Confined-interface-directed synthesis of Palladium single-atom catalysts on graphene/amorphous carbon

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The maximized atomic efficiency of supported catalysts is highly desired in heterogeneous catalysis. Therefore, the design and development of active, stable, and atomic metal-based catalysts remains a formidable challenge. To tackle these problems, it is necessary to investigate the interaction between single atoms and supports. Theoretical calculations indicate that the Pd binding strength is higher on graphene/amorphous carbon (AC) than that on graphene or AC substrate. Based on these predictions, we present a facile confined-interface-directed synthesis route for the preparation of single-atom catalysts (SACs) in which Pd atoms are well-dispersed on the interface of double-shelled hollow carbon nanospheres with reduced graphene oxide (RGO) as the inner shell and AC as the outer shell. Owing to the synergetic effect of the RGO/AC confined interface and the atomically dispersed Pd, the as-made RGO@AC/Pd SAC achieves the maximum atomic efficiency (catalytic activity) of Pd species and exhibits an excellent stability in chemical catalysis. This confined-interface-directed synthesis method provides a novel direction to maximize the atomic efficiency, improve the activity, and enhance the stability of metal-based catalysts.

1. Introduction

Supported noble metal catalysts are widely used in industry owing to their high activity and/or selectivity for many key chemical reactions [1]. However, industrial catalysts base on precious metal suffer from several drawbacks, including scarcity and the resulting high cost as well as poor stability and recyclability. Consequently, extensive research efforts have focused on strategies for increasing the active sites, either by reducing the size of catalyst clusters [2] or by producing particles with externally exposed high index facets [3]. Downsizing noble metals to ultrafine clusters or even single atoms has recently emerged as a new research frontier [4]. In this way, full atom utility can be obtained from the lowest size limit in a catalyst. Thus, metals are usually finely divided into nanometer-sized particles [5], subnanometer-sized clusters [6] or even single atoms [7] and dispersed onto high-surface-area support to maximize the metals' atomic efficiency and achieve the desired catalytic performance [8]. Despite the effectiveness of this strategy, the size reduction often generates unsaturated coordination sites on the metal species that enhances activity but makes them structurally unstable [9]. Consequently, dispersed metal clusters or single atoms require optimized anchoring to mitigate unfavorable aggregation or coarsening during the catalytic process owing to their increased surface free energy [4]. As is known, the interaction between single atoms and supported catalysts is crucial to stabilizing these active single atoms [2]. As a result, much effort has been focused on this strategy by embedding the downsized single atoms into supported catalysts, which have shown excellent catalytic performance [2,10]. However, a clear understanding of the formation mechanism and of the maximized atomic efficiency of single-atom catalysts (SACs) is still lacking. Therefore, the design and development of active, stable, and atomic metal-based catalysts remains a formidable challenge. To tackle these problems, it is necessary to investigate the interaction between single atoms and supports.

Carbon materials, such as amorphous carbon (AC) and graphene have been widely used to disperse metal particles for advanced supported catalysts [11–14]. Nevertheless, the processes involved in

anchoring single metal atoms on carbon materials have not been intensively investigated. To design and prepare novel carbon supported SACs, density functional theory (DFT) calculations were conducted to investigate the interaction between single atoms and carbonaceous supports. According to our calculation results, Pd atoms are prone to adsorption and deposition on the confined interface between graphene and AC and preferentially separate from each other. Inspired by the theoretical predictions, we designed and fabricated a new type of Pd-based SAC by a reduced graphene oxide@AC (RGO@AC) confined-interface-directed synthesis method. This atomically dispersed Pd catalyst was constructed with a double-shelled hollow carbon nanosphere (HCN) of RGO@AC with Pd single atoms loaded onto its confined interface, and this catalyst exhibited extremely high activity and stability for 4-nitrophenol (4-NP) reduction and the Suzuki coupling reaction.

2. Experimental section

2.1. Computational methods

The computations were performed through Tianhe-2JK at the Beijing Computational Science Research Center (CSRC). Our calculations were performed with DFT, as implemented in the Vienna ab initio package (VASP) [15]. The general gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) was adopted for the exchange-correlation functional [16]. Moreover, the electron-wave functions were expanded by a plane-wave cutoff of 400 eV. The $(4 \times 4 \times 1)$ supercell RGO with a stoichiometry of C_{50} was constructed by the periodic boundary condition (PBC), and the vacuum layers were set to be larger than 20 Å to avoid periodic interaction. The initial structure of the amorphous carbon (AC) structure studied here was obtained from a previous study with bulk a-C with a density of 3.0 g/cm^3 [17]. A two-dimensional slab of a-C was obtained by removing the periodicity in the z direction (surface normal direction) using a supercell of dimensions $12.5 \times 12.5 \times 20.0$ Å^3 instead of the bulk a-C supercell of $12.5 \times 12.5 \times 5.4$ Å^3. The dangling bonds at the bottom of the slab were terminated with 23 pseudo-hydrogen atoms, yielding an initial surface structure with a total of 163 atoms (128C and 23 H-terminations). The strategy of using the pseudo-hydrogen atoms to saturate the dangling bonds to maintain the bulk coordination environment has also been widely used in the studies of metal, metal oxide and carbon-based catalysis [18–20]. The reciprocal space was performed by the Monkhorst-Pack special k-point scheme with $2 \times 2 \times 1$ grid meshes for structural relaxation for the AC slab. Atomic relaxation was performed until the total energy variation was smaller than 10^{-6} eV and all forces on each atom were less than 0.01 eV/Å.

