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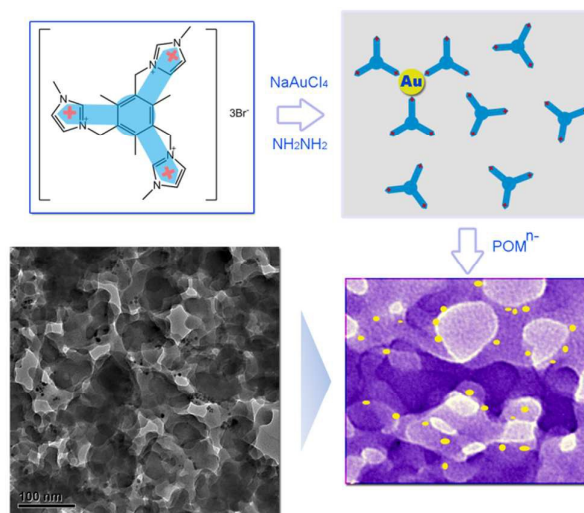
# Sustainable Catalytic Oxidation of Alcohols over the Interface between Air and Water

Zhijun Huang, Fengbo Li\*, Bingfeng Chen and Guoqing Yuan\*

**Alcohols are oxidized to aldehydes or ketones in water by directly using air as the oxidant. The catalytic conversions are based on a hybrid nanocatalyst with monodispersed Au nanoparticles embedded in polyoxometalate self-assembly matrix. The oxidation processes exhibit excellent activity and selectivity.**

Sustainability of chemical processes is a rapidly emerging issue as promoted by the European Technology Platform on Sustainable Chemistry (ETP SusChem) <sup>1</sup> and the twelve principles of Green Chemistry <sup>2</sup>. The development of new catalysts is the core technology to improve process sustainability. Well-designed catalysts might lead to improvements in yield/productivity and abate process costs through longer catalyst life, milder or sustainable reaction conditions, and reduction of environmental costs <sup>3</sup>. Selective oxidations of primary and secondary alcohols to the corresponding carbonyl compounds are important conversions in modern organic synthesis. However, widely used methods are based on hazardous stoichiometric reagents, such as chromium-based reagents, Activated dimethyl sulfoxide, hypervalent Iodine Compounds, permanganate, and highly toxic ruthenium tetroxide (RuO<sub>4</sub>) <sup>4</sup>. All these processes inevitably lead to stoichiometric wastes. Molecular oxygen or air is the environmentally benign oxidant with the only byproduct of water. Highly selective oxidation reactions of molecular oxygen occur every moment in every aerobic organism in nature. However, selective activation of molecular oxygen under mild condition is still a great challenge for the synthesis of complicated molecules. Activation of oxygen is thermodynamically favorable, but kinetically inert <sup>5</sup>. Under harsh conditions, molecular oxygen can be easily activated to burn off organic compounds and such quick and complete oxidation shows no applicability for synthesis of target organic molecules. Well-designed catalysts are the central issues of the selective oxidation with molecular oxygen. Significant progresses have been witnessed in catalytic oxidation based on metal complex catalysis <sup>6</sup>, organocatalysis <sup>7</sup>, biocatalysis <sup>8</sup>, and heterogeneous catalysis <sup>9</sup>. Homogeneous catalysts, such as metal complex catalysts, organocatalysts, biocatalysts, provide powerful solutions for selective green oxidation, but the use of organic solvent and the problems related to handling, recovery, and reuse of the catalyst limit application of these processes. Green oxidants (molecular oxygen and H<sub>2</sub>O<sub>2</sub>) and efficient heterogeneous catalysts could provide reliable solutions for improving sustainability of selective oxidation of alcohols.

Many polyoxometalates are effective catalysts for green oxidations using H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub> as oxidants <sup>10</sup>. Phosphovanadomolybdate Keggin-type polyoxometalates (H<sub>3+*x*</sub>PV<sub>*x*</sub>Mo<sub>12-*x*</sub>O<sub>40</sub> (*x* = 1-6)) have the redox potential of about 0.7 V vs. SHE, which is lower than that of O<sub>2</sub>. These compounds can activate molecular oxygen for homogeneous oxidation under mild conditions <sup>11</sup>. In the practical application, there is a quest for the development of recoverable and recyclable heterogeneous oxidation catalysts. There are two strategies for heterogenizing: 1) solidification of polyoxometalates through formation of insoluble solid ionic materials with selected counteranions <sup>12</sup>; 2) immobilization of polyoxometalates through adsorption, covalent linkage and ion-exchange <sup>13</sup>. Polyoxometalates can be used as building blocks for many novel functional materials. This is a new horizon for the development of heterogeneous polyoxometalate-based oxidation catalysts <sup>14</sup>. Self-assembly is an efficient and low-cost method for exploring novel nanocatalysts based on POM building units. Supported gold nanoparticles have attracted tremendous interest recently and many findings reveal their great potential to be sustainable oxidation catalysts with dioxygen <sup>15</sup>. In this work, well-dispersed Au nanoparticles are *in situ* introduced into polyoxometalate-based supramolecular arrays and a hybrid nanocatalyst is obtained in this way.

