Sub-10 nm Platinum Nanocrystals with Size and Shape Control: Catalytic Study for Ethylene and Pyrrole Hydrogenation

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Abstract: Platinum nanocubes and nanopolyhedra with tunable size from 5 to 9 nm were synthesized by controlling the reducing rate of metal precursor ions in a one-pot polyl synthesis. A two-stage process is proposed for the simultaneous control of size and shape. In the first stage, the oxidation state of the metal ion precursors determined the nucleation rate and consequently the number of nuclei. The reaction temperature controlled the shape in the second stage by regulation of the growth kinetics. These well-defined nanocrystals were loaded into MCF-17 mesoporous silica for examination of catalytic properties. Pt loadings and dispersions of the supported catalysts were determined by elemental analysis (ICP-MS) and H2 chemisorption isotherms, respectively. Ethylene hydrogenation rates over the Pt nanocrystals were independent of both size and shape and comparable to Pt single crystals. For pyrrole hydrogenation, the nanocrystals demonstrate different physical and chemical properties. The most important aim of heterogeneous catalysis is to design catalysts with high selectivity for the desired product without sacrificing activity. Transition metal nanocrystals with size and shape control are very promising for this goal. For example, alkane hydrogenolysis rates showed sensitivity to Pt nanocrystals size.1-4 Our group further demonstrated the size sensitivity for carbon-nitrogen ring-opening reactions.5 Catalytic activity and selectivity dependence on nanocrystal shape have also been demonstrated. For instance, both cyclohexene and cyclohexane formed on cuboctahedral nanocrystals during benzene hydrogenation, while only cyclohexane formed on cubic nanocrystals.6 These observations were consistent with previous results for Pt single-crystal studies. To further investigate the roles of nanocrystal size and shape in transition metal heterogeneous catalysis, it is essential to simultaneously control the size and the shape of the nanocrystals.

Introduction

The well-defined (100) facets on Pt nanocube surfaces make the Pt nanocubes an ideal material for understanding the influence of nanocrystal facets on catalytic performance.6,7 Several synthetic methods for cubic Pt nanocrystals were reported previously; however, sizes of these shaped nanocrystals were typically around 10 nm or larger.7-10 Sub-10 nm nanocrystals demonstrate different physical and chemical properties from large nanocrystals.11-18 Previous research unambiguously showed that the structure dependency of activity and selectivity is more significant for nanocrystals smaller than 10 nm.7-5 Also, smaller nanocrystals have higher dispersion than larger ones, and this fact permits more efficient use of precious metals. The lack of a synthetic method for shaped nanocrystals in single

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digit nanometer range reflects that size reduction while main-
taining the shape is challenging. The difficulty is partly because
the shape-controlled nanocrystals are normally kinetically stable,
but not thermodynamically stable. Therefore, change of any
synthetic factor that reduces the size also causes shape change.19

The development of a general strategy for simultaneous control
of size and shape is critical for synthesis of nanocrystals with
shape control in the single-digit nanometer range.

In this work, we report a facile method to synthesize sub-10
nm Pt nanopolyhedra and nanocubes dominantly enclosed in
six (100) facets. The size and the shape of these sub-10 nm Pt
nanocrystals were both tuned by simply controlling the reducing
rate of metal precursors at different stages of the synthesis.
Nanocubes with tunable size from 5 to 9 nm and nanopolyhedra
with size of 3.5 and 5.0 nm were synthesized and then supported
into an inert mesoporous silica support (MCF-17) for shape-
and size-dependent catalytic studies. The Pt nanocrystals with
different size and shape displayed similar turnover frequencies
for ethylene hydrogenation, which was consistent with previous
studies3,4 on Pt nanocrystals and single crystals. Normalized
per mass of Pt, the activities of the 5 nm nanopolyhedra and
nanocubes were higher than that of the 9 nm nanocubes, which
demonstrated that the smaller Pt nanocubes were advantageous
as compared to the larger nanocubes due to its higher surface-
to-bulk ratio. Shape-dependent selectivity was clearly demonstrat-
ed for the nanopolyhedra and nanocubes by pyrrole
hydrogenation. The dominant product over the Pt nanocubes
was n-butylamine. Over Pt nanopolyhedra of similar size, a
mixture of pyrrolidine and n-butylamine formed, and this
selectivity difference represents a significant result in shape-
controlled selectivity. To further understand this shape sensitiv-
ity, sum-frequency generation (SFG) surface vibrational spectra
of pyrrole adsorbed onto Pt single crystals were compared. The
study showed that, consistent with our catalytic results, n-
butylamine formation is enhanced on the Pt (100) surface, the
dominant surface of the nanocubes, relative to the Pt (111)
surface.