The ab initio molecular dynamics (AIMD) simulations were performed using the CP2 K/QUICKSTEP package [21]. The wave functions of the valence electrons were expanded in terms of Gaussian functions with molecularly optimized double-ζ polarized basis sets (m-DZVP), which ensures a small basis set superposition error [22], and core electrons were described with norm-conserving Goedecker, Teter, and

Hutter (GTH) pseudo potentials [23]. The AIMD simulations were conducted with the NVT ensemble at a target temperature along with a Nose-Hoover thermostat (Fig. S1). A simple cubic lattice was chosen as the initial configuration of the atoms, as this structure is highly unstable for carbon. Once molten, the sample was equilibrated at 5000 K for 0.36 ps, where the liquid was highly diffusive with a diffusion constant of 7×10^{-5} cm^2/s. The liquid sample was then cooled to 300 K over 0.5 ps; following this, the system was equilibrated for a further 0.5 ps to gain temporal averages. The cooling rate of 10^{16} K/s is similar to that used in other simulations of carbon [24,25].

2.2. The detailed fabrication process of the RGO@AC/Pd atomic catalyst

2.2.1. Synthesis of GO-wrapped SiO_2 (SiO_2@GO) spheres

SiO_2 spheres (100–200 nm) were synthesized as templates by the Stöber method [26]. GO was prepared according to a modified Hummers method [27]. In a typical synthesis, 0.2 g of SiO_2 spheres was first dispersed in 100 mL of ethanol by sonication for 20 min. Next, 1 mL of 3-aminopropyltrimethoxysilane was added and refluxed for 5 h to obtain amine-functionalized SiO_2 nanospheres. After the products were centrifuged and redispersed in 100 mL of DI water, 30 mL of 0.2 mg/mL GO aqueous solution was added and stirred vigorously for 1 h. During this process, the amino-functionalized SiO_2 nanospheres were tightly wrapped by GO nanosheets through electrostatic interactions and hydrogen bonds between the amino groups and the oxygen-containing groups on the GO sheets (step 1 in Fig. S4) [28]. Finally, the products were collected by centrifugation, washed with water several times, and then dried at 60 °C overnight.

2.2.2. Synthesis of double-shelled hollow carbon spheres (RGO@AC)

The surface of the SiO_2@GO nanospheres was further coated by AC precursor layers via the pyrolysis of glucose under hydrothermal conditions and a subsequent thermal treatment procedure (step 2 in Fig. S4), accompanying the thermal reduction of GO to RGO [29]. Typically, 150 mg of as-prepared SiO_2@RGO spheres were dispersed in 16 mL of a water/ethanol (volume ratio = 3/1) mixture by ultrasonication. Then, 4 mL of 0.5 M aqueous glucose solution was added under vigorous stirring for 30 min. After that, the suspension was transferred to a 25 mL Teflon-lined autoclave and heated in an oven at 180 °C for 16 h. The dark gray products were collected by centrifugation and washed with ethanol and DI water six times. After drying at 60 °C overnight, the resulting dark gray powder was carbonized at 900 °C for 4 h under an inert atmosphere. Finally, the as-prepared SiO_2@RGO@AC spheres were then transformed into RGO@AC HCNs by etching the SiO_2 cores with HF solution ($\approx$ 2%) twice (step 3 in Fig. 1).

2.2.3. Synthesis of double-shelled hollow carbon spheres with the pd catalyst (RGO@AC/Pd)

RGO@AC composites (50 mg) were dispersed in 50 mL of DI water. Then, 0.5 mg of K_2PdCl_4 were added to the suspension and stirred vigorously for 2 h in an ice bath. During this process, Pd atoms were
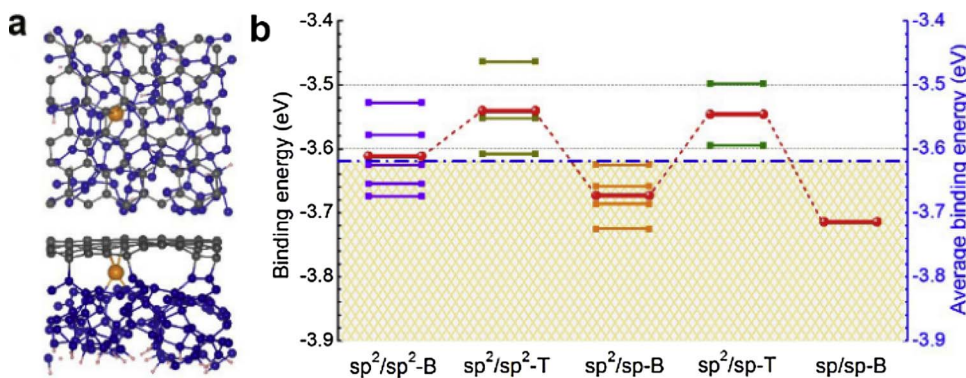
Fig. 1. (a) Top (above) and side (bottom) views of the representative sites for Pd intercalated in AC/graphene. The blue, gray, yellow and light red balls indicate C (AC), C (graphene), Pd and H, respectively. (b) Binding energies of the Pd atom intercalated in 16 different positions. The average binding energies of five different types of adsorption structures are shown in red, and the blue dashed line indicates the total average binding energy of the AC/Pd/graphene system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)