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Surfactant Removal for Colloidal Nanocrystal Catalysts Mediated by N-Heterocyclic Carbene

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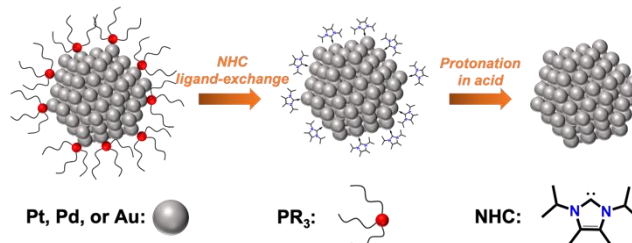
Abstract We report the facile removal of surfactants from colloiddally synthesized nanocrystals *via* a ligand exchange with N-heterocyclic carbene (NHC). Subsequent protonation of the NHC ligand in acid efficiently cleans the nanocrystal surface while preserving their uniform morphology and structure for catalysis. The broad efficacy of this strategy is validated using monodisperse Pt, Pd, and Au nanocrystals, each prepared with strongly bound phosphine stabilizers. The surface activated nanocrystals exhibit significantly improved catalytic activities, superior to other surface cleaning methods, as demonstrated in two centrally important electrochemical reactions (glycerol oxidation and CO₂ reduction). This work highlights a new surface activation strategy for catalysis and other applications that enables the efficient use of well-defined nanocrystal libraries prepared by colloidal chemistry.

Well-defined nanocrystals prepared by colloidal synthesis provide opportunities to exploit the physical properties and applications that are dependent on nanoscale dimensions and atomic structures.¹⁻⁵ Surfactants, such as trioctylphosphine (TOP), oleic acid (OA), and oleylamine (OAm), are typically long hydrocarbon molecules attached to a functional headgroup and are critical components in colloidal synthesis.^{6, 7} These molecules function to stabilize the nanocrystal high-energy surfaces against aggregation. Moreover, the use of surfactant may allow the control of nanocrystal shape⁸⁻¹² and size¹³⁻¹⁵ by modulating the crystal growth kinetics.^{6, 16, 17} Despite the essential role in the synthesis, the bulky surfactants surrounding nanocrystals create barriers for many applications, especially for catalysis, as the necessary surface active sites are blocked. Consequently, several surfactant removal methods, such as ligand exchange with small carboxylate or amine ligands (e.g., acetic acid¹⁸ and hydrazine¹⁹), thermal annealing^{20, 21}, and UV-ozone/plasma treatments^{22, 23}, have been reported in an attempt to liberate active sites. However, these methods are insufficient for strongly bound surfactants like phosphines, which are a common component of nanocrystal syntheses,^{24, 25} and can lead to incomplete cleaning, generation

of undesirable impurities (e.g., metal phosphide/phosphate due to annealing/ozone treatment), or uncontrollable atomic structure changes under harsh conditions.^{20, 26}

Herein, we present a room-temperature washing strategy mediated by an N-heterocyclic carbene (NHC) ligand for efficient nanocrystal surface cleaning. There has recently been interest in the surface modification of nanomaterials with NHCs,²⁷⁻²⁹ as NHCs are strong σ -donors and π -acceptors and can effectively modulate nanomaterials electronic structures.²⁹⁻³² As NHCs are generally stronger ligands than phosphines,^{30, 33} we envision that NHCs are promising candidates to replace phosphines in a ligand exchange process than conventional carboxylate or amine reagents (acetic acid and hydrazine). Furthermore, NHCs are prone to protonation in acidic conditions,³⁰ which allows for their conversion to a non-binding ligand for the easy removal from the nanocrystal surface. The two-step washing process we have developed is illustrated in **Scheme 1**. Using Pt, Pd, and Au nanocrystals prepared with TOP surfactants as model systems, we demonstrate that this approach enables nanocrystal surface activation for diverse electrocatalytic reactions while preserving their monodisperse sizes and structures. The nanocrystals treated with NHC were characterized by a suite of spectroscopic probes and showed much improved electrocatalytic activities toward glycerol oxidation reaction (GEOR) and CO₂ reduction reaction (CO₂RR), compared with other surface cleaning methods including acetic acid washing, hydrazine washing, and thermal annealing.

Scheme 1. NHC-mediated surfactant removal for colloidal nanocrystals.



