Ultrathin palladium nanosheets with selectively controlled surface facets†

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We report a facile bottom-up synthetic approach to preparing ultrathin two-dimensional (2D) palladium nanosheets (PdNSs) with selectively exposed surface facets. Our synthetic strategy is based on the utilization of the nanoconfined lamellar mesophases of amphiphilic functional surfactants to template the growth of PdNSs in aqueous solution. Preferential adsorption of functional groups (e.g., COOH, pyridyl and quaternary ammonium) and halide counter ions (e.g., Br− and Cl−) in the long-chain surfactants onto different Pd planes results in the epitaxial growth of {100}, {110} and {111}-exposed surface facets of ultrathin PdNSs. Our synthetic approach is a general, powerful and scalable method to precisely control the surface facets of ultrathin 2D PdNSs, thus providing an opportunity to evaluate facet-dependent catalytic performance of Pd nanocrystals. Ultrathin PdNSs have been examined as the electrocatalysts for hydrogen evolution reactions (HERs). We show that {100}-exposed PdNSs display superior catalytic activity and stability for HERs, compared to that of {110} and {111}-exposed ones as well as their bulk counterparts. Conceivably, our findings will offer a general guideline in rational design of surfactant templates for other 2D metal nanosheets.

Ultrathin two-dimensional (2D) noble metal nanomaterials with atomic thickness have received considerable interest due to their unique electronic, catalytic, electrochemical, and optical properties, compared to their bulk nanoscale counterparts. Those 2D nanosheets with a large portion of exposed surface atoms show superior catalytic activity for a number of chemical transformations. The surfactant-directed synthetic approach has been utilized to engineer the nanostructures of ultrathin 2D noble metal nanosheets in the presence of specific adsorbates. One example is the synthesis of Pd nanosheets with {111}-exposed crystal facet (denoted as PdNSs{111} hereafter) using cetyltrimethylammonium bromide and poly(vinylpyrrolidone) as templates and capping agents, and CO as reductant and facet-selective adsorbate. Preferentially strong adsorption of CO onto Pd{111} plane inhibited the growth of Pd along {111} plane, and facilitated the epitaxial growth on uncovered {110} and {100} planes. This resulted in the formation of ultrathin PdNSs{111} with the hexagonal shape. Other adsorbates, e.g., halide ions and amines, have also been utilized to assist the control of exposed facets of Pd nanoparticles. However, it is largely unsuccessful when extending the methodology to expose other low-index surface facets of ultrathin 2D PdNSs (e.g., {110} or {100}), although there are some examples on controlling the exposed facets in Pd nanocubes, polyhedrons and nanorods. This may be originated from the complexity in tuning the interactions between the surfactants/adsorbates and specific Pd planes while simultaneously maintaining confined 2D nanostructures during the synthesis. Therefore, a simple and general synthetic methodology to precisely control the specific exposed surface facets of ultrathin 2D PdNSs is exceedingly desired.

We herein demonstrate a facile yet powerful bottom-up synthesis of ultrathin PdNSs with efficiently controlled surface facets through a template-assisted solution-phase growth. In comparison to the conventional surfactant templates, our design features the precious control of binding between metal precursors and surfactants by tuning the functionality on the head groups of the long-chain amphiphilic surfactants (see Fig. S1 and Table S1† for chemical structures of the surfactants). When varying the hydrophilic head groups, preferential adsorption on different crystal planes can direct the epitaxial growth along plane directions to control the exposed surface facets of PdNSs. Three functional groups, including carboxyl (COOH), pyridyl (Py) and quaternary ammonium (QA), are designed as surfactants having different lengths of alkyl tails to tune the surface crystal facets of 2D PdNSs. The functional surfactants used as the templates include three structural...
features: (i) the long-chain alkyl hydrophobic tails \( (i.e. \text{C}_{22}) \) that
direct the self-assembly into lamellar mesophases, (ii) the
hydrophilic heads which stabilize the lamellar mesophases,
bind/confine metal precursors with specific planes, and
drive the epitaxial growth along plane directions into
ultrathin 2D nanosheets, and (iii) the halide counter ions that
assist the control of the exposed surface facets of 2D nanosheets
(see Fig. 1a, b, S2 and S3†). Our synthetic method does not
require any other additional adsorbates. As shown in Fig. 1b, all
three types of the low-index exposed facets of \{100\}, \{110\} and
\{111\} in ultrathin 2D nanostructures have been successfully
obtained using a family of the surfactants with various functional
groups of COOH, Py and QA, respectively. Facet-
dependent catalytic performances of as-resultant PdNSs were
finally evaluated as the electrocatalysts for hydrogen evolution
reactions (HERs).