Experimental Section

Chemicals. Triblock copolymer Pluronic P123 (Aldrich), 1,3,5-
trimethylbenzene (Sigma-Aldrich), tetraethyl orthosilicate
(Si(OC2H5)4, Sigma-Aldrich), ammonium fluoride (Sigma-Aldrich),
chloroplatinic acid hexahydrate (H2PtCl6·6H2O, ≥ 97.50% Pt basis,
Sigma-Aldrich), ammonium hexachloroplatinate(IV) ((NH4)2PtCl6,
99%; Sigma-Aldrich), ammonium tetrachloroplatinate(II) ((NH4)2-
PtCl4, 99%; Sigma-Aldrich), poly(vinylpyrrolidone) (PVP,
99%; Sigma-Aldrich), ammonium hexachloroplatinate(IV) ((NH4)2-
PtCl6, 99%; Sigma-Aldrich), poly(vinylpyrrolidone) (PVP, Mw =
29 000; Sigma-Aldrich), tetramethyammonium bromide
(N+(CH3)4)Br-, 99%; Sigma-Aldrich), ethylene glycol (>98%,
EMD), and solvents (analytical grade) including acetone, ethanol,
hexanes, and chloroform were used without further purification.

Sub-10 nm Pt Nanocrystal Synthesis. A total of 0.05 mmol
of Pt ions (NH4)2PtCl6 and (NH4)2Pt(H2O)6Cl4. 0.75 mmol of
tetramethylammonium bromide, and 1.00 mmol of poly(vinylpyr-
rolidone) (in terms of the repeating unit; Mn = 29 000) were
dissolved into 10 mL of ethylene glycol in a 25 mL round-bottom flask at
room temperature. The same results were obtained if
(NH4)2PtCl6 was replaced by H2PtCl6·6H2O as the Pt(IV)
ion source. The Pt(IV) to total Pt (Pt(II) + Pt(IV)) molar ratios
were 0, 20%, 50%, 80%, and 100% for synthesis of 3.5 nm
nanopolyhedra, 5 nm nanocubes, 6 nm nanocubes, 7 nm nanocubes,
and 9 nm nanocubes, respectively. The mixed solution was heated
to 180 °C in an oil bath at 60 °C/min. For 5 nm Pt spherical
nanopolyhedra, the Pt(IV) to Pt (Pt(II) + Pt(IV)) molar ratio was
0.2, and the temperature was 140 °C. The solutions were held at
these respective temperatures for 20 min under argon protection
and magnetic stirring, resulting in a dark brown solution. After
the solution was cooled to room temperature, acetone (90 mL) was
then added to form a cloudy black suspension, which was separated
by centrifugation at 3000 rpm for 10 min. The black product was
collected by discarding the colorless supernatant. The products were
further washed three times by precipitation/dissolution (redispersed
in 20 mL of ethanol and then precipitated by adding 80 mL of
hexanes). The nanocrystals were then redispersed in 10 mL of
ethanol for characterization and catalyst preparation.

MCF-17 Synthesis. The synthesis of MCF-17 followed the
previous reports.20,21 In a typical preparation, 4 g of 1,3,5-
trimethylbenzene (TMB) was added into a 75 mL aqueous solution
that contained 4 g of triblockcopolymer Pluronic P123 and 10 mL
of concentrated HCl. The solution was stirred at 40 °C for 2 h,
and 9.2 mL of tetraethylxysilane (TEOS) was then added. After
being stirred for 5 min, the solution was aged at 40 °C for 20 h
under a quiescent condition. Next, 46 mg of NH4F was added, and
the solution was transferred to an autoclave and was aged at 100 °C
for another 24 h. The precipitate product was filtered, washed with
water and ethanol, and calcined in air at 600 °C for 6 h. The white
powder was kept in desiccator for further use.