Monodisperse Pt,³⁴ Pd,³⁵ and Au³⁶ nanocrystals were prepared by modifying previously reported methods {Supporting information (SI)}. To highlight our ability to remove strongly bound surfactants, TOP was used as the capping agent either directly in the synthesis (for Pt and Au) or via a post-synthesis exchange with weaker surfactant OAm (for Pd). The nanocrystals were supported onto conductive carbon material (Vulcan-72X) to enable electrocatalytic applications. The NHC, 1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene, chosen for its ease of preparation, shelf stability, and high solubility in hydrocarbon solvents, was prepared via an established procedure.³⁷ It was then dissolved in anhydrous hexanes, and added to the carbon-supported nanocrystals for ligand exchange (Scheme 1). The mixture was stirred for 4 hours in N₂-filled glovebox before collection via centrifugation. Protonation of the bound NHC was achieved by stirring the NHC-washed sample in glacial acetic acid at the room temperature.

Figure 1 shows the transmission electron microscopy (TEM) images of as-synthesized Pt, Pd, and Au nanocrystals and the NHC-washed carbon-supported Pt after protonation. The TEM images show that the two-step NHC treatment causes negligible size and shape change of nanocrystals, and a size analysis confirms this: the NHC-washed Pt exhibited an average size of 2.3 nm, consistent with the as-synthesized Pt of 2.4 nm (Figure S1). As control experiments for subsequent electrocatalysis, we also treated carbon-supported nanocrystals using conventional methods, including acetic acid washing (at 60 °C for 12 hours), hydrazine washing (room temperature for 12 hours), and annealing in air (300 °C for 4 hours). The sample morphologies after these treatments are shown in Figure S2.

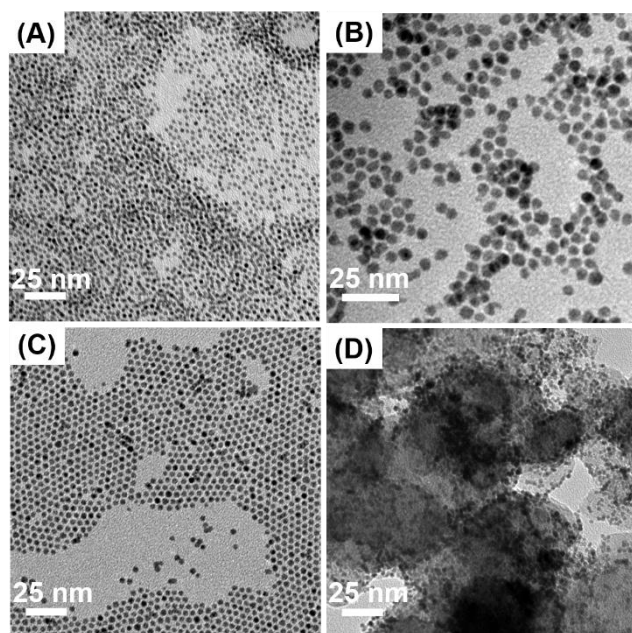


Figure 1. (A-C) TEM images of TOP-bound Pt (A), Pd (B), and Au (C) nanocrystals. (D) TEM image of NHC-washed carbon-supported Pt nanocrystals after protonation.

Direct observation of the removal of TOP on the nanocrystal surface was achieved with X-ray photoelectron spectroscopy (XPS). Four carbon-supported samples were tested: untreated Pt, acetic acid washed Pt, NHC-washed Pt without protonation, and NHC-washed Pt with protonation (Figure S3). The Pt 4f peaks (Figure S4) display unchanged peak positions in these samples (Table S1). High resolution P 2p and N 1s spectra were highlighted in Figure 2A and 2B. The NHC-washed Pt without protonation is the only sample to exhibit N signal, indicating NHC is surface bound and is removed after protonation. The ligand exchange of NHC is clear as the P signal disappears after NHC washing, even before protonation, suggesting substantial decrease of TOP on the Pt surface. The acetic acid washed Pt also shows decreased P signal below the XPS detection limit. However, later DRIFTS and electrochemical characterization indicates acetic acid's removal ability for TOP is not as effective (vide infra).

Scanning transmission electron microscopy-coupled electron energy loss spectroscopy (STEM-EELS) was also conducted on untreated Pt and NHC-washed Pt after protonation. Comparison of EELS spectra reveals that the P signal is reduced below detection after NHC-washing and protonation treatment, further confirming that TOP is indeed largely removed (Figure 2C). Such a difference was also visualized by comparing the EELS P-elemental mappings and STEM high-angle angular dark field (HAADF) images in Figure 2D-G, where the cleaned Pt nanoparticles show the unaltered morphology and lattice fringe (Figure S5) but negligible P signal compared with untreated Pt.

