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Engineering Metallic Nanoparticles for Enhancing and Probing Catalytic Reactions

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Abstract

Recent developments in tailoring the structural and chemical properties of colloidal nanoparticles (NPs) have led to significant enhancements in catalyst performance. Controllable colloidal NP synthesis has also allowed tailor-made NPs to also serve as mechanistic probes for catalytic processes. The innovative use of colloidal NPs to gain fundamental insights into catalytic function will be highlighted across a variety of catalytic applications. The future engineering of catalyst NPs is also moving beyond size, shape and composition considerations. Advancements in understanding structure-property relationships have enabled incorporation of complex features such as tuning surface strain to influence the behaviour of catalytic NPs. Exploiting plasmonic properties of NPs and altering colloidal surface chemistry through functionalization are also emerging as important areas for rational design of catalytic NPs. This news article will highlight the key developments and challenges to future design of catalytic NPs.

Introduction

Colloidal noble metal nanoparticles (NPs) have long been used as model systems for studying catalytic processes.^[1] The emergence of shape controlled synthesis enabling the growth of nanocrystals with well-defined morphologies from simple geometries to complex shapes such as anisotropically branched structures and NPs with high index surface facets has led to intensive studies of shape dependent catalytic activity, which has been subject to many excellent reviews.^[2] Parallel developments in the synthesis of bimetallic colloids has led to core-shell NPs, heterostructures, intermetallic and alloyed NPs, also with controllable size and shape.^[3] Judicious design of NPs through colloidal synthesis presents unique opportunities to enhance catalytic performance and selectivity by tailoring structural and chemical features at the atomic scale. The ability to decouple size, shape and compositional effects in catalytic systems has enabled unambiguous correlations about structure-property relationships in variety of catalytic processes from liquid phase synthesis, gas phase reactions, energy conversion and storage.

In this Research News we will address some recent developments in tailoring the chemical and physical properties of colloidal NPs with a focus on probing reaction mechanisms through rational catalyst design. First, designing NPs to probe the origin of enhanced reactivity will be discussed, with an emphasis on studies where colloidal catalysts are combined with other investigatory techniques to provide new mechanistic insights. The report will then illustrate how additional effects such as optical properties can be utilized for enhancing and probing catalytic processes and the future role of catalyst design. Finally the growing interest in tailoring colloidal surface chemistry at a molecular level to optimize activity, selectivity and durability for catalytic applications will be addressed.

Designing Catalytic Nanoparticles to Probe Reaction Mechanisms

The unique NP morphologies accessible through colloidal growth provides a convenient approach to probe reactions through monitoring the structural and/or chemical evolution of NPs in catalytic processes. Combining catalyst design with additional spectroscopy or microscopy techniques can be very beneficial to understanding reaction mechanisms. An insightful experiment into the complex behaviour of shaped selective NPs, involved single molecule super-fluorescence microscopy, which was used to spatially map catalytic events occurring on the surfaces of Au catalysts with different morphologies (nanocrystals, nanoplate, nanorod).^[4] The analysis revealed that catalytic activity is not constant on a particular facet but displayed an activity gradient, which is dependent on the catalyst shape. For example, Au triangular nanoplates exhibited a 2D radial gradient with the highest activity at the corners, followed by the edges and then the flat surfaces. The activity trend was related to the spatial distribution surface defects. The use of three dimensional compositional mapping by energy dispersive X-ray (EDX) tomography with scanning tunnelling transmission electron microscopy (STEM) was used to elucidate the composition dependent catalytic properties of hollow AgAu alloy NPs in the liquid phase synthesis of propargylamines.^[5] The analysis revealed the role of surface segregation in the catalysts and that optimal catalytic reactivity correlated with the maximum Au surface coverage of the NPs, which was present for AuAg alloys with ~25% atomic Au.