Pt on MCF-17 Catalysts Preparation. Pt colloidal solution (1
mg/mL) was diluted by ethanol (0.1 mg/mL). The desired amount
of solution (0.25 wt % Pt) was added to mesoporous MCF-17 and
sonicated for 3 h at room temperature by a commercial ultrasonic
sonicator (Branson, 1510R-MT, 70 W, 42 kHz). The brown precipi-
tates were separated by centrifugation (3000 rpm, 20 min),
thoroughly washed with ethanol two more times, and dried in an
oven at 373 K overnight.22

Characterization Methods. Shape, size, and lattice structure
of the nanocrystals were analyzed using a FEI Tecnai G2 S-Twin
transmission electron microscope (TEM) and Philips CM200/FEF
high-resolution TEM (HRTEM), operated at 200 kV. X-ray
photoelectron spectroscopy (XPS) experiments were performed on
a Perkin-Elmer PHI 5300 XPS spectrometer with a position-
sensitive detector and a hemispherical energy analyzer in an ion-
pumped chamber (evacuated to 2 × 10-10 Torr). The Al Kα (BE =
1486.6 eV) X-ray source was operated at 300 W with 15 kV
acceleration voltage. Binding energies (BE) were calibrated by
setting the measured BE of C 1s to 285 eV. Elemental analyses by
inductively coupled plasma atomic emission spectroscopy (ICP-
AES) were conducted at Galbraith Laboratories, Inc. (Knoxville,
TN). Dispersions were determined at 303 K by H2 chemisorption
(Autosorb I, Quantachrome Instruments) using the total isotherm.

Ethylene and Pyrrole Hydrogenation. For catalytic studies,
samples were diluted with low surface area quartz and loaded into
glass reactors. Temperature was controlled by a PID controller
(Watlow 96) and a type-K thermocouple. Gas flows (all from
Praxair and UHP) were regulated using calibrated mass flow
controllers. Before the reaction, samples were reduced in 50 mL
min-1 of 76 Torr of H2 with a He balance for 1 h at 100 °C. For
ethylene hydrogenation, the gases were 10 Torr of ethylene, 100
Torr of H2 with a balance of He. For pyrrole hydrogenation, the
feed was 4 Torr of pyrrole (Sigma-Aldrich, >98%) and 400 Torr
of H2 with a balance of He. The desired partial pressure of pyrrole
was achieved by bubbling He through pyrrole and assuming
saturation. For both reactions, gas composition was analyzed with
flame ionization (FID) and thermal conductivity (TCD) detectors
on a HP 5890 Series II gas chromatograph (GC). Turnover
frequencies were determined by normalizing the conversion to
the number of Pt surface atoms determined by hydrogen chemisorption.

(22) Lettow, J. S.; Han, Y. J.; Schmidt-Winkel, P.; Yang, P. D.; Zhao,
Sum-Frequency Generation (SFG) Surface Vibrational Spectroscopy Study. For SFG measurements, an active/passive mode-locked Nd:YAG laser (Leopard D-20, Continuum) with a pulse width of 20 ps and a repetition rate of 20 Hz was used. The fundamental output at 1064 nm was sent through an optical parametric generation/amplification (OPA/OPG) stage where a tunable IR (2300–4000 cm⁻¹) and a second-harmonic VIS (532 nm) beam were created. The IR (150 µJ) and VIS (200 µJ) beams were spatially and temporally overlapped on the crystal surface at angles of incidence of 55° and 60°, respectively, with respect to the surface normal. The generated SFG beam was collected and sent through a monochromator to a photomultiplier tube to detect the SFG signal intensity.