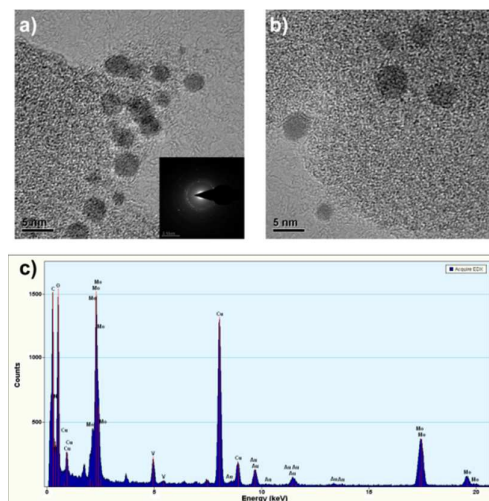


**Fig. 1** The preparation procedure and Transmission Electron Microscope (TEM) image of the hybrid nanocatalyst.

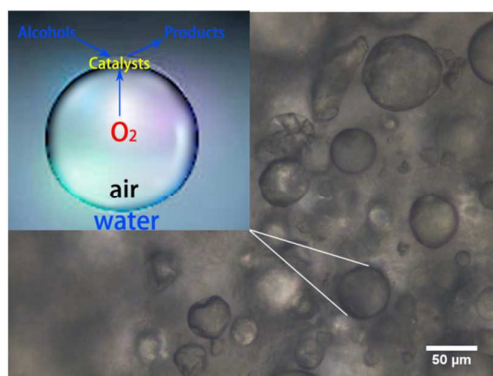
The hybrid nanocatalyst was prepared and the catalytic oxidation of alcohols proceeded through air microbubbles suspended in the aqueous medium, which were generated with well-selected stirring model and speed. The catalysts were dispersed over the interface between the air microbubble and the aqueous phase. Molecular oxygen in the air microbubble was used as the oxidant and alcohol molecules in the aqueous phase diffused onto the phase interface. The reactions took place with the aid of the catalysts over the interface between air and water. After the given reaction time, the reaction mixture was treated in an ultrasonicator and then centrifugated to recover and recycle the catalysts into the next reaction batch. Most high boiling point alcohols are poorly soluble in water. Oxidation of these substrates is performed in organic solvents such as toluene, THF, CH<sub>3</sub>CN (Table S1). The organic-inorganic hybrid catalyst in our work is amphiphilic and facilitates the oxidation in water. For alcohol oxidation over supported Au catalyst, addition of several equiv. bases is required to get acceptable yield (Table S2). For the conversion over our hybrid catalyst system, base additives are avoided and the catalyst shows high activity and selectivity. These are two improvements in “green aspects” of aerobic oxidation of alcohols over heterogeneous Au catalysts.

Fig. 1 shows the preparation procedure of the hybrid nanocatalyst. A rigid tripodal anion receptor based on 1, 3, 5-trisubstituted benzene spacer (**1**; 1, 3, 5-tris [(3-methylimidazolio) methyl]-2, 4, 6-trimethylbenzene tribromide)<sup>16</sup> was used as the organic structure directing agent. **1** was precipitated from the aqueous solution by introducing [AuCl<sub>4</sub>]<sup>-</sup> anion. After being reduced, Au nanoparticles stabilized by **1** were dispersed in the aqueous solution. Polyoxometalate anion [PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub>]<sup>5-</sup> was then added and organic-inorganic hybrid nanocomposites were gradually precipitated. The floccule solids were collected by centrifugation. Transmission Electron Microscope (TEM) image in Fig. 1 shows the morphology of the as-synthesized nanocomposites. Porous nanostructures are formed by electrostatic-interaction-directed self-assembly between the rigid tripodal ligands and polyoxometalate anions. Au nanoparticles are embedded in the nanostructure and kept in a monodispersed state.