Synergistic effects observed in alloy NP catalyst have been long noted in catalysts and are generally attributed to ligand, geometric and ensemble effects.^[6] Ligand effects arise from charge transfer between the two different chemical species altering the electronic band structure. Geometric effectives give rise to strain, influencing the interaction of reacting species or products. Ensemble effects arise when one or more of the metal atoms or clusters (ensembles) catalyse distinct steps in the reaction. Often, a combination of these effects contribute to the overall activity observed. Rational catalyst design is emerging a promising

tool to identify, isolate and even tune these effects as demonstrated by tailoring surface strain in core-shell Pt alloys for oxidation reduction reaction (ORR).^[7] Atomic electron energy loss spectroscopy (EELS) mapping of Pt-Ni NPs surrounded by a Pt shell, revealed the formation of Ni-rich inner sub-shell, which was dependent on the NiPt ratio of the core. The higher Ni content of the core, produced greater compressive strain at the Pt surface, leading to enhanced catalytic activity due to geometric effects. Engineering NPs to maximise structure-induced surface strain as a strategy to enhance activity is excellently illustrated by a recent study where face centred cubic (fcc) FePt NPs, were annealed to form face centred tetragonal (fct) intermetallic FePt NPs.^[8] Deposition of a thin (~ 3 monolayer) Pt shell produced fct-FePt@Pt NPs, which showed higher activity compared to their fcc-analogues due to release of overcompressed Pt strain. Further refinement of the catalyst chemistry by partial replacement of Fe with Cu to form FeCuPt@Pt NPs, resulted in a 10 fold increase in ORR activity compared to commercial Pt catalysts. The use of electrochemical techniques provide a complimentary analysis to microscopy and spectroscopy based characterization and was used to evidence ensemble effects as the origin of enhanced activity observed in Ag-rich AgPd alloy NPs for ORR.^[9] Colloidal AgPd alloy NPs with tuneable composition were prepared by simultaneous reduction of metal salts. CV and CO stripping were used to probe the local environment of the surface atoms as a function of composition. Specifically, the electrochemical signatures were used to identify if the Pd was present as Pd-Pd domains or single atoms. For Ag-rich alloys ($\text{Ag}_{\geq 4}\text{Pd}$) the surface consisted of discrete Pd atoms surrounded by Ag-rich domains which amplified the activity of each Pd atom. This approach can be used as a general strategy to elucidate synergistic effects in alloy NPs.

The origin of enhanced activity is not always attributed to the chemical or structural nature of the as-synthesized NPs but due to changes that occur under the reaction conditions. Cui and co-workers^[10] studied the origin of the enhanced activity observed for ORR using bimetallic

PtNi octahedra. Combining HRTEM and EELS, as shown in Figure 1 (a)-(d), the structural and chemical evolution of the electrocatalysts could be tracked at the atomic scale and correlated to catalytic activity. EELS analysis revealed chemical segregation occurred during potential cycling as Ni atoms selectively leached from the central (111) surface facets during catalytic cycling with higher Ni content-alloys (40-47%) being more resistant to dissolution. The dissolution of Ni transformed the alloy octahedral to concave Pt nanostructures which are a highly activate surface structure for ORR, shown in Figure 1(d). Dissolution behaviour of catalyst NPs and the role of dissolved species in the mechanism is often debated in liquid phase reactions. NP catalysed Suzuki coupling reaction being a well-studied, yet controversial reaction. The mechanism is typically characterized by a complex semi-heterogeneous process, although controversy remains over the exact mechanism. Several studies have used structure-tailored NPs to serve as catalytic probes for the reaction mechanism. Fing *et al.*^[11] used Au core Pd shell NPs as catalysts and showed the surface Pd shell was partially dissolved to expose the Au core, which was monitored by surface-enhanced Raman spectroscopy (SERS) and by cyclic voltammetry (CV). Shape selective catalysis using cubic, cuboctahedral and octahedral Pd NPs supported on carbon, provided new mechanistic insights into the role of oxygen in the reaction.^[12] The structure dependent activity trend was found to be cubic > cuboctahedra > octahedral NPs. A combination of TEM, inductively coupled plasma (ICP) and x-ray photoelectron spectroscopy (XPS), revealed that the reactivity trend originated from the facet-preferred dissolution of the (100)-enclosed cubic NPs. Molecular oxygen played a key role in facilitating leaching of Pd atoms, which resulted in greater dissolution from (100) surface compared to (111) surfaces and so catalytic activity correlated with NPs shapes possessing (100) surface facets. NPs with high index surface facets were also useful catalytic probes for Suzuki coupling.^[13] Concave Pd nanocubes exhibited a nearly 7-fold increase in the surface normalized turn over frequency compared to the cubic counterparts. Analysis of the catalysts

post reaction showed that the structural integrity of the concave catalysts appeared well preserved at high catalysts loadings, but only at lower catalysts loadings was dissolution of the NP and morphological evolution to small diameter NPs was apparent as shown in Figure. 1 (e)-(h). The high index facets of the concave NPs were more susceptible to dissolution compared to planer (100) surfaces, leading to the observed enhanced catalytic activity. [13]