Results and Discussion

Synthesis and Characterization of Shaped Sub-10 nm Pt Nanocrystals. The addition of foreign metal ions is effective for controlling the shape of metallic nanocrystals. Several Fe or Ag ion-mediated syntheses of shape-controlled Pt nanocrystals have been reported. However, the role of the foreign metal ions is not clear, and the final state of the foreign metal is hard to confirm. Moreover, in the Ag-mediated synthesis, the catalytic activity is greatly affected by the presence of foreign ions even though the foreign ion was barely detectable. In the present approach, bromide ions were used as the shape directing agent. The bromide-mediated strategy is more favorable catalytically because the bromide species are only on the nanocrystal surface and are easily removed after synthesis by washing. In general, the metal salts (Pt(IV) and Pt(II)), the surfactants (PVP), and the shape directing agent (bromide ions) were dissolved in ethylene glycol at room temperature to form a precursor solution. Previous studies have shown that the bromide species selectively adsorbed onto Pt (100) crystal faces and induced the formation of Pt nanocrystals. The mixed precursor solution was then rapidly heated to the desired temperature (140 and 180 °C for nanopolyhedra and nanocubes, respectively) and maintained at this temperature for 20 min with vigorous stirring. The formation of 9 (8.8 ± 1.2) nm (edge) Pt nanocubes (85% cubes, 15% tetrahedra or irregular crystals) is revealed by the transmission electron microscopy (TEM) images (Figure 1a) when the Pt(IV) salt [(NH₄)₂PtCl₆] was used in the precursor solution. High-resolution (HR) TEM image indicates that the Pt nanocubes are single crystals and enclosed by six [100] faces (Figure 1b). During the synthesis, the solution instantaneously turned brown after 2 min of heating and then turned darker with increasing time. By monitoring the crystal growth process with TEM (Figure 2), we hypothesized that the 9 nm Pt nanocube growth was a two-stage process. During the initial stage, the Pt nuclei (around 3.5 nm) formed rapidly in the solution (Figure 2a). In the second stage, the remaining Pt ions were reduced onto these nuclei with preferential growth direction along the [111] direction because bromide ions stabilized the (100) faces (Figure 2b and c). If this assumption were true, smaller nanocubes should form by increasing the number of the nuclei in the initial stage and decreasing the remaining Pt ions in the second stage. To demonstrate this concept, we introduced Pt(II) salt (NH₄)₂PtCl₆, which can be reduced more easily than Pt(IV), to partially replace the Pt(IV) salt in the initial solution. By doing so, the number of nuclei in the initial stage increased without changing the kinetics of the second stage (Scheme 1). TEM images show the monodispersity and well-defined shape of these Pt nanocubes synthesized by altering the concentration ratios of Pt(II) to Pt(IV) in the initial solution (Figure 1c, e, and g). Pt nanocubes with sizes of 7 (6.9 ± 1.8) nm, 6 (5.9 ± 0.7) nm, and 5 (5.0 ± 0.4) nm were obtained when the ratios of Pt(IV) to total Pt ions (referred to as Pt(IV) ratio in the following) were 0.8, 0.5, and 0.2, respectively. The high yield and well-defined shape of these sub-10 nm nanocubes synthesized by this method were clearly revealed by TEM and HRTEM. Regardless of size, the yields of cubic nanocrystals are more than 80%. HRTEM images revealed that these nanocrystals with different sizes are all enclosed by six (100) faces (Figure 1d, f, and h). The observation of mainly [100] direction-oriented nanocrystals (more than 70% of ~50 measured nanocrystals in each size) under HRTEM without any sample tilting indicated the high yield and well-defined shape. Size control of the Pt nanocrystals is demonstrated as a function of thePt(IV) ratios in Figure 3. When all of the Pt(IV) ions were replaced by Pt(II) ions in the initial solution, the 3.5 (3.5 ± 0.3) nm single-crystalline Pt nanocrystals were obtained (Figure 1k) and (1), which are similar to the nucleus nanocrystals (Figure 2a) that were observed in the initial stage of 9 nm nanocubes synthesis. We believe that these 3.5 nm single-crystalline nanocrystals were also formed by reducing Pt(II) ion in the syntheses of 5, 6, and 7 nm single-digit nanocubes. These rapidly formed nanocrystals served as nuclei in the synthesis, and the increase of these nuclei density significantly helps to reduce the size of the nanocubes.

The shape of these sub-10 nm nanocrystals was tuned by changing the growth rate. Nanocubes are kinetically stabilized by bromide ions, while the growth rate of the second stage can be reduced via decreasing the reaction temperature. Next, the more thermodynamically stable polyhedral nanocrystals were obtained rather than cubic nanocrystals (Scheme 1). For example, 5 nm single-crystalline Pt spherical nanopolyhedra were synthesized while the Pt(IV) ratio was 0.2 and the temperature was 140 °C (Figure 1i and j). The much slower color change of the solution during the synthesis at 140 °C indicated the slower reducing rate of Pt ions. The Pt nanopolyhedra oriented randomly under TEM grids, and the [111] oriented crystals were observed more frequently due to the larger lattice space (Figure 1j).