Au nanoparticles were further investigated through HRTEM (Fig.2 a, b). The average particle size was 5.0 nm. Crystal lattice of Au nanoparticles can be clearly observed. Au nanoparticles were stabilized by organic-inorganic hybrid nanocomposite structure of 1, 3, 5-trisubstituted benzene spacer and polyoxometalate anion [PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub>]<sup>5-</sup>. EDS of the selected region was acquired to analyze chemical composition of the as-synthesized nanocomposite. The survey spectrum clearly describes chemical elements of the tripodal ligand, polyoxometalate anion ([PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub>]<sup>5-</sup>), and Au nanoparticles.



**Fig. 2** a) and b) High-resolution TEM images of the embedded Au nanoparticles. c) EDS spectrum of the selected region of the catalyst sample.



**Fig. 3** Optical Microscopy image of the microbubble system. The insert is schematic illustration of its mass transfer mechanism.

The selective oxidation was performed in an aqueous solution containing the suspended nanocatalyst. A given amount of alcohol was added into the mixture, which was directly open to air to supply oxygen. The reaction mixture was stirred gently to form a microbubble system. Air microbubbles were suspended in the aqueous solution and the hybrid catalyst was dispersed over the interface of two phases (Figure 3). The catalytic oxidation proceeded over the interface through a multiphase reaction model (Figure 3). Alcohol substrates and products were contained in the aqueous phase. The oxidant (molecular oxygen) was from the air microbubbles. The organic-inorganic hybrid catalyst was amphiphilic and dispersed over the interface between air and water. As the oxidation proceeded, molecular oxygen was consumed and the pressure drop collapsed the microbubble. The hybrid catalyst was delivered to form new air bubbles and guaranteed continuous supply of oxygen in the reaction mixture. After the reaction, microbubbles were destroyed by ultrasonic treatment. The catalyst was separated by centrifugation and recovered by water washing and directly recycled to the next reaction batch.

**Table 1** Experimental results of alcohols' oxidation.

Substrate	Aldehyde or ketone yield (%)	
	(45°C)	(75°C)
n-C <sub>3</sub> H <sub>11</sub> CH <sub>2</sub> OH	81	96
n-C <sub>7</sub> H <sub>15</sub> CH <sub>2</sub> OH	75	93
n-C <sub>6</sub> H <sub>13</sub> CH(CH <sub>3</sub> )OH	71	91
PhCH <sub>2</sub> OH	90	>99
(4-Cl) PhCH <sub>2</sub> OH	80	97
(4-MeO) PhCH <sub>2</sub> OH	83	98
PhCH(CH <sub>3</sub> )OH	89	>99
Cyclooctanol	72	91
(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> OH	91	>99
PhCH=CHCH <sub>2</sub> OH	92	>99

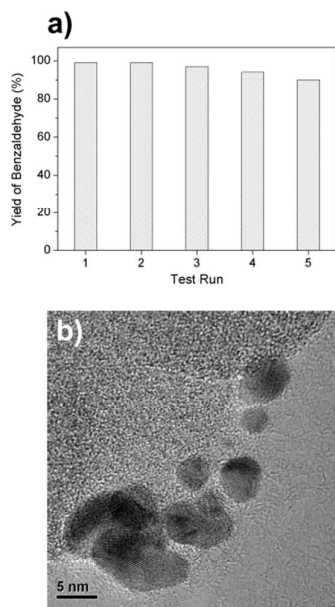
Reaction conditions: 10ml deionized water, 1.0 mmol substrate, 10 mg catalyst (approximately 1.0 mol% of the substrate), stirred in open air, reaction time: 3.0 h.

Ten typical alcohols with high boiling point were tested over the catalyst. Table 1 lists the experimental results obtained under the given reaction conditions. The catalytic oxidation shows high activity and selectivity in converting the substrates to aldehydes or ketones. In all conversions, there are no over-oxidized products (carboxylic acids) in the final reaction mixtures. The oxidation degree of the reaction is well controlled by the hybrid nanocatalyst. The catalytic activity is markedly influenced by reaction temperature. The yield of target products is sharply improved when reaction temperature increases from 45 to 75. For active substrates with conjugate groups, the yields to aldehydes or ketones are more than 99%. The yield values of long-chain alkyl alcohols are all above 90%. The results in Table 1 reveal that oxygen can be efficiently activated and the oxidation degree is precisely controlled through the three-phase microbubble system.

