

CHIRAL Au NANOCCLUSERS - A STEP TOWARDS HETEROGENEOUS ASYMMETRIC CATALYSIS

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INTRODUCTION AND MOTIVATION

Monolayer protected Au nanoclusters (NCs) usually consist of less than 100 metal atoms stabilized by organic ligands. Unlike nanoparticles, they can be synthesized with atomic precision, leading to monodisperse clusters of specific size, structure and properties^[1]. Therefore, these clusters are perfect materials to be applied in catalysis, in particular to study structure-activity relationships.

For some Au nanoclusters, existence of intrinsic structural chirality has been reported. Besides, the chirality can also be introduced to previously achiral clusters by binding of chiral protecting ligands^[1]. Thus, combining this with the possibility to obtain atomically defined structures, chiral Au nanoclusters are ideal candidates as catalysts in asymmetric catalysis. This research area is currently dominated by homogeneous catalysis featuring mainly chiral coordination complexes. However, moving towards heterogeneous systems would yield several benefits, e.g. concerning catalyst stability, separation or recyclability.

We therefore aim to find a suitable strategy for preparing chiral Au nanocluster surfaces. As shown in Figure 1, there are two different routes possible: (1) deposition of chiral Au nanoclusters on suitable support materials or (2) supporting of precursor clusters and introducing of chirality by ligand exchange on the surface with chiral ligands. In both cases, prior investigations must be carried out: To pursue pathway (1), the chiral clusters

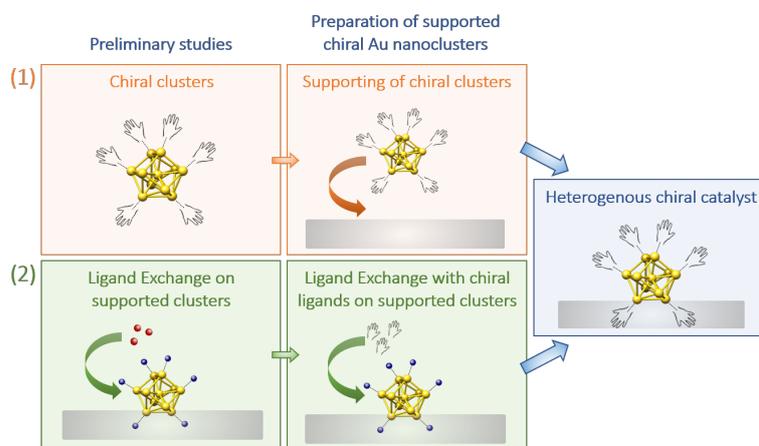


Figure 1: Strategies for obtaining chiral Au nanocluster surfaces must first be synthesized and thoroughly characterized in solution; for (2), the feasibility of ligand exchange on a surface must be determined. Within this work, we therefore want to present our first steps towards well-defined supported chiral Au NCs, investigating the accessibility of both routes.

EXPERIMENTAL

The Au nanoclusters in this study were prepared by modified Brust procedures^[2]. For the preparation of chiral clusters, different cluster sizes and geometries (Au₁₁, Au₂₅ and biicosahedral Au₂₅) and chiral ligands (thiols and phosphines; mono- and bidentate) were used. Thorough analysis was performed (UV-Vis, MS, NMR, IR, elemental analysis, stability tests), with special emphasis on probing the chiral properties by (vibrational) circular dichroism ((V)CD) spectroscopy.

For the ligand exchange-on-surfaces approach (2), the model reaction of Au₁₁ and two different thiols (L-glutathione (GSH) and 2-phenylethanethiol (2-PET)), which is well documented in liquid

phase^[3,4], was chosen. Therefore, the Au₁₁(PPh₃)₇X₃ clusters were supported on Al₂O₃ and SiO₂ and then exposed to solutions of the thiol exchange ligands. The samples before and after reaction were analyzed by several techniques, including PM-IRRAS, STEM, EXAFS, ss-NMR and DRS.

RESULTS AND DISCUSSION

All synthesized Au nanoclusters with chiral ligands showed signals in CD spectroscopy, proving the chirality of the system. However, the signal intensities differed strongly depending on the specific cluster-ligand system. In general, higher degree of chirality transfer from the ligands to the whole cluster structure could be achieved using bidentate chiral ligands. This is mainly confirmed by the fact that these clusters do not only exhibit a CD signal in areas where the chiral ligands are absorbing, but also in the higher-wavelength areas of Au nanocluster HOMO-LUMO transitions. In addition, these clusters are also generally more stable, which makes them ideal candidates for the following catalytic tests and supporting experiments.

As is shown in Figure 2, very interesting data could be obtained for the ligand exchange on surfaces: Contrary to the same reaction in solution, when the cluster size is increasing from Au₁₁ to Au₂₅ regardless of the chemical nature of the exchange thiol^[3,4], the supported Au₁₁ preserved its small core size when reacted with GSH. However, the samples reacted with 2-PET showed alterations of the cluster structure, which are related to etching and decomposition processes. Moreover, the presence of thiolates in all reacted samples could be confirmed by PM-IRRAS and elemental analysis (LA-ICP-MS, ICP-OES), indicating at least partial ligand exchange^[5].

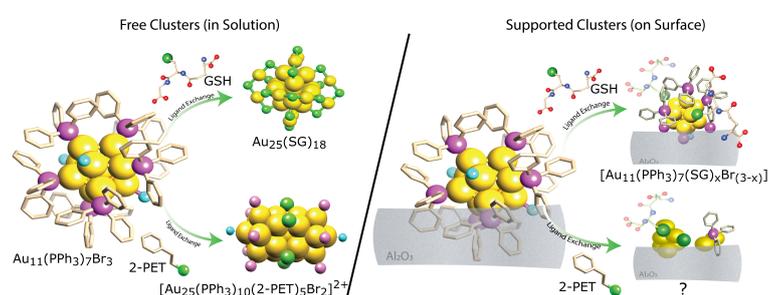


Figure 2: Ligand exchange of Au₁₁ in solution vs. on a surface

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CONCLUSIONS

In our work, we aim to obtain supported chiral Au nanoclusters for application in heterogeneous catalysis. We thereby focused on two different routes for their preparation and approached them by performing necessary preliminary studies. For the supporting approach (1), we managed to synthesize and characterize a set of chiral clusters, whose most promising candidates will be selected for catalytic testing and supporting. In addition, we were able to prove the feasibility of ligand exchange on surfaces (2) by studies on an Au₁₁-thiol model system. However, to apply this as a general synthesis tool, further tests and refinement of the method will be necessary.

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