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Engineering Nanoporous Organic Frameworks to Stabilize Naked Au Clusters: A Charge Modulation Approach

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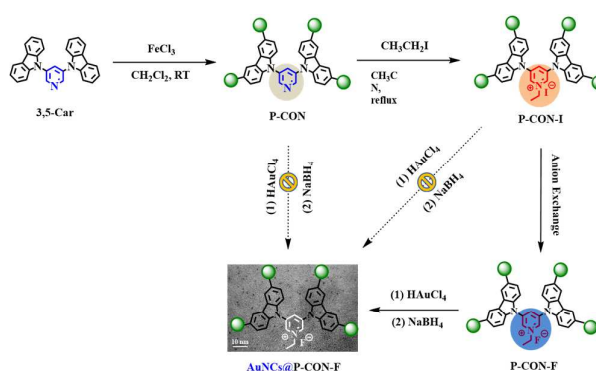
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A simple charge modulation approach has been developed to stabilize naked Au clusters on a nanoporous conjugated organic network. Through engineering pore walls with regulated charges, the controllable growth of Au nanoclusters has been realized. The resulting supported catalyst exhibits excellent performance in the aerobic oxidation of alcohols.

Metal nanoclusters (NCs) are of significant research interest for their unique physical and chemical properties which originate from possessing dimensions between a single metal atom and 2 nm nanoparticles.¹ The intrinsic electronic structure, large fraction of surface atoms, and quantum size effect render small metal NCs attractive candidates for catalysis. Specifically, a great deal of research has focused on the rational design and construction of Au NCs, enabling catalysis of a wide range of important chemical reactions,² such as hydrogenation of olefins, CO oxidation, water-gas shift reaction and selective alcohol oxidation. Unfortunately, the high surface energies of Au NCs promote severe aggregation and particle growth, resulting in the drastic loss of their catalytic activity;³ the controllable synthesis of naked Au NCs remains a great challenge. One popular solution to enhance aggregation resistance is to confine naked Au NCs inside a nanoporous support,⁴ where the inherently narrow pore dimensions provide an external physical barrier to mitigate the aggregation and growth rate of Au species.^{4a} However, conventional nanoporous supports, such as inorganic oxides and carbon materials, are usually lack of capping agents, and are therefore unable to stabilize Au NCs against aggregation.^{2c,5} In this regard, the search and development of new nanoporous

great interest.

In this work, we report a charge modulation approach in engineering nanoporous conjugated organic networks to stabilize naked Au clusters, and their employment as a new family of highly-active heterogeneous supported Au NC nanocatalysts. Conjugated organic networks constitute a very promising class of advanced porous materials and have attracted great attention in the field of catalysis due to the accessibility of diverse nanopore regimes through the rational design of active sites at the molecular scale.⁶ Although numerous nanoporous frameworks have been well developed through conventional organic synthetic protocols, the use of them as a novel stabilizer to immobilize naked Au clusters has never been explored. The key to our success lies in the installation of abundant regulated charged species within the framework, inducing strong surface interactions against Au NC aggregation. This innovative strategy not only provides a facile means to control the growth of Au species inside a nanoporous framework, but simultaneously opens up new possibilities for the development of new nanoclusters catalysts possessing long-term stability and activity.



Scheme 1. A charge modulation approach of preparing conjugated organic networks to stabilize Au NCs.

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supports capable of stabilizing Au NCs is highly important and of

As shown in **Scheme 1**, our initial attempts to install small Au NCs involved a pyridine-functionalized conjugated organic network (**P-CON**). **P-CON** was prepared through a facile FeCl_3 -catalyzed oxidative coupling polymerization approach, with synthetic details available in the supporting information.⁷ The structure of **P-CON** was identified at the molecular level by solid state ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR, with the peak around 145 ppm arising from the aromatic carbons can indicate the presence of the pyridine rings. Two peaks at ~ 125 and 110 ppm are ascribed to the aromatic carbons in the carbazolic ring (Figure S1).^{7a} **P-CON** possessed a high Brunauer-Emmett-Teller (BET) surface area of $1538 \text{ m}^2 \text{ g}^{-1}$, as determined by nitrogen adsorption-desorption isotherms (Figure S2a and Table S1), affording sufficient space for the immobilization of Au species. Au nanoparticles were physically impregnated through a facile process where HAuCl_4 was reduced by NaBH_4 . A high loading of 2.0 wt% was successfully loaded on the surface of the material (**Au@P-CON**), as determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Unfortunately, intense peaks associated with large Au nanoparticles were apparent in the X-ray diffraction (XRD) pattern (Figure 1), indicating formation of large Au domains (12.7 nm, Table S1) and a failure of **P-CON** to stabilize the NCs. We reasoned that the limited number of functions on the **P-CON** surface results in facile aggregation and ripening. Transmission electron microscopy (TEM) images further confirmed this result (Figure S3).

