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Redox-Active Catalyst Based on Poly(Anilinesulfonic Acid)-Supported Gold Nanoparticles for Aerobic Alcohol Oxidation in Water

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Abstract: The hybrid consisting of gold nanoparticles and poly(2-methoxyaniline-5-sulfonic acid), which works as a redox mediator for transferring protons and electrons, catalyzed the oxidation reaction of various alcohols in water under molecular oxygen.

Keywords: aerobic oxidation; gold; green chemistry; redox chemistry

Sustainable molecular transformation reactions are found in biological systems. For example, catalytic oxidation reactions are allowed with the help of redox mediators *in vivo* using molecular oxygen as a terminal oxidant.[1] On the other hand, oxidation of alcohols is one of the most important transformations in organic chemistry and biochemistry. The discovery of the catalytic properties of gold nanoparticles (NPs) for aerobic alcohol oxidation[2] has activated this research field for a decade. Generally, metal NPs need a stabilizer (polymers are often used) to prevent metal NPs from aggregation in the catalytic reaction.[3] We envisioned the idea to give the function of redox actitivity to the stabilizer to mediate the redox reaction, such as aerobic alcohol oxidation. For this purpose, we chose polyanilines as a redox-active π-conjugated polymer. We have constructed artificial multi-redox systems based on d,π-conjugation of polyanilines or polypyrroles with various transition metals or metal nanoparticles (NPs), and developed some catalytic oxidation reactions (Figure 1, a).[4] In the present sudy, we decided to use the water-soluble polyaniline, poly(2-methoxyaniline-5-sulfonic acid) (PMAS)[5] from the ecological point of view. PMAS has three representative oxidation states as follows, completely oxidized form PMAS (ox), half oxidized form PMAS (half ox), and completely reduced form PMAS (red), and usually exists in the state of PMAS (half ox) (Figure 1, b). Au NPs were employed for the catalytic aerobic alcohol oxidation. To the best of our knowledge, there are no reports of such a catalyst design for the alcohol oxidation reaction using a

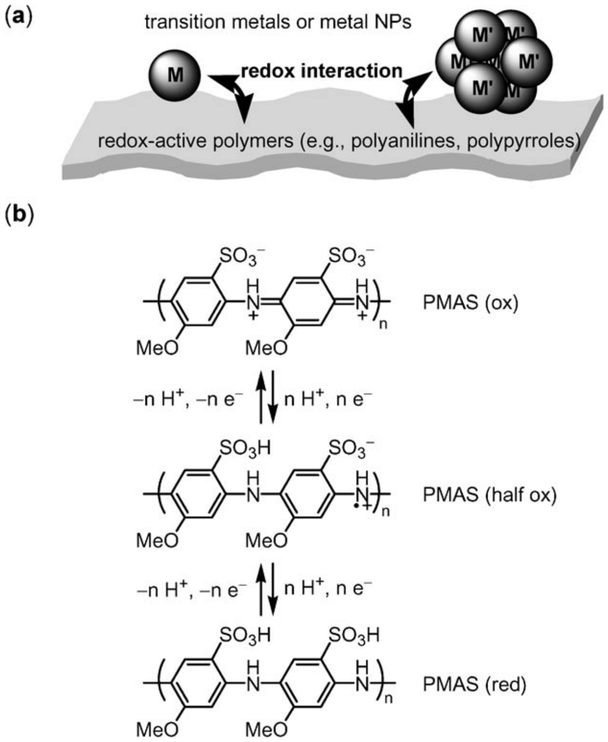

Figure 1. (**a**) Concept for the catalyst design based on the redox-active conductive polymers with various transition metals or metal NPs. (**b**) Three representative oxidation states of PMAS: complete oxidized form PMAS (ox), half oxidized form PMAS (half ox), and complete reduced form PMAS (red).

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redox-active polymer as the catalyst support, in spite of a variety of investigations on the metal NPs-catalyzed alcohol oxidation reactions.[6] Herein, we report on the reusable PMAS/Au NPs catalyst for the oxidation reaction of alcohols under molecular oxygen in water, where PMAS works as a redox mediator for transferring protons and electrons.

PMAS/Au NPs were prepared according to the process shown in Figure 2, a. PMAS was treated with $N_2H_4{\cdot}H_2O$, then $NaAuCl_4$ was added to the reaction mixture to give PMAS (half ox)/Au NPs. The transmission electron microscopy (TEM) image and the diameter histogram of the PMAS/Au NPs are shown in Figure 2, b. Each particle was dispersed and the average diameter was 7.9 nm. The thus-obtained aqueous solution of the PMAS/Au NPs was used for the catalytic reaction, and could be stored without the particles growing in size for at least 6 months (the TEM image is shown in the Supporting Information, Figure S1).