The oxidation state of these nanocrystals was measured by X-ray photoelectron spectroscopy (XPS). A thin layer of washed nanocrystals was deposited on a single-crystal silicon wafer for XPS, and the Pt 4fου peaks of different samples were compared. The XPS results revealed that all of the nanocrystals are mainly in metallic state, regardless of the size and shape (Table 1). The small amount of oxidized Pt (~20%) was contributed by a thin layer of oxidized Pt on the surfaces. Only trace amounts of bromide ions were detected. The ratios of bromide ions to total Pt atoms were below 10%. The amounts of oxidized Pt and bromide ions both increased with decreasing nanocrystal size, which correlated to a higher surface-to-bulk ratio. This
trend supported that oxidized Pt and bromide ions are mainly on the surfaces of the nanocrystals. This one-pot synthetic strategy allowed the synthesis of shape-controlled nanocrystals without foreign metal ions and also the continuous size control in the single-digit nanometer regime. The ability to continuously tune the size of shape-controlled nanocrystals in this regime is very important for studying catalytic properties and is the focus of the rest of this Article.

**Loading Pt onto MCF-17 Mesoporous Silica.** To study the catalysis over the Pt nanocrystals, ethylene and pyrrole hydrogenation over the 9 nm nanocubes, 5 nm nanocubes, and 5 nm nanopolyhedra supported on the 3D inert mesoporous silica...
The size and the shape of the nanocrystals are controlled by reduction rate kinetics during the two stages.
selectivity dependency of these nanocubes and nanopolyhedra was demonstrated using pyrrole hydrogenation (Scheme 2). Because it has been shown that the ring-opening of pyrrole to n-butylamine is structure sensitive,5 it is suitable for probing shape-dependent reaction selectivity in catalysts. Also, this reaction is an important model reaction for fuel processing involving removal of N from N-containing organics. In Figure 5, the structure sensitivity for hydrogenation of pyrrole to pyrrolidine, n-butylamine, and butane is presented at equal conversions at each given temperature, which is necessary for selectivity comparisons. The shape of the nanocrystals led to clear selectivity differences. For both 5 and 9 nm Pt nanocubes, n-butylamine was the dominant product at all studied temperatures. For the 5 nm nanopolyhedra, however, pyrrolidine (up to 30%) and n-butylamine were both formed at lower temperatures.

To study this structure-sensitive selectivity and determine the intermediates on the surfaces of nanocubes, sum-frequency generation (SFG) surface vibrational spectroscopy was performed to study the adsorption species of pyrrole hydrogenation over Pt (100) single crystal. Under the catalytic reaction conditions, SFG is a much more effective technique for interfacial chemical analysis than is conventional linear spectroscopy, such as infrared absorption or Raman.36–41 In linear spectroscopy, the absorption is mainly contributed by bulk gases, and therefore the absorption generated by adsorbed species at the catalyst surface is relatively small. In contrast, due to the second-order nonlinear optical process of SFG, the absorption of isotopic bulk gases does not appear in the SFG spectrum, and the absorption of adsorbed species, the symmetry of which is broken at the surface, is solely enhanced. Most importantly, previous SFG35 and NEXAFS studies42 have shown that the reaction intermediates (pyrroline, pyrrolidine, and n-butylamine) of pyrrole hydrogenation bind through the nitrogen to the metal surface in an upright orientation on Pt single crystal surface (Scheme 2) and can be recorded by SFG. The SFG spectrum recorded during pyrrole hydrogenation over Pt (100) single crystal is shown in Figure 6. By comparing the spectra of Pt (111)35 and Pt (100) single crystals for pyrrole hydrogenation at the same temperature (298 K), we observed that the CH2 group bands contributed by disorder in the butyl chains of n-butylamine and the CH3 group bands on Pt (100) single crystal were relatively stronger than the ones on Pt (111) single crystal. The result suggested that the amount of n-butylamine on the Pt surface was greatly enhanced on the (100) crystal surface. On the basis of this observation, the shape-controlled selectivity of pyrrole hydrogenation should be caused by the hydrogenation of pyrrolidine to n-butylamine being promoted by the Pt (100).