First-principles calculations were first used to estimate the
surface binding behaviors of the functional surfactants on
different crystal facets of Pd (Fig. S4†). To simplify the
simulations, we used COOH, Py and QA with methyl tails to
examine the binding energy \( \Delta E_b \) between functional head
groups of the surfactants and different Pd crystal planes (see
details in ESI†). A more negative \( \Delta E_b \) is indicative of thermo-
dynamically favourable binding. Among three functional
groups, a more negative \( \Delta E_b \) is observed for COOH-containing
surfactants preferentially bound to Pd\{100\} plane, compared to
\{110\} and \{111\} planes (Fig. 1c). Similarly, Py-containing
surfactants favor the binding to Pd\{110\} plane. Nearly no
differences for QA-containing surfactants on three planes were
seen. Based on above rationales from simulation, those three
groups have been examined to modify the bulky surfactants to
tune the surface facets of \{100\}, \{110\} and \{111\} in PdNSs.

PdNSs\{100\}, which has not been experimentally synthesized,
were grown using COOH-containing surfactants of \( \text{C}_{22}\text{H}_{22n+1}\text{N}^+\text{CH}_2\text{COOH (Br}^-)\text{ (C}_{22}\text{N–COOH (Br}^-)\text{, n = 14–22) as}
templates. COOH group of surfactants thermodynamically favors the adsorption onto Pd\{100\} planes.\(^{30–32}\) The synthetic
details of the surfactants and ultrathin PdNSs\{100\} are given in
ESI (see Fig. S5† for time-dependent experimental). In a typical
synthesis, the Pd precursor (\( \text{H}_2\text{PdBr}_4 \)) obtained by the rapid
ligand exchange between PdCl\(_4^{2–}\) and Br\(^–\))\(^{33}\) was mixed with
\( \text{C}_{22}\text{N–COOH (Br}^-) \) in aqueous solution, to direct the self-
assembly into lamellar mesophases at 35 °C (see Fig. S3† for
small-angle X-ray diffraction (XRD) and small-angle X-ray scat-
tering (SAXS)). Then, the fresh-prepared ascorbic acid was
injected into the above solution to start reduction of PdBr\(_4^{2–}\)
into metallic Pd \textit{in situ}. The color of reaction mixture changed
from light-brown, to blue and eventually to dark-blue in 3 h,
indicative of the formation of Pd nanocrystals. The solution-
phase synthetic route is in one step, and it can be easily scale-
up to 1 L (Fig. S3†).

The nanostructures of as-resultant PdNSs\{100\} are revealed
by electron microscopy. As shown in Fig. 2, the representa-
tive low-magnification scanning electron microscopy (SEM) and
transmission electron microscopy (TEM) images clearly show
the ultrathin nanosheets of Pd with a high purity and uniform-
ity (see Fig. S6 and S7† for more low-magnification SEM and
TEM images). PdNSs\{100\} are in nearly square shapes with an
average edge length of \( \sim 80 \text{ nm} \) (Fig. 2i), although slightly curly
edges with higher contrast can be seen. The square morphology
of ultrathin 2D PdNSs is confirmed by high-angle annular dark-
field scanning TEM (HAADF-STEM) and corresponded
elemental mapping (Fig. 2c). High-resolution TEM (HRTEM)
of PdNSs shows the square lattice fringes with an inter-planar

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**Fig. 1** Schematic illustration for surface facet-controlled synthesis of ultrathin PdNSs. (a) Scheme to show the assembled lamellar meso-

phases between long-chain alkyl surfactants and the growth of Pd nanocrystals. (b) Surface binding behaviours and (c) corresponded \( \Delta E_b \)
of functional head groups onto different Pd crystal planes based on first-principles calculations.