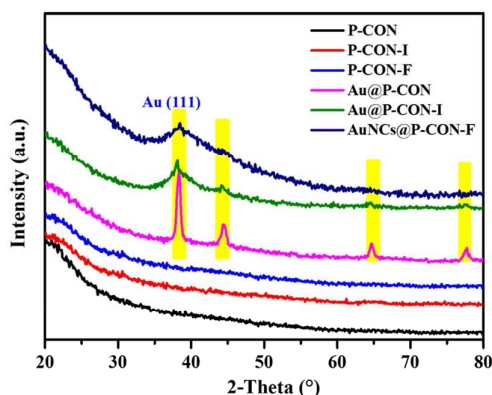


Figure 1. XRD patterns of the as-prepared conjugated organic networks and Au-loaded hybrid materials.

We subsequently performed a charge modulation approach to address this obstacle through engineering pore walls of **P-CON**. A recent work by Yuan et al., demonstrated that polymeric ionic liquid (PIL) can serve as a promising platform capable of stabilizing a variety of metal clusters.¹¹ Their success relies on the an unusual synergy between the heterocyclic cations in PIL and an *in situ* generated polycarbene structure. Inspired by this work, we sought to create charged species within the framework of **P-CON**, inducing an electrostatic charge to promote the stabilization of Au species. We reasoned that the post-synthesized anions will be bound to the Au surfaces and form a “protective shell” layer immediately adjacent to the nanocluster, thus providing the Columbic repulsion component of Dergaugin-Landau-Verwey-Overbeek (DLVO)-type

stabilization.⁸ Additionally, the existence of rich pyridine rings gives rise to a facile nucleophilic reaction with iodoethane for the incorporation of desired charges (**Scheme 1**). Halides have been considered as one of the most promising small monoanions to generate DLVO-type stabilization.^{8a} As expected, the ^1H - ^{13}C CP-MAS NMR confirms a successful postsynthetic modifications inside the framework (**P-CON-I**). Two peaks at ca. 14 and 59 ppm, attributed to the existence of alkyl groups, were observed (Figure S1). Additionally, **P-CON-I** shows a decrease of BET surface area of $1115 \text{ m}^2 \text{ g}^{-1}$ as a result of successful pore wall engineering (Figure S2b). The x-ray photoelectron spectroscopy (XPS) study also indicates a high containing of iodide species (0.92 at%). As shown in Figure S4b, the binding energy at ca. 618 eV was assigned to $\text{I}(3d_{5/2})$ and at ca. 630 eV to $\text{I}(3d_{3/2})$, respectively.⁹

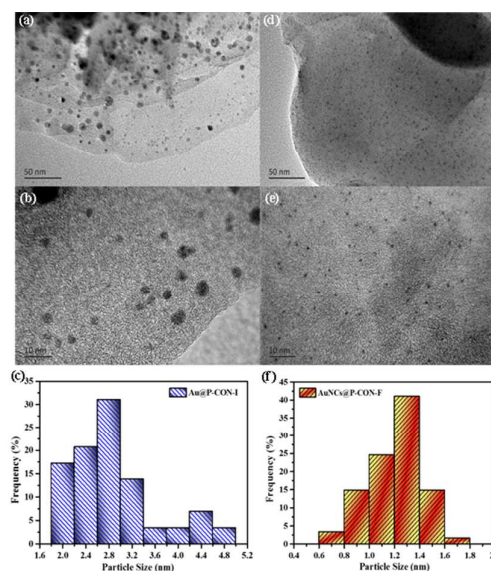


Figure 2. TEM images and the corresponding size distribution histogram of the as-prepared Au materials. Scale bars: 50 nm (a and d)/10 nm (b and e).