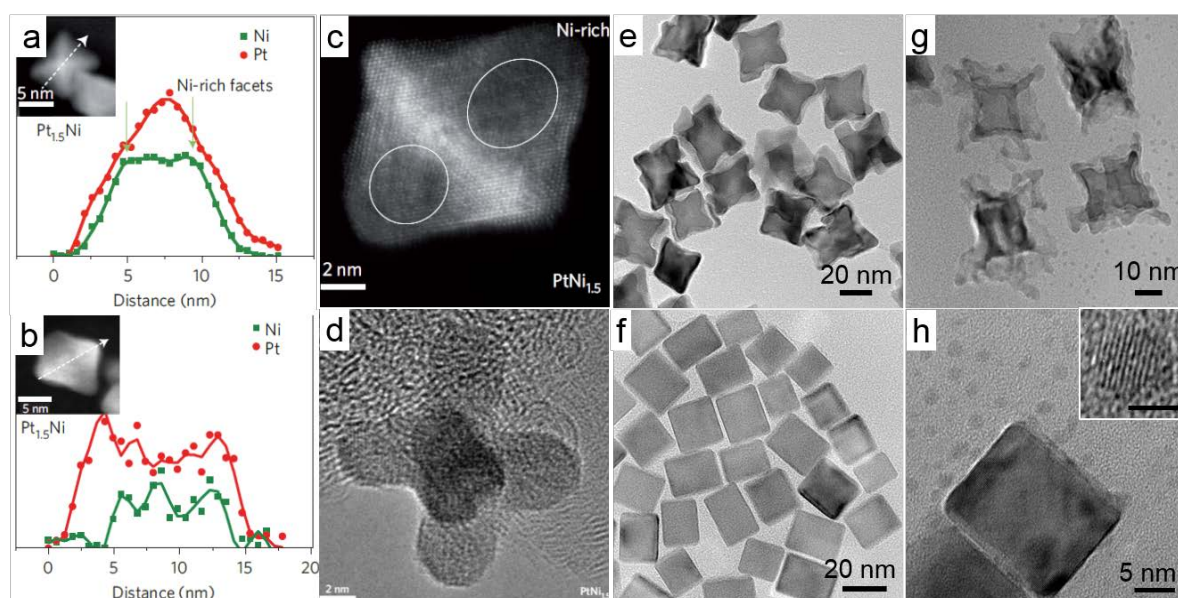


Figure 1. EELS line scans of $\text{Pt}_{1.5}\text{Ni}$ octahedral (a) before and (b) after 25 potential cycles. (c) High resolution STEM image of $\text{PtNi}_{1.5}$ octahedra before and (d) after selective leaching during potential cycling. Reproduced with permission from [6]. Copyright 2013 Nature Publishing Group. (e)-(f) TEM image of concave Pd nanocubes and cubic Pd NPs before reaction. (g)-(h) TEMs images showing preferential dissolution from high index surface facets in the reaction environment. Reproduced from [10] © 2014 American Chemical Society

Designing Plasmonic NPs for Enhanced Catalysis and In-situ Monitoring

Plasmonic metals in catalytic NPs has seen a surge in recent years motivated by two developments in particular. Firstly, incorporating plasmonic metals into catalytic NPs provide highly sensitive, label-free, in-situ monitoring of chemical reactions by SERS.^[14] With the advancements in bimetallic colloidal synthesis, current efforts are focusing on engineering NPs that serve as a bifunctional platform, incorporating both plasmonic and catalytically active phases, as shown in the schematic in Figure 2. Complex structures such as Ag@Pd-Ag nanocubes and Au/Pt/Au core-shell nanoraspberries have been prepared for quantitative operando SERS monitoring.^[15] An innovative approach was shown by Huang *et al.*^[16] who used site-specific epitaxial growth of Pd on the corners of Au nanorods. The resulting structures consisted of AuPd alloy horns characterized by index surface facets, which showed excellent catalytic activity for hydrogenation of 4-nitrothiophenol, while the anisotropic Au rod morphology resulted in a strong SPR localized at the ends to the rod for in-situ reaction monitoring.^[16] A second related motivator for the development of plasmonically active and catalytically active NPs has been the emergence of plasmon mediated photocatalysis which is based on using the localized surface plasmon resonance (LSPR) of nanostructures to drive catalytic chemical transformations through visible light.^[17] Several mechanisms exist to exploit the LSPR for light harvesting in a variety of catalytic applications and the area has been subject to recent review.^[18] Direct plasmonic photocatalysis is where the NP serves as both the light absorber and catalytically active site and most work as centred on Ag and Au as their absorption maxima are in the visible spectrum. As an example, reaction rates for ethylene epoxidation, CO oxidation and NH₃ oxidation were enhanced with Ag nanocubes irradiated by low intensity visible light.^[19] While Au and Ag are active catalysts for some organic transformations, the application of light harvesting catalysts to the key catalytic metals such as Pd and Pt are highly desirable. The LSPR modes of Pd and Pt are typically in the UV spectral range, but can be shifted towards the visible region by altering NP size and shape.^[20] Ultrathin Pd nanosheets