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**Fig. 2** Structural characterizations of ultrathin 2D PdNSs\{100\} synthesized using \( \text{C}_{22}\text{N–COOH (Br}^-) \) (a) Low-magnification SEM

and (b) TEM images of PdNSs\{100\}. Inserted in (b) is TEM image of an individual PdNS and the scale bar is \( 20 \text{ nm} \). (c) STEM image

and elemental mapping of PdNSs\{100\}. (d) HRTEM image and corre-

sponded FT pattern of PdNSs\{100\}. (e) SAED pattern of an individual

PdNS\{100\} (shown in the inset). (f) HRTEM image taken from the curly

edge of a PdNS (the insert) which stands vertically on the TEM grid. (g)
Pd 3d XPS spectrum, and (h) wide-angle XRD pattern of PdNSs\{100\}. (i) The average size and its distribution of PdNSs\{100\}.
spacing of 1.96 Å (Fig. 2d), which can be assigned to the \{200\} plane of face-centered cubic (fcc) Pd (see wide-angle XRD in Fig. 2h). Fourier transform (FT) pattern further confirms the growth in [100] plane direction. We examined the lattice fringes of >20 different nanosheets (Fig. S9|) and all nanosheets show identical crystal structures, suggesting the same exposed surface facet of PdNSs. HRTEM images of different domains in an individual PdNS exhibits uniform spacings and orientations of the lattice fringes (Fig. S10|), indicating the single-crystalline feature of PdNSs. Selected-area electron diffraction (SAED) pattern in Fig. 2e displays a series of spots of single-crystalline structure, corresponding to the [100] zone diffraction of the fcc Pd. The thickness of PdNSs is measured to be ca. 2.5 nm with \~{}12 atomic layers, when taking TEM images perpendicular to the nanosheet (Fig. 2f). The fringes with a lattice spacing of 1.99 Å can be indexed to the Pd \{002\} facet. The high-resolution X-ray photoelectron spectroscopy (XPS) of Pd 3d shows two asymmetric peaks at 335.4 and 340.6 eV (Fig. 2h), slightly higher than the values of PdNSs capped by quaternary ammonium groups or pyridyl groups (Fig. S11|) and the reported value of commercial Pd nanoparticles,\(^4^a\) possibly because of strong surface dipole induced by carboxyl groups. Those findings suggest the first successful preparation of ultrathin PdNSs with \{100\}-exposed surface facet using the functional surfactant of C\(_{22}\)N-COOH (Br\(^{−}\)) simultaneously as the templates and capping agents.

To synthesize PdNSs with \{110\} and \{111\}-exposed surface facets, a set of functional surfactants were further examined by varying binding interactions of hydrophilic head groups with Pd crystal planes. Surfactants having functional Py groups that favor to interact the Pd\{110\} crystal planes,\(^35\text{-}37\) were designed (C\(_{22}\)-Py (Br\(^{−}\)). The as-designed functional surfactant of C\(_{22}\)-Py (Br\(^{−}\)) thus directed the growth of ultrathin PdNSs\{110\}. On the other hand, the surfactants with only QA groups and Cl\(^{−}\) as counter ion (C\(_{22}\)-QA (Cl\(^{−}\)) were designed to decrease the chemisorption interactions with the Pd\{100\} or \{110\} planes, and to expose the Pd\{111\} planes with low surface energy.\(^38\) In addition, CO with strong preferential chemisorption onto the Pd\{100\} or \{110\} planes, will destabilize the initial lamellar mesophases thermodynamically, thus disrupting the epitaxial growth of ultrathin PdNSs along plane direction.\(^39\text{-}40\)