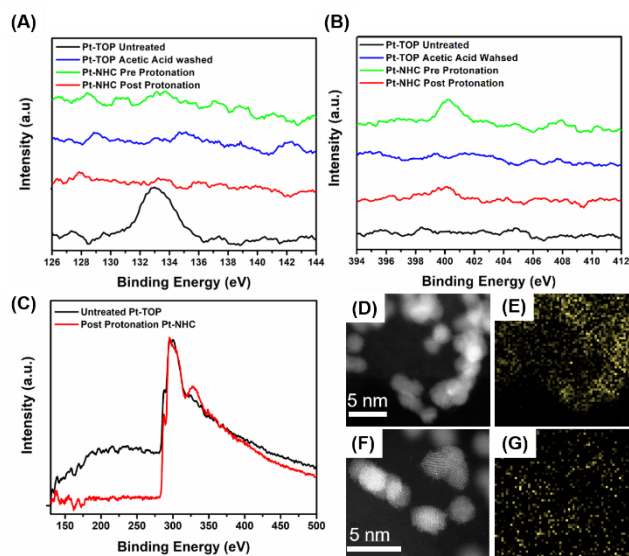


Figure 2. (A, B) High resolution P 2p XPS spectra (A) and N 1s XPS spectra (B) of carbon-supported Pt samples. (C) EELS spectra of carbon-supported Pt before and after NHC-mediated treatment. (D-G) STEM HAADF images and EELS P-elemental mappings of carbon-supported Pt with TOP capping agent (D, E) and after NHC-mediated treatment (F, G).

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed to monitor the ligand profile change on our nanocrystal surfaces. In order to achieve a clean spectrum, the NHC ligand-exchange was performed on colloidal nanocrystal suspensions in hexanes as opposed to carbon-supported nanocrystals. Upon exchange, the NHC-bound nanocrystals are prone to agglomeration due to insufficient steric hinderance from NHC. These nanocrystal agglomerates could be collected via centrifugation for DRIFTS study.

The NHC-bound Pt, Pd, and Au show vibrational bands that are in good agreement with oxidized NHC (**Figure S6**). After protonation with glacial acetic acid and subsequent purification to remove any residual acetic acid, the isolated samples show no or very weak signs of organic material in DRIFTS spectrum (**Figure S7**). These spectra, in addition to XPS and EELS results, strongly support that a) NHC replaces almost all detectable TOP on the surface regardless of nanocrystal composition, and b) that protonation leads to the stripping of NHC and therefore a cleaned nanocrystal surface. Similar DRIFTS tests were performed using acetic acid washed samples, but clearly less organics were removed, leaving a substantial amount of TOP on all samples (**Figure S8**).

To evaluate the efficacy of NHC-mediated cleaning strategy, we studied carbon-supported Pt, Pd, and Au nanocrystals that were treated with different surfactant removal methods for different electrocatalytic reactions. All nanocrystal catalysts were investigated for GEOR, a reaction that enables the utilization of bio-renewable glycerol as a fuel in fuel cells or a feedstock for fine-chemical production. Pt, Pd, and Au have been found to be active for this reaction in previous studies.³⁸⁻⁴⁰ Additionally, Au nanocrystal catalysts were used in the CO₂RR, another reaction central to clean energy and environmental sustainability with extensive recent interest.^{3, 38, 39} The combination of two catalytic reaction studied here was designed to confirm the broad applicability of this new cleaning strategy.

Figure 3A shows the cyclic voltammetry (CV) curves of Pt with different cleaning treatments in N₂ saturated KOH (1 M). The two conventional ligand-exchange methods, acetic acid and hydrazine washing, demonstrate an increased peak area in the hydrogen adsorption/desorption region (0 - 0.4 V vs. reversible hydrogen electrode (RHE)), compared with the untreated catalyst. Remarkably, the NHC-washed catalyst after protonation shows an additionally increased peak intensity and area, suggesting a more effective cleaning. Thermal annealing has the reverse effect, decreasing the apparent electrochemical active surface area (ECSA), probably due to coking of residual surfactant or nanoparticle aggregation at high temperature (**Figure S2B**). Increased current density can also be observed in Pt oxidation/reduction region (0.5 - 1.0 V), which confirms the improved ECSA after new NHC treatment. Moreover, the shape of the CV curves remains similar for all tests, suggesting that the

removal is not facet specific and that negligible morphological rearrangement takes place.