**Table 2** Screening experiments of the roles of the catalyst components.

Catalyst	Yield of oxidation product (%)
Blank	0
Tripodal ligand <b>1</b>	0
Au NPs/PVP	54
Au NPs/ <b>1</b>	57
POM	52
POM/ <b>1</b>	68
POM/ <b>1</b> + Au NPs/PVP	76
Au NPs/ <b>1</b> /POM	>99

Reaction conditions: 10ml deionized water, 1.0 mmol benzyl alcohol, 10 mg catalyst (approximately 1.0 mol% of the substrate), stirred in open air, reaction temperature: 75°C, reaction time: 3.0 h.



**Fig. 4** a) A five-run recycling test of benzyl alcohol oxidation. b) TEM image of the spent catalyst after the fifth recycling run.

The stability and recyclability of the hybrid catalysts were investigated by a five-run recycling test of benzyl alcohol oxidation (Fig. 4a). There is approximately 9% loss of catalytic activity after the fifth recycling test for the reported catalyst. There are two inevitable reasons for this changing trend. Firstly, the manual operation cannot guarantee 100% recycle of the catalyst. There is inevitable loss of catalyst amount during transferring operation between containers, cleaning, separation and purification. Secondly, the performance of catalysts is time and process dependent. The adsorbate and catalyst interaction during catalytic reactions may induce the reconstruction and localized compositional variation, which have subtle impact on the performance of heterogeneous catalysts. The concentrations of leached Au and Mo species in the final aqueous solution were detected by inductively coupled plasma atomic emission spectroscopy (ICP-OES) and the values of each test run are negligible. This is further confirmed by hot filtration test (Fig. S1). The morphology of the spent catalyst after the fifth run was characterized by TEM (Fig. 4b). Agglomeration of Au nanoparticles is clearly revealed and directly leads to loss of catalytic active surfaces. This is the inherent mechanism of catalytic deactivation during the batch by batch recycling test.

The catalytic roles of Au nanoparticles, polyoxometalates, and tripodal ligand (**1**) were further investigated through control experiments of benzyl alcohol oxidation over eight model catalysts: blank, tripodal ligand (**1**), poly(vinylpyrrolidone) stabilized Au nanoparticles (Au/ PVP), tripodal ligand (**1**) stabilized Au nanoparticles (Au/ **1**), polyoxometalate (POM), polyoxometalate/ tripodal ligand composite (POM/ **1**), POM/ **1** +Au/ PVP, and the as-synthesized catalyst (Au/ **1**/ POM) (Table 2). Stabilized Au nanoparticles can catalyze the oxidation of benzyl alcohol with air. The yield of oxidation products is approximately 50% and there are over-oxidized products in product mixture. Polyoxometalate anions  $[PV_2Mo_{10}O_{40}]^{5-}$  and polyoxometalate/ tripodal ligand composite (POM/ **1**) are also active catalysts, but their performances are relatively mediocre. Direct physical mixture of Au nanoparticles and POM/ **1** shows some improvement in the catalytic activity. However, only Au nanoparticles embedded in the matrix of polyoxometalate/ tripodal ligand composite exhibit the synergetic catalytic effect. The as-synthesized catalyst (Au/ **1**/ POM) show the catalytic conversion of approximately 100%.



## Conclusions

In summary, a sustainable process was developed for selective oxidation of alcohols with molecular oxygen. A multifunctional catalyst was prepared by electrostatic interaction directed self-assembly between the rigid tripodal ligand and polyoxometalate anion  $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ . Au nanoparticles are embedded in the nanostructure and kept in a monodispersed state. Molecular oxygen is used as the oxidant and the only side product is water. The reaction medium is water. The catalytic reaction proceeds through microbubbles suspended in the aqueous solution, which provide a microreactor for the reaction. The organic-inorganic hybrid catalyst is amphiphilic and dispersed over the interface of microbubbles. The catalytic process has high activity and the selectivity to aldehydes or ketones is more than 99% for some active substrates. The catalyst exhibits good recoverability and recyclability during a five-run recycling test.

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## Notes and references

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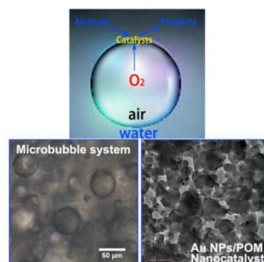
† Electronic Supplementary Information (ESI) available: Experimental details about catalytic materials' preparation, characterization, and activity testing. Fig. S1, Table S1, and Table S2.

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## Graphic Abstract



Alcohols are oxidized to aldehydes or ketones in water over a hybrid nanocatalyst dispersed over the interface between air and water.