(<10 atomic layers) exhibit a strong and tunable (826–1,068 nm) SPR in the near IR region.^[21] Plasmonic photocatalysis with these metals is more readily achieved using bimetallic NPs such as Au(Ag)M (M=Pt, Pd) alloys, core shell and heterostructures, which have enabled light enhancement for a variety of Pd and Pt catalysed reactions including oxidations, C-N and C-C bond formation.^[22] The easily tuneable size, shape and composition of plasmonic NPs, means that it is possible to design nanostructures that interact with the entire solar spectrum, thereby offering potential to optimize reaction pathways and selectivity at different excitation wavelengths. The origin of the catalytic enhancement for alloy NPs is yet to be fully elucidated but the proposed mechanism is that light irradiation excites electrons to higher energy levels which then transfer from the NP to the lowest unoccupied molecular orbital (LUMO) of the surface absorbed reactant molecule, as shown in Figure 2. Catalytic enhancement is influenced by size, alloy composition, support material, light intensity and wavelength, so rational NP design to optimise the architecture of NPs with plasmonic and catalytically active components will be a key challenge.^[23] Furthermore, while catalysis generally favours small diameters (< 5 nm) for large surface-area to volume ratios, tuning plasmonic resonances favours larger dimensions (~10-100 nm). One possible strategy to satisfy both requirements is the use of hollow or porous nanostructures such as nanorings, cages and boxes for creating additional active surface area for catalysis but also tunability of the SPR. A further synthesis challenge is successfully combining non-plasmonic metals without quenching the SPR of the plasmonic component as maintaining a large plasmonic cross section is critical for efficient light harvesting. The ability to independently tailor size, shape and optical properties of NPs present many opportunities for a multidimensional approach to integrate several features into catalyst design, as illustrated by Jing et al.^[24] Their tuneable plasmonic Ag@Au core shell nanodumbbells for 4-nitrothiophenol reduction exhibited the optimal structure for enhanced catalytic activity through both the SPR and high index surface facets, coupled with highly

sensitive time-resolved SERS monitoring of the reaction. Thus there will be considerable overlap between engineering NPs for probing reactions to gain fundamental insights into the mechanisms operating in plasmon mediated photocatalysis and also developing integrated SERS and catalysis active NPs for operando monitoring. Many approaches to the design of plasmonic mediated photocatalysts combines size, shape and composition controlled colloidal NPs which invariably utilize capping ligands or surface directing species during synthesis. Their impact on plasmonic enhancement and catalytic performance also need to be evaluated. The role of surface species is often understudied but is gaining interest as a component of catalyst design, which will be addressed in the following section.