We extended our investigations to understand whether the alkyl lengths and reaction temperatures affect the nanostructures of as-resultant PdNSs. As shown in Fig. 2a, the longer alkyl length favors to stabilize lamellar structures assembled from functional surfactants, promoting the formation of ultrathin 2D nanosheets (see Fig. S15\textendash}S17| for TEM images). Similarly, the more ordered nanosheet structures were obtained at the lower reaction temperature (Fig. S18|). This may be because the shorter alkyl chains and the higher reaction temperature will destabilize the initial lamellar mesophases thermodynamically, thus disrupting the epitaxial growth of ultrathin PdNSs along plane direction.\(^39\text{-}40\)

In addition, the effect of functional head groups and halide counter ions of the surfactants on surface facets of the PdNSs were systematically investigated. To this end, surfactants with long alkyl chain of C\(_{22}\) were used to form stable lamellar lattice fringe of 2.42 Å, well-matched to the 1/3 (422) reflection of fcc Pd (Fig. 3e). The result indicates that the PdNSs have exposed \{111\} facets, similarly in the FT pattern (Fig. 3f).

We extended our investigations to understand whether the alkyl lengths and reaction temperatures affect the nanostructures of as-resultant PdNSs. As shown in Fig. 4a, the longer alkyl length favors to stabilize lamellar structures assembled from functional surfactants, promoting the formation of ultrathin 2D nanosheets (see Fig. S15\textendash}S17| for TEM images). Similarly, the more ordered nanosheet structures were obtained at the lower reaction temperature (Fig. S18|). This may be because the shorter alkyl chains and the higher reaction temperature will destabilize the initial lamellar mesophases thermodynamically, thus disrupting the epitaxial growth of ultrathin PdNSs along plane direction.\(^39\text{-}40\)

In addition, the effect of functional head groups and halide counter ions of the surfactants on surface facets of the PdNSs were systematically investigated. To this end, surfactants with long alkyl chain of C\(_{22}\) were used to form stable lamellar
mesophases; while the head groups and halide counter ions were varied (Fig. 4b). As reported previously, halide ion of Br\textsuperscript{−} preferentially chemisorbed onto Pd{100} and Pd{110} planes, while no favorable binding for Cl\textsuperscript{−}.\textsuperscript{16,22,41} We found that C\textsubscript{22}–QA (Br\textsuperscript{−}) led to the formation of PdNSs with the mixed surface facets of \{100\} and \{110\} planes with a ratio of 39 : 61, confirming the preferential interaction of Br\textsuperscript{−} ions with Pd{100} or \{110\} planes (Fig. S19†). Those findings suggest that the weak adsorption of both quaternary ammonium groups and Cl\textsuperscript{−} ions on Pd crystal planes is the key to the formation of PdNSs with the lower crystal facets of Pd\{111\}. On the contrary, when Cl\textsuperscript{−} on Pd crystal planes is the key to the formation of PdNSs with C\textsubscript{22}–QA (Cl\textsuperscript{−}) and C\textsubscript{22}–Py (Cl\textsuperscript{−}), PdNSs\{111\} mixed with PdNSs\{100\} (\{111\} : \{100\} = 46 : 54) and PdNSs\{110\} (\{111\} : \{110\} = 32 : 68) were simultaneously observed (Fig. S20†). Given slight difference of ΔH\textsubscript{a} in COOH and Py-containing surfactants (Fig. 1c), the results further suggested that the halide ion of Br\textsuperscript{−} has a synergistic effect on controlling exposed facets of the resultant PdNSs.