Motivated by these promising results, we initiated the same Au-growth process to attempt the preparation of Au NCs on **P-CON-I**. To our delight, a broad reflection at 38° in the XRD pattern was observed (**Figure 1**), attributed to (111) reflection of the cubic (fcc) gold lattice and indicating the formation of small Au nanoparticles (2.8 nm, Table S1).¹⁰ TEM images also display small Au nanoparticles with mean size of ca. 2.8 nm, supported on the surface of the polymer (**Figure 2a-c**). The BET surface area of this new sample (**Au@P-CON-I**) was measured to be $938 \text{ m}^2 \text{ g}^{-1}$ (Figure S1). Nevertheless, Au NCs were not successfully constructed, similar to the initial attempts with **P-CON**. Despite this, this progress in achieving much smaller Au nanoparticles ranging from 12.7 nm in **Au@P-CON** to 2.8 nm in **Au@P-CON-I** indicates a profound effect of introducing charge to the frameworks and the effect on the stabilization and growth of Au NPs species. We hypothesized that

modulating the charged species could enable controlled synthesis of monodisperse supported Au NCs.

To confirm this, we prepared another **P-CON-F** analog through a simple ion-exchange procedure to substitute fluoride as the counter anion in place of iodide (**Scheme 1**). We reasoned that anionic species could also influence the stabilization of Au NCs complementing the cationic effect proposed by Yuan et al.¹¹ According to XPS analysis (Figure S4), a complete exchange was accomplished and no iodide residue was detected. Accordingly, a high F content of 0.89 at% was measured, with the binding energy of F1s at ca. 690 eV corresponding to fluoride (Figure S4c). Understandably, **P-CON-F** exhibits a higher BET surface area ($S_{\text{BET}} = 1210 \text{ m}^2 \text{ g}^{-1}$) compared to **P-CON-I**, consistent with the exchange of a heavy element for a lighter one and demonstrating the stability of the organic framework. We then followed the same process to grow Au species on **P-CON-F**. As expected, small Au NCs with mean size of ca. 1.3 nm were homogeneously dispersed on the surface, evidenced by the TEM image (**Figure 2d-f**). This promising result matches well with the broadening observed in the corresponding XRD pattern (**AuNCs@P-CON-F**). The Au $4f_{7/2}$ peak at ca. 84.5 eV in the XPS spectra shows that Au NCs are in the zero oxidation state (Figure S5). The BET surface area was measured to be $1060 \text{ m}^2 \text{ g}^{-1}$, thus suggesting good potential implementations in catalysis.¹¹

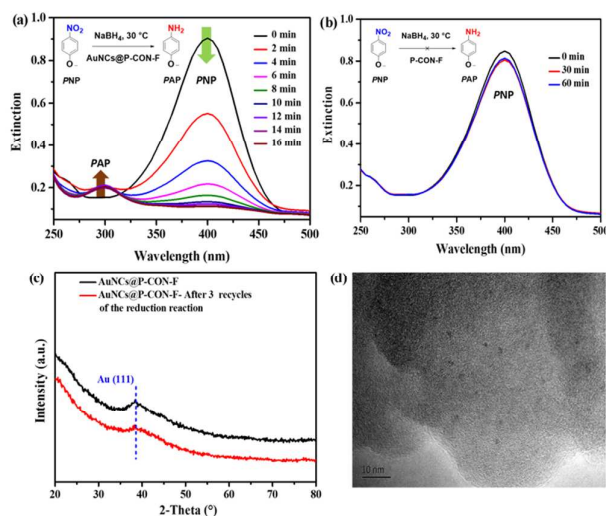


Figure 3. Time-dependent UV-vis spectra of the reduction of 4-nitrophenol catalyzed by **AuNCs@P-CON-F** (a) and **P-CON-F** (b). (c) The XRD patterns before and after reduction reaction. (d) TEM images of supported Au species after reduction reaction.

This simple yet efficient charge modulation approach opens up new possibilities for the controlled synthesis of Au species on the surface of nanoporous networks. We anticipated that it will advance the development of a variety of naked metal clusters through implementation of diverse framework materials, such as

metal-organic frameworks (MOFs). In addition, **AuNCs@P-CON-F** contains 2.0 wt % Au NCs, constituting a comparatively large quantity metal and enabling higher loading for catalytic processes. Nitrophenol reduction, as a model reaction, was examined. As shown in **Figure 3a** and **b**, the existence of small Au NCs on **AuNCs@P-CON-F** successfully afforded the formation of aminophenol, whereas no catalytic activity was observed on **P-CON-F**. As confirmed by the XRD and TEM analysis, the sizes of Au species maintain very well (**Figure 3c** and **d**). This stability can be further supported by **AuNCs@P-CON-F**-catalyzed CO oxidation. Although the material exhibits a poor CO oxidation performance, ca. 15% conversion at a high temperature of 180 °C, no significant aggregation of Au was observed under this condition (Figure S6).