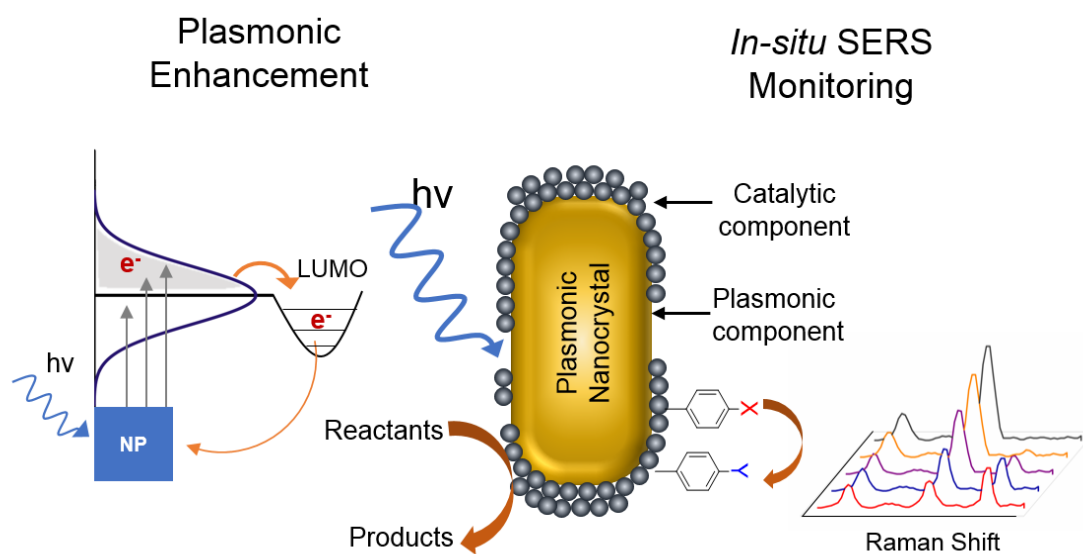
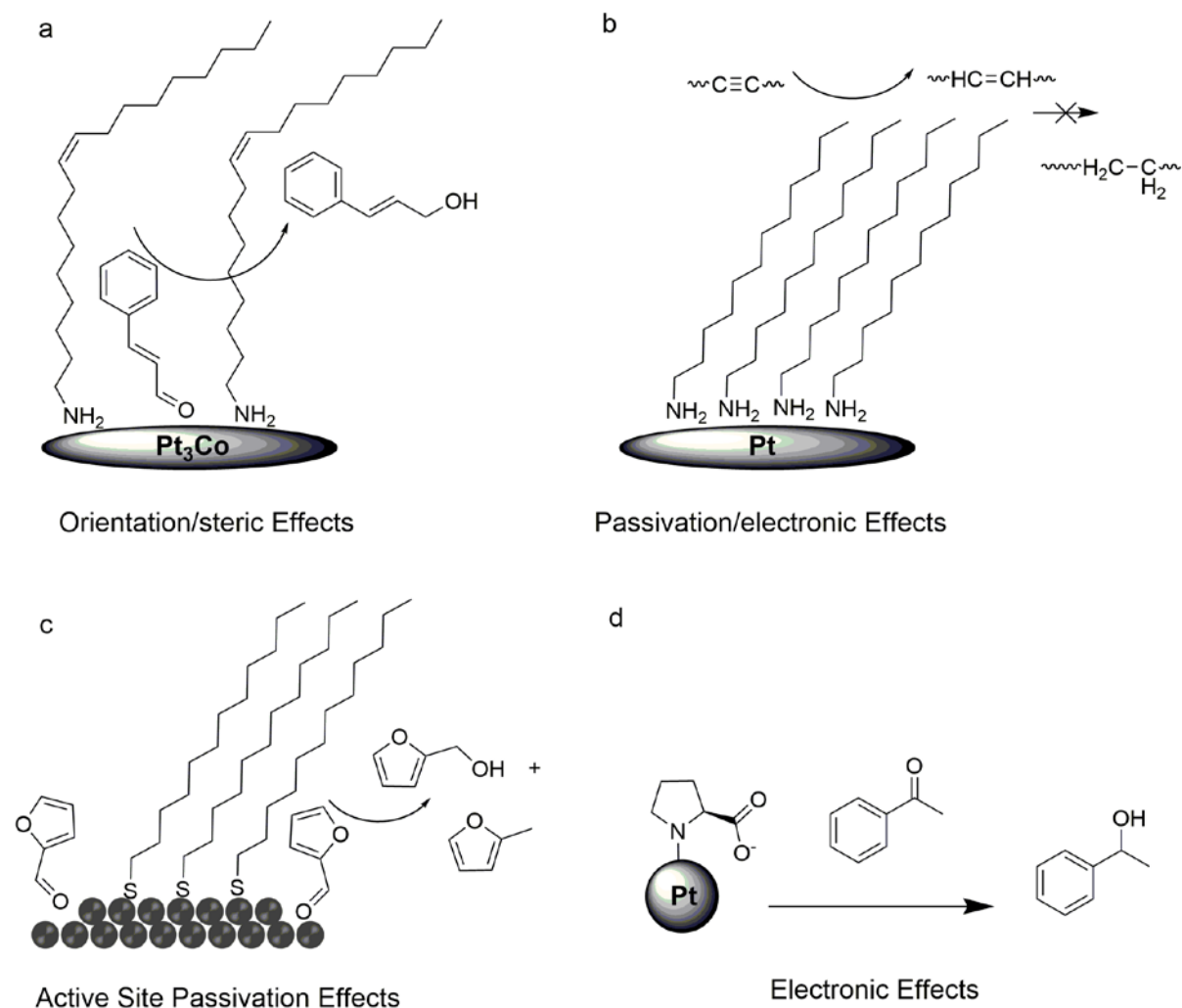


