Unprecedented Single-Layered Rhodium Nanosheets: Metallene

Despite significant advances in the fabrication of two-layered materials, the preparation of single-layered metal materials remains a challenge. We report a solvothermal synthesis of novel single-layered rhodium nanosheets (Rh NSs) with large dimensions. Atomic force microscopy shows that the Rh NS is less than 4 Å thick. Electron diffraction and X-ray absorption spectroscopy measurements suggest that the ultrathin Rh NS has only a single-atom layer. Density functional theory (DFT) studies reveal that the single-layered Rh NS possesses a unique δ-bonding framework formed via Rh 4d orbitals that stabilizes the ultrathin structure. Similar to graphene, we propose to call the single-layered metal nanosheet "metallene".

Table 1: Structural parameters obtained from the curve fitting analysis of the EXAFS spectra
[a]X-ray absorbing and scattering atoms, [b]Coordination number, [c]Atomic distance, [d]Mean-square disorder in the distribution of inter-atomic distances, [e]defined; Range $\Delta k = 2–13$ Å^{-1}, $\Delta R = 1.8–2.8$ Å.

Sample	Ab–Sc[a]	C.N.[b]	r^c/Å	σ^{2d}	R factor
Rh foil	Rh–Rh	12[e]	2.687 ± 0.003	0.0038 ± 0.0004	0.0019
Rh NPs	Rh–Rh	10.4 ± 0.8	2.687 ± 0.003	0.0045 ± 0.0004	0.0015
ultrathin Rh sheets	Rh–Rh	6.4 ± 0.7	2.692 ± 0.004	0.0063 ± 0.0006	0.0041

The discovery of ultrathin materials, such as graphene [1], molybdenum disulfide, and boron nitride [2], has aroused considerable research interest due to their fascinating properties, such as high electron mobility, quantum Hall effects, extraordinary thermal conduction, magnetic resonant mode, and superconductivity. Up to now, the fabrication of ultrathin materials has mainly relied on the strong intra-layer chemical bonding and weak inter-layer interactions. In contrast, metal atoms have strong preferences for three-dimensional close-packed structures, making it challenging to prepare ultrathin metallic materials.

Herein, we report the fabrication of single-layered rhodium nanosheets (Rh NSs) with an edge length of ca. 500–600 nm by using a simple solvothermal synthetic approach [3]. These semi-transparent Rh NSs are highly sensitive to electron beam irradiation in high-resolution transmission electron microscopy (HRTEM), suggesting an ultrathin structure. Aberration-corrected electron microscopy, atomic force microscopy (AFM), and X-ray adsorption spectroscopy further reveal that the Rh NSs are composed of planar single-atom-