The linear scan voltammetry (LSVs) curves of different Pt catalysts in the presence of glycerol are summarized in **Figure 3B**. Acetic acid and hydrazine washing improve the peak mass activity by 23% and 37% compared with untreated TOP-bound Pt. The NHC-washed Pt after protonation results in a 77% enhancement, which is 30% better than acetic acid-washed Pt. When Pd nanocrystals were tested, the trend remained similar, with a peak mass activity order of NHC-treatment (~340% enhancement) > hydrazine washing (~260% enhancement) ≥ acetic acid washing (~250% enhancement) (**Figure 3C**). Similarly, Au showed an approximately 500% increase in peak mass activity for GEOR after NHC-mediated treatment (**Figure S9**).

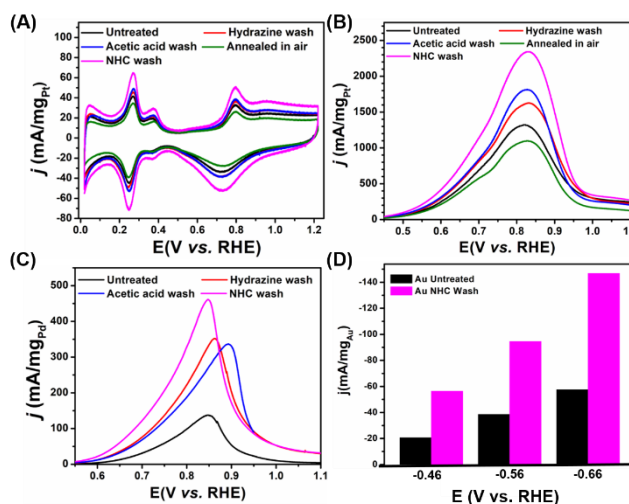


Figure 3. (A) CVs of different Pt catalysts in N₂-saturated 1 M KOH (1 M). (B) LSVs of different Pt catalysts in N₂-saturated 1 M KOH containing glycerol (1 M). (C) LSVs of different Pd catalysts in N₂-saturated 1 M KOH containing glycerol (1 M). (D) Mass activities of untreated Au and NHC-treated Au after protonation for the CO₂RR at three potentials.

Interestingly, when dilute acetic acid (~2.5 wt%) was used to remove the bound NHC on Pd, the mass activity was worse than the TOP-bound sample (**Figure S10**). This suggests a strong Pd-NHC interaction formed in the NHC-exchange, and that dilute acetic acid was too weak to effectively protonate the NHC. Glacial acetic acid was found to be efficient in protonating and removing bound NHC in the present condition. Additionally, we found that cleaned Pd and Au exhibited excellent stability against agglomeration after GEOR catalysis (**Figure S11-S12**), while Pt did show morphology change. However, the control experiment also resulted in Pt sintering, confirming that the Pt sintering was not related to the NHC treatment but rather an intrinsic property of small-sized Pt itself. (**Figure S13-S14**).

When these Au catalysts were tested in the CO₂RR in 0.1 M HKCO₃, an improved mass activity was seen at all

potentials from -0.46 V to -0.66 V (**Figure 3D**). Au is a known catalyst for the selective reduction of CO₂ to CO.^{29, 32, 41-43} Our strategy allows the increase in current density by exposing more surface sites, while causing negligible change in product selectivity for Au, as revealed by the close faradaic efficiencies toward CO for both NHC-treated and untreated catalysts (**Figure S15**).

This work presents a facile, widely applicable, and effective chemical method to remove strongly bound surfactant on colloidal nanocrystal surfaces using NHCs. The demonstrated improved removal efficiency over conventional methods enables the nanocrystals to be surface activated for catalysis, as exemplified by two different electrocatalytic reactions with gas and liquid phase substrate molecules. This method is strategically important for well-defined nanocrystals that can only be prepared by colloidal chemistry, including atomically precise core/shell, alloy, porous, and other hierarchical nanocrystals, to facilitate the study of structure-property relationship and maximize their potential in catalysis.

ASSOCIATED CONTENT

Supporting Information

Experimental. Table S1. Figures S1-S15. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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