Figure 2. Plasmonic-catalytic nanocrystals for enhancing and probing catalysis. Schematic depicts NP with plasmonic and catalytically active components. The left schematic illustrates the proposed mechanism of visible light enhancement in alloy NPs. The right schematic depicts *in-situ* SERS monitoring of catalytic reactions.

Molecular Engineering of the Nanoparticle Surfaces

Capping ligands are an integral part of controlled NPs synthesis, with a diverse variety of capping ligands including polymers, long chain amines, thiols, phosphines and carboxylic acids commonly used. Despite their importance to colloidal synthesis the impact of capping agents on catalytic performance is not well understood. Initiatively, the adverse effects of capping ligands are obvious in that they block access to precious active sites, thereby lowering catalytic activity. While ligand removal is certainly preferential for some catalytic systems, there is a growing interest in modifying the surface environment through functionalization to promote a specific reaction pathways controlling chemo- or regio-selectivity, remains a key challenge for heterogeneous catalysis^[25]. Several mechanisms exists to exploit surface functionalization effects such as passivation of active sites, steric and orientation effects and electronic effects, as illustrated in Figure 3. Thiol self-assembled monolayers (SAMs) on Pd surfaces can be used to block specific active sites which increased selectivity of 1-epoxybutane from 1-epoxy-3-butene from 11% to 94%,^[26] however a decrease in reaction rate was observed due to the strongly binding thiol groups. Selectivity can also be tuned by engineering noncovalent interactions between reactant molecules and surface capping ligands, as demonstrated in the hydrogenation of cinnamaldehyde (CAL).^[27] Thiol SAMs containing an aromatic tail group can preferentially orientate CAL molecules through interaction with the phenyl ring, into a configuration to promote selective hydrogenation to cinnamyl alcohol over Pd. Similar effects were observed with oleylamine (OAm) capped Pt₃Co NPs due to steric effects favouring the upward adsorption of C=O.^[28] Passivation of Pt and Pt₃Co with primary amines for hydrogenation of alkynes significantly increases the selectivity for the alkene from 0 to 90% with 99.99% conversion. Selectivity can also be achieved through steric effects by limiting surface access of sterically hindered functional groups or reaction intermediates, as demonstrated in the hydrogenation of polyunsaturated fatty acids. Hydrogenation of the

polyunsaturated linoleic acid produces the bulkier monounsaturated reaction intermediate (oleic acid), which has limited access to the catalyst surface preventing further hydrogenation.^[29] Recently, Schrader et al.^[30] synthesized Pt NPs functionalized with L-proline for selective hydrogenation of acetophenone that were not only highly chemoselective but displayed enhanced rates compared to bare Pt NPs. The origin of the enhanced activity and chemoselectivity were attributed to electronic effects of the amine proton in of the proline ligands. Functionalization of metal NPs using chiral ligands have been used for enantioselective catalysis.^[31] These developments are opening new aspects in tailoring colloidal NPs for catalytic processes whereby ligands are not merely spectator species but play a role in mediating the reaction through specific interactions with reacting species, similar to ligand acceleration effects in homogeneous systems. From a NP design perspective, manipulating surface chemistry through functionalization can be achieved by ligand exchange in many colloidal systems. However, the specific chemistry of the capping ligands, their surface coverage and surface-ligand charge transfer effects further add a level of complexity to understanding, let alone designing capping agents in catalysis. The impact of capping species on catalytic function is complex and reaction dependent for example, residual PVP significantly improved the activity of Au catalysed hydrogenation of p-chloronitrobenzene, while decreased the activity for hydrogenation of (CAL).^[32] Successive removal of PVP also shifted the selectivity of CAL to favour to reduction at the alkene. Further progress in the development of surface modified catalysts will require a greater understating of interfacial surface chemistry in colloidal NPs in specific reaction environments.