layer sheets of Rh atoms. As shown in Fig. 1, AFM visualization and the corresponding height profiles display a large sheet-like morphology with a height of ca. 4 Å, in accordance with the diameter of a Rh atom of 3.46 Å, suggesting that the as-prepared Rh NSs are layers of only one atom in thickness. Taking advantage of its ability to provide statistical significance, extended X-ray absorption fine structure (EXAFS) was used to elucidate the local coordination environment of Rh atoms and to determine the thickness of Rh NSs. As shown in Table 1, the coordination number (CN) for close-packed nanoparticles (NPs) is 10.4 ± 0.8, in agreement with the expected value for normal nanoparticles. In contrast, a much smaller CN value of 6.4 ± 0.7 is obtained for the Rh NSs, fitting well with the CN of a single-layered structure. Additionally, the average Rh–Rh bond length in Rh NSs is estimated as 2.692 ± 0.004 Å from the EXAFS spectra, which is similar to that of Rh foil (2.687 ± 0.003 Å), indicating that the single-layered Rh NSs consist of close-packed Rh atoms.
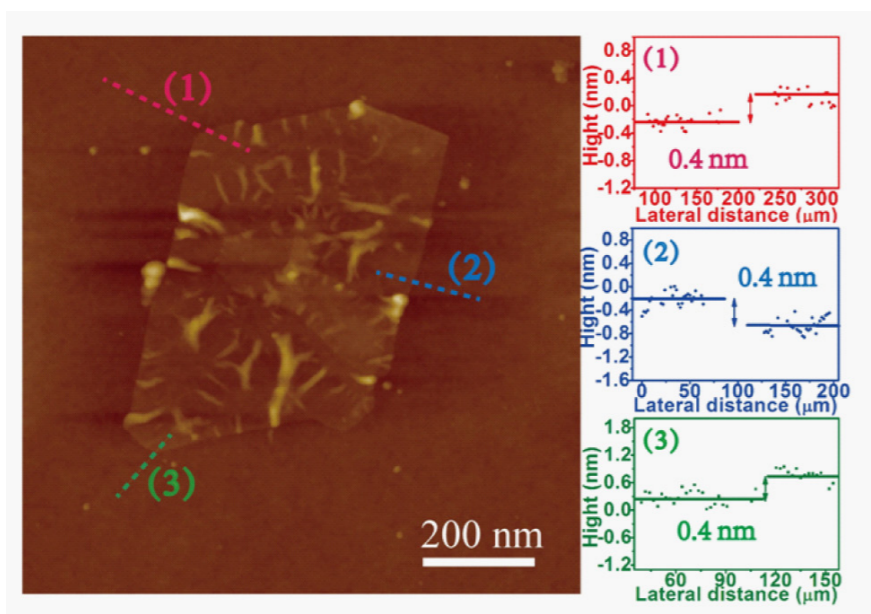
To elucidate the nature of the unexpected stability of the Rh NSs, theoretical studies were carried out by using density functional theory (DFT) and *ab initio* molecular dynamics (AIMD) simulations. It is shown that the single-layered Rh NSs possess a delocalized δ-bonding framework, constructed from 4d$_{z^2}$–5s hybrid orbitals of Rh atoms, which stabilizes the single-layered structure together with the external poly(vinylpyrrolidone) ligands. The δ-bonding in single-layered Rh NSs has high similarity with the π-bonding in graphene. As shown in Fig. 2(a), Rh 4d orbitals split into e$_{2g}$ (d$_{xy}$, d$_{x^2-y^2}$), e$_{1g}$ (d$_{xz}$, d$_{yz}$), and a$_{1g}$ (d$_{z^2}$) species upon interacting with six peripheral Rh atoms in a Rh$_7$ (D_{6h}) cluster. The highest half-filled a$_{1g}$ orbital forms the shoulder-to-shoulder δ-bonding framework. In contrast, in graphene, each C atom has half-filled (sp^2)^3 hybrid orbitals that form the σ-skeleton and a (p$_z$)^1 orbital that forms the delocalized π-bonding framework. Based on the analogy with graphene, we have chosen to call the Rh NSs "metallene". AIMD simulations at 21 ps show that the structure of single-layered Rh is stable even at T = 300 K [Fig. 2(b)].

To investigate the catalytic properties of ultrathin Rh NSs, hydrogenation processes of phenol and hydroformylation of 1-octene were employed as probe reactions. Commercial Rh/C and Rh NPs were chosen as the benchmark catalysts. In the hydrogenation of phenol, the best performance was achieved with ultrathin Rh NSs, which gave >99.9% conversion within 4 h near room temperature (30°C) under low H$_2$ pressure (1.0 MPa) and showed an activity that was, respectively, four and seven times greater than those of commercial Rh/C and Rh NPs (based on conversion at 1 h). In the hydroformylation of 1-octene, ultrathin Rh NSs were found to give both superior catalytic activity and selectivity towards the target product (aldehyde) compared with commercial Rh/C and Rh NPs. The high performance of Rh NSs in catalysis is attributed to the 100% proportion of surface atoms, which is not possible in commercial Rh/C or Rh NPs.
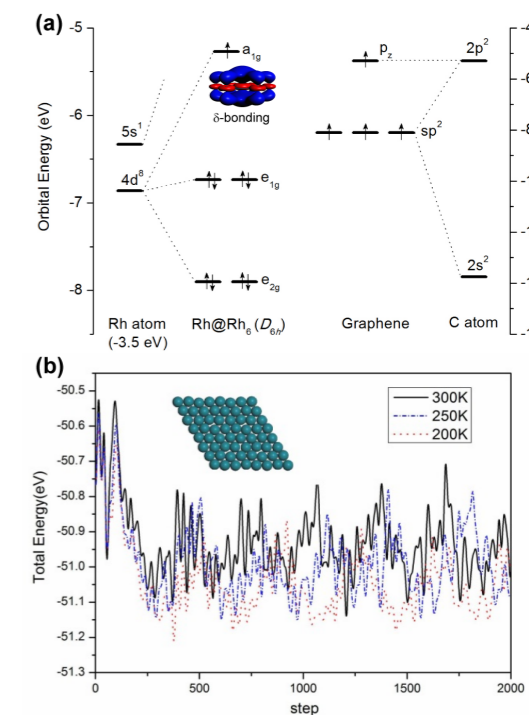

Figure 1: Atomic force microscope image of an individual rhodium nanosheet with height profiles for three different areas.

Figure 2: (a) Molecular orbitals of Rh$_7$ (D_{6h}) cluster constructed by central Rh atom and peripheral Rh$_6$ frame (left) and schematic molecular orbitals of change to graphene (right). (b) Total energies of a single-layered Rh of the last 6 ps of AIMD simulations at 200, 250 and 300 K.

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