Electrocatalytic HERs were further used as a model reaction to evaluate the surface facet-dependent catalytic performances using PdNSs as the electrocatalysts. The commercial Pt (cPt) and Pd black (PdB) (see TEM images in Fig. S21†) were also tested as controls. Fig. 5a shows HER linear sweep voltammetry (LSV) curves under acidic condition (0.5 M H\textsubscript{2}SO\textsubscript{4}) at a scan rate of 5 mV s\textsuperscript{−1}. PdNSs with different exposed surface facets exhibited completely different HER activities, following an order of PdNSs\{100\} > PdNSs\{110\} > PdNSs\{111\}. The lowest overpotential of 67 mV was seen for PdNSs\{100\} at a current density of 10 mV cm\textsuperscript{−2}, which is 91 and 160 mV lower than that of PdNSs\{110\} and PdNSs\{111\}, respectively (Fig. 5b). Besides, PdNSs\{100\} exhibited a comparable HER activity to the state-of-the-art catalyst of cPt (the overpotential of PdNSs\{100\} is only 49 mV higher than that of cPt at 10 mV cm\textsuperscript{−2}). The similar trends of HER activities were also observed at current densities at 50 and 100 mV cm\textsuperscript{−2} (Fig. 5b). The better electrocatalytic performance of PdNSs\{100\} may be originated from the optimal balance between adsorption and desorption of H on the Pd\{100\} planes during HER.\textsuperscript{42,43} By contrast, commercial PdB exhibited the lowest HER activity due to their large sizes.

The electrocatalytic stability of ultrathin 2D PdNSs\{100\} was further examined. As shown in Fig. 5c, negligible shifts of LSV curves were observed for PdNSs\{100\} after continuous potential sweeps for 15 000 cycles. The result indicated the superior stability of ultrathin PdNSs. No significant change on the nanosheets shape of the PdNSs\{100\} was also observed after test for 15 000 cycles (see the TEM image as the inset in Fig. 5c), further confirming the superior stability. The current–time (i–t) chronocoulometric response was also recorded by a continuous potential of 42 mV at the current density of 50 mV cm\textsuperscript{−2} (Fig. 5d). A respectable current retention of 96.7% was maintained for 21 h, further indicating the superior electrocatalytic durability of PdNSs\{100\} in an acidic solution. In contrast, only 65.4% of current retention was maintained (~20 h) for commercialized PdB nanoparticles. The improved electrocatalytic stability of ultrathin PdNSs can be ascribed to the anisotropic ultrathin 2D nanostructures which retarded the dissolution and ripening processes of PdNSs and strengthened the physical interaction between catalysts and the carbon support/electrode.\textsuperscript{3,44}

In summary, we reported a novel but facile surfactant-assisted synthetic approach for epitaxial growth of ultrathin 2D nanosheets with well-controlled exposed surface facets, for the first time. The key to the synthesis of ultrathin PdNSs with specific exposed facets is the utilization of surfactants having functional hydrophilic head groups as the templates and capping agents. The change in hydrophobic carbon chain lengths, functional head groups and halide counter ions of the surfactants resulted in specifically exposed surface facets of ultrathin metal nanosheets. As a result, all three low-index exposed crystal facets of \{100\}, \{110\} and \{111\} in ultrathin PdNSs were synthesized using the surfactant of C\textsubscript{22}–N–COOH (Br\textsuperscript{−}), C\textsubscript{22}–Py (Br\textsuperscript{−}) and C\textsubscript{22}–QA (Cl\textsuperscript{−}), respectively. Lastly, the surface facet-dependent electrocatalytic activity of ultrathin PdNSs was also examined by HERs. We found that the PdNS\{100\} exhibited much better electrocatalytic activity and stability, compared to the PdNS\{110\} and PdNS\{111\}. This work represents the first successful example for facet-controlled synthesis of ultrathin PdNSs. We believe that the concept of 2D-templated strategy deriving from the self-assembly of novel designed functional surfactants could provide new insight in the prospective construction of other kinds of ultrathin noble metals or related inorganic nanomaterials.

**Conflicts of interest**

There are no conflicts to declare.
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Notes and references