![Scheme 2. Pyrrole Hydrogenation Network and Proposed Molecular Adsorption over a Pt Surface](image)

![Figure 5. Pyrrole hydrogenation selectivity for Pt nanocrystals with different size and shape as a function of temperature. The color of the line coordinated to Scheme 2. –“□”, “△”, and “○” represent 9 nm nanocubes, 5 nm nanocubes, and 5 nm nanopolyhedra, respectively. Feed was 4 Torr of pyrrole and 400 Torr of H2 with a He balance.](image)

![Figure 6. SFG vibrational spectra recorded during pyrrole hydrogenation (3 Torr pyrrole, 30 Torr H2) over Pt (100) at 298 K. CH2(FR) represents Fermi resonance of the methyl group.](image)

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**Table 2. Ethylene Hydrogenation Rates and Kinetic Parameters on MCF-17 Supported Pt Nanocrystals**

<table>
<thead>
<tr>
<th>catalyst</th>
<th>loading</th>
<th>dispersion</th>
<th>activity (mmol C2H4 gPt (-1) s(^{-1}))</th>
<th>TOF (s(^{-1}))</th>
<th>(E_a) (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0 nm Pt nanopolyhedra</td>
<td>0.2%</td>
<td>0.19</td>
<td>5.3</td>
<td>5.5</td>
<td>7.4</td>
</tr>
<tr>
<td>5.0 nm Pt nanocubes</td>
<td>0.2%</td>
<td>0.20</td>
<td>6.2</td>
<td>6.0</td>
<td>7.2</td>
</tr>
<tr>
<td>9.0 nm Pt nanocubes</td>
<td>0.2%</td>
<td>0.08</td>
<td>2.0</td>
<td>5.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Pt (111)(^\circ)</td>
<td>N/A</td>
<td>N/A</td>
<td>6.1</td>
<td>6.1</td>
<td>10.8</td>
</tr>
</tbody>
</table>

* Loaded on MCF-17. \(^a\) Elemental analyses determined by ICP-MS. \(^b\) Based on total H\(_2\) isotherm. \(^c\) Initial TOF at 10 Torr C2H4, 100 Torr H2, and 298 K. \(^d\) Zea, F.; Somorjai, G. A. J. Am. Chem. Soc. 1984, 106, 2288–2293 with data corrected to our conditions.

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surface. Because the Pt nanocubes are mainly enclosed in (100) surfaces, pyrrolidine was converted into n-butylamine on the surface of the nanocubes. Therefore, our nanocubes promote the formation of n-butylamine at lower temperatures. As compared to the (100) surface-rich nanocubes, the polyhedral nanocrystals contain more thermodynamically stable (111) surfaces, which inhibit turnover of n-butylamine. Detailed descriptions of SFG theory and peak assignment can be found elsewhere, and detailed SFG studies on single-digit nanocrystals for further understanding the mechanism of the selectivity are currently under investigation. Two important points should be highlighted in this selectivity behavior study. First, the selectivity difference between the 3D mesoporous material supported Pt nanopolyhedra and nanocubes was significant and agreed with the single crystal studies. Second, the comparable selectivity for pyrrole hydrogenation over the 5 and 9 nm single-digit Pt nanocubes revealed that the (100) crystal surfaces were still dominant for these nanocubes with size as small as 5 nm. It clearly indicated that we successfully decreased the size of the nanocubes to the single-digit nanometer region without sacrificing the well-defined surface structure.

Conclusion

Sub-10 nm Pt nanocubes and nanopolyhedra with tunable size were synthesized by controlling the reducing rate of Pt ions in our one-pot synthetic system. This synthetic method allowed us to synthesize Pt nanocrystals with tunable size and shape, which are ideal for catalysis studies. Ethylene hydrogenation rates over the mesoporous silica supported Pt nanocrystals indicated similar catalytic activities as compared to Pt single crystals, which suggested a clean and accessible catalytic surface. The nanocubes showed significant product selectivity difference from the nanopolyhedra during pyrrole hydrogenation due to the well-controlled crystal surfaces. These observations clearly indicate the importance of size and shape control of nanocrystals in catalytic research.

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