ZnO nanowires. The details of synthesizing ZnO nanowires are discussed in the (Xu and Liu, 2016). In this work, we used the ZnO nanowires as templates to synthesize mesoporous h-NCs. The pre-formed ZnO nanowires were loaded into a high temperature furnace tube, which was then heated to 500 °C. A mixture of nitrogen, water and ethanol was then introduced into the furnace tube. Ethanol reforming as well as decomposition occurs on the surfaces of the ZnO nanowires. Such catalytic reactions result in residues of carbonaceous species uniformly coating the ZnO nanowires. Because of this coking induced deactivation, the thickness of the deposited carbonaceous layers is self-limiting. By controlling the reaction time, one can control the thickness of the deposited carbonaceous layers. After the desired thickness of the carbonaceous layers was obtained the ZnO (nanowires) were evaporated at a temperature of 750 °C for 6 h with a flowing gas mixture of H2/Ar to produce the hollow carbon tubes with mesopores on the sidewalls.

2) Pt/h-NC preparation. The h-NCs were firstly dispersed in the ethanol and then the corresponding Pt precursors were slowly dropped into the ethanol. After being stirred at room temperature for 2 hours, the ethanol was slowly evaporated off and then the obtained precipitates were dried at 60 °C for 12 hours in air without further calcination. The actual Pt loading is 0.93 wt.% by ICP-MS.

3) Pt/XC-72 preparation. The carbon black powders (Vulcan XC-72) were firstly dispersed in the ethanol and then the corresponding Pt precursors were slowly dropped into the ethanol. After being stirred at room temperature for 2 hours, the ethanol was slowly evaporated off and then the obtained precipitates were dried at 60 °C for 12 hours in air. The actual Pt loading is 0.08 wt.% by ICP-MS.

4) Nano-Pt/h-NC preparation. The h-NC supported Pt nano particle catalyst (nano-Pt/h-NC) was prepared as control catalyst. The corresponding Pt precursors were firstly reduced by the NaBH4 to form nano-meter sized Pt particles and then the above solution was slowly dropped into the ethanol to mix with the pre-synthesized h-NCs. After being stirred at room temperature for 2 hours, the ethanol was slowly evaporated off and then the precipitates were dried at 60 °C for 12 hours in air without further calcination. The actual Pt loading is 0.84 wt.% by ICP-MS.

Evaluation of the catalytic performance

The hydrogenation of 3-nitrostyrene was conducted in a Parr reactor. Before the activity test, the catalyst was first put into the reactor, to which 8 ml ethanol was added, and then the reactor was charged with 5 bar hydrogen and heated at 40 °C for 40 min to allow for the reduction treatment of the catalyst. After that, the 3-nitrostyrene substrate, internal standard O-xylene and 8 ml ethanol, were put into the reactor. Then, the reactor was flushed with 5 bar hydrogen for 11 times. After being sealed, the autoclave was charged with H2 until 5 bar, then it was heated to 40 °C under stirring to initiate the reaction. The molecular ratio of Pt atoms to 3-nitrostyrene molecules is 0.078%. After reaction, the products were analyzed by gas chromatography (Agilent GC 7890A with HP-5 column) equipped with the Agilent auto sampler. The peaks were calibrated by the standard chemicals from Sigma-Aldrich. The turnover number (TON) value was measured by keeping the substrate conversion below 25% by tuning the molecular ratio of Pt atoms to 3-nitrostyrene molecules and the corresponding TON was calculated based on the total Pt loading in the catalyst, and the yields at the corresponding low conversion rate.
Catalyst Characterization

The loading level of the Pt was measured by a ThermoFinnegan iCAP Q quadrupole ICP-MS with CCT (Collision Cell Technology). Samples were run in KED (Kinetic Energy Discrimination) mode, with inline aspiration of a multi-element internal standard.

Sub-angstrom resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images were obtained on a JEM-ARM200F TEM/STEM with a guaranteed resolution of 0.08 nm. Before microscopy examination, the catalyst powders were ultrasonically dispersed in ethanol and then a drop of the solution was put onto a copper TEM grid coated with a thin lacey carbon film.

The X-ray photoelectron spectroscopy (XPS) investigation was conducted on a Vacuum Generators 220i-XL using a mono-chromated Al Kα X-ray source (1486.6 eV). The samples were mounted onto the double-sided adhesive tape on the sample holder. The XPS spectra of the selected elements were measured with the constant analyzer pass energy of 20.0 eV. All binding energies (BEs) were referred to the C 1s peak (284.6 eV). The deconvolution protocol of the spectra is similar to our previous work (Lou et al., 2014; Lou et al., 2014). Raman experiments were conducted on LabRam HR 800 using 532 nm laser. The deconvolution protocol of the spectra was similar to that reported in literature (Wen et al., 2017).

The BET surface areas were measured by nitrogen adsorption at liquid nitrogen temperature by using a surface area and porosity analyzer (Quantachrome NOVA 4000e apparatus). Before measurement, the samples were degassed at 180 °C for 6 h in vacuum.

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