(b)

Figure 3. Selective hydrogenation of (a) CAL over amine capped Pt_3Co NPs. (b) alkynes over primary amine functionalized Pt NPs and (c) furfural hydrogenation favouring furfuryl alcohol and methylfuran formation. (c) Enhancing catalytic activity and selectivity in acetophenone hydrogenation using L-proline capped Pt NPs.

While the utilization of capping ligands is emerging a promising area in catalyst design, removal of surface stabilizers still remains a key requirement for many catalytic systems. The main methods are thermal annealing, oxidative treatment such as UV-ozone (UVO), chemical washing and ligand exchange. The nature of the pre-treatments can significantly impact on catalytic performance due to changes in size, shape, surface faceting or surface oxidation.^[33]

Thermal treatment can be effective for small molecular weight organic adsorbates but high temperatures (250-650 °C) are required for polymer based stabilizers commonly used in colloidal synthesis, which is problematic as annealing treatments often result in loss of NP size and/or shape uniformity. Noble metal NPs such as Au and Pt can be subjected to harsher treatments such as UVO or H₂SO₄/H₂O₂ for PVP removal, but more reactive metals such as Pd are prone to oxidation and require milder cleaning procedures.^[34] A practical issue noted for UVO removal of PVP on Pd nanocubes was the inability to clean the surface facing away from the UV lamp. The formation of surface PdO was detected, however the cubic morphology was reasonably well maintained and a 4-fold increase in the hydrogenation of acetylene was observed after surface cleaning.^[35] Solvent washing in good/poor solvent such as hexane-methanol system for oleylamine (OAm), is often reported however, the efficiency of this approach is usually not accompanied by surface analysis such as XPS. Refluxing in water was shown to partially remove (~20% based on wt% C) polyvinyl alcohol (PVA) from Au NPs, which was sufficient to enhance catalytic performance in CO and alcohol oxidation.^[36] Chemical washing with reagents is based on weakening the interaction of the capping ligands with the surface so they can be more readily washed away. Washing dodecanethiol Au NPs on oxide and carbon supports with KMnO₄ or K₂MnO₄ solutions partially removes thiol ligands allowing for mild thermal treatment of 300 C.^[37] Removal of amine species on Pd and Pt can be achieved by protonation with acetic acid treatment, which significantly weakens the surface interaction. Ligand exchange using *tert*-butyl amine can displace OAm, PVP and Br- species on Pd and Pt NPs and nanocubes, while maintaining the cubic morphology.^[38] Nitrosonium tetrafluoroborate NOBF₄ removes oleic and OAm and allows subsequent secondary surface functionalization.^[39] A versatile general approach for the removal of capping ligands including from Au NPs is treatment with NaBH₄.^[40] The strong binding affinity of the hydride ions

generated by decomposing NaBH_4 in water effectively displaces capping ligands (PVP, thiols, and anions such as Br^- and I^-) under very mild conditions.

Outlook

Controllable NP synthesis enables reactivity to the enhanced and catalytic mechanisms to be studied in a range of catalytic systems. The partnership between colloidal NP synthesis and microscopy and spectroscopy techniques have led to some of the most progressive developments for rational catalyst design. Advancements such as aberration corrected TEM/STEM, environmental TEM, particularly when coupled with X-ray and energy loss spectroscopic techniques (EELS, EDX etc.), ambient pressure XPS and ambient pressure high temperature STEM are revealing the dynamic nature of NPs by ex-situ and in-situ characterization.^[41] The emergence of electron tomography, allowing 3D analysis is particularly valuable for NPs with complex shapes or hollow morphologies. Multidimensional microscopy and spectroscopy techniques will undoubtedly continue play an important role in bridging the pressure and materials gap in catalysis.

Engineering high performing catalyst NPs is being expanded to new platforms. The ability to harvest visible light in catalytic reactions through the use of plasmonic metals will present challenges in tailoring both the optical and catalytic properties of NPs. However, there is potential for parallel enhancements in activity and selectivity through combining facet dependent reactivity and plasmonic harvesting. Ligand effects in colloidal catalysts have already demonstrated the remarkable ability to tune selectivity, while not sacrificing on activity, which can benefit many important industrial catalytic processes. Probing the binding modes of capping ligands and elucidating their interaction, not only with the NP surface but

species within the reaction environment will be critical for developing positive ligand effects to enhance activity, selectivity and stability of colloidal NPs.

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