Furthermore, we investigated the aerobic oxidation of cyclohexanol to cyclohexone, a key step for Nylon-6 and Nylon-66 production, to assess the catalytic activities of our supported Au NCs. **AuNCs@P-CON-F** (10 mg) was combined with cyclohexanol (1 mmol) and toluene (3 ml) in a reaction flask. With the heat treatment at 60 °C for 24 h under air, the conversion on **AuNCs@P-CON-F** reached as high as 98.4 % (**Table 1**, Entry 1) with a high selectivity (> 99%). Control experiments performed with materials devoid of any Au species displayed no activity (Entry 2-5), demonstrating the critical role of the Au- sites in catalysis. To gain a better understanding regarding the influence of the Au size on oxidation performance, we also performed the controlled experiments using **Au@P-CON** and **Au@P-CON-I**. Clearly, the **AuNCs@P-CON-F** afforded the best yield and highest turnover number (TON, Entry 6-9), which we attribute to the smallest Au size generating a greater number of catalytic sites with optimal accessibility by the substrates (Figure S7).

Table 1. Performances of different catalysts in the cyclohexanol oxidation reaction.^a

Entry	Catalyst	t (h)	Conversion (%)	Selectivity (%)	TOF (h ⁻¹)	TON ^c
1	AuNCs@P-CON-F	24	98.4	>99	129	984
2	Blank	40	<0.1	-	-	-
3	P-CON	40	<0.1	-	-	-
4	P-CON-I	40	<0.1	-	-	-
5	P-CON-F	40	<0.1	-	-	-
6	Au@P-CON	40	7.8	>99	-	78
7	Au@P-CON-I	24	95.2	>99	92	952
8	Au@P-CON-I	6	34.6	>99	92	346
9	AuNCs@P-CON-F	6	44.6	>99	129	446
10	AuNCs@P-CON-F	1	12.9	>99	129	129

^a Reaction conditions: cyclohexanol (1 mmol), anisole (internal standard, 1 mmol), catalyst (10 mg), toluene (3 ml), 60 °C under dry air and 1 atm; ^b TOF = [reacted mol alcohol]/[(total mol gold) * (reaction time)]. The TOFs were measured after the first 1 h of reaction; ^c TON = [reacted mol alcohol]/[total mol gold].

Inspired by these promising results, we proceeded to investigate the effects of reaction time on cyclohexanol oxidation. After 1 h, the conversion reached 12.9 %, whereas the selectivity was as high as 99% (Entry 10, **Table 1**). The conversion yield increased

continuously during the following 6 h and reached to be 44.6 % (Entry 9). These results are summarized in Table 1. As recyclability has been considered to be one of most advantageous features of heterogeneous catalysts over to homogeneous catalysts, the recyclability of **AuNCs@P-CON-F** was also studied. When simply collected by centrifugation, dried, and added to a new reaction, the recovered catalyst still displayed excellent catalytic performance, with a negligible drop in conversion activity over five recycles while maintaining the high selectivity as well (Figure S8). The sizes of Au NCs maintain very well based on the XRD patterns and TEM image (Figure S9). Au NCs supported in charged nanoporous networks thus show outstanding performance in the aerobic oxidation of alcohol.

Seeking to probe the generality of our **AuNCs@P-CON-F** heterogeneous catalyst, we investigated the oxidation of a range of other alcohol substrates. As displayed in Table S2, these reactions afford high conversion to the desired ketone products, clearly demonstrating the accessibility of bulky substrates within the pore structure of the **AuNCs@P-CON-F** system and the diversity of this novel heterogeneous catalyst.

In conclusion, a simple yet efficient charge modulation approach is reported as a new strategy for the stabilization of naked small Au clusters in conjugated organic networks. The successful installation of regulated charges inside the nanoporous architecture has effectively tuned the surface properties of the support framework suppressing the aggregation of the Au NC species. The resulting heterogeneous Au nanoclusters exhibit excellent performance in the aerobic oxidation of alcohols, suggesting great promise for catalytic applications. This innovative strategy not only provides a facile means to control the growth of Au species inside nanoporous frameworks, but simultaneously enables new avenues for the development of novel metal nanoclusters catalysts displaying long-term stability and high-activity.

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