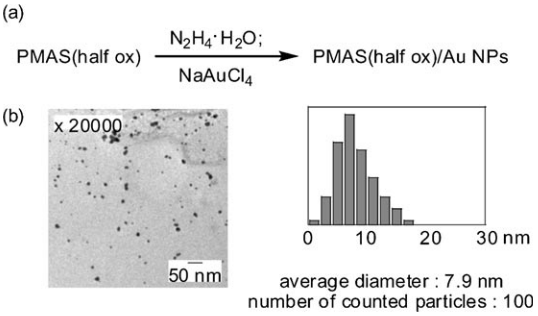
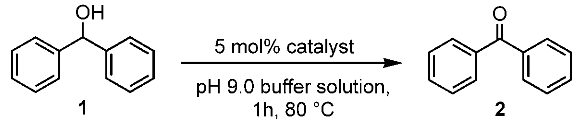


Figure 2. Preparation of PMAS/Au NPs. (**b**) TEM image and diameter histogram of PMAS/Au NPs.

Table 1. Oxidation of benzhydrol (**1**).



Entry	Catalyst	Atmosphere	Yield[a] [%]
1	PMAS/Au NPs	O_2	quant
2	PMAS[b]	O_2	0
3	PMAS/Au NPs	Air	quant[c]
4	PMAS/Au NPs	Ar	3
5	PMAS/Au NPs (400 mol%)	Ar	quant
6	PVP/Au NPs[d]	O_2	47

[a] Determined by ^{1}H NMR.

[b] Amount of PMAS was calculated based on the aniline monomer unit.

[c] 6 h.

[d] Prepared by treatment with $N_2H_4{\cdot}H_2O$ in the presence of PVP and $NaAuCl_4$.

To examine the catalytic function of PMAS/Au NPs prepared according to the process in Figure 2, a, the oxidation of benzhydrol (**1**) was conducted in pH 9.0 aqueous buffer solution at 80 °C, where no organic solvent was used (Table 1). Under an oxygen atmosphere, **1** was quantitatively transformed into benzophenone (**2**) in the presence of 5 mol% PMAS/Au NPs (based on Au atom) for 1 h (entry 1). On the other hand, PMAS showed no catalytic activity in the absence of Au NPs (entry 2). Even under air, PMAS/Au NPs transformed **1** into **2** quantitatively (entry 3). In contrast, the reaction under an argon atmosphere showed a sharply decreased yield of **2** of merely 3% with PMAS/Au NPs (entry 4), suggesting that molecular oxygen is essential for the oxidation reaction. Poly(*N*-vinyl-2-pyrrolidone) (PVP)/Au NPs were tried as a representative catalyst in which the polymer does not have redox-active function (average diameter: 7.7 nm, see Supporting Information, Figure S2). The yield was lower than with PMAS/Au NPs whereas the average particle size is similar, indicating that the reaction was enhanced by the presence of PMAS. The redox-mediating effect by PMAS may be discussed to account for the results (entry 6).

In order to investigate the redox behaviour of PMAS in the oxidation reaction, the selected entries of Table 1 were followed by using UV-vis-NIR spectroscopy. In the catalytic reaction under an argon atmosphere (Table 1, entry 4), a significant spectral change was observed after the reaction (Figure 3, a), whereas the yield was poor. The characteristic polaron band (747 nm)[7] disappeared after the reaction, in the meantime a sharp peak appeared at 402 nm, which is assigned to the reduced form of PMAS[8] (Figure 3, a). The surface plasmon band of Au NPs was observed after the reaction. These results suggest the hydrogen transfer from **1** to PMAS. In other words, the reoxidation of PMAS (red) is essential for the catalytic cycle. In the stoichiometric reaction under an argon atmosphere (Table 1, entry 5), PMAS was reduced, while the alcohol **1** was quantitatively oxidized to **2** *via* stoichiometric hydrogen transfer.[9] On the other hand, under an oxygen atmosphere, the UV-vis-NIR spectra after the reaction did not show any significant changes (Figure 3, b). The catalytic reaction proceeded quantitatively under these conditions (Table 1, entry 1), suggesting the involvement of molecular oxygen in the reoxidation of PMAS (red). With these results in hand, the proposed multi-catalytic cycles were proposed as shown in Figure 4. The latest mechanistic research of alcohol oxidation with Au NPs has revealed that the catalyst restoration depends on the abstraction process of hydride species from Au–H by molecular oxygen.[10] However, the availability of molecular oxygen on the Au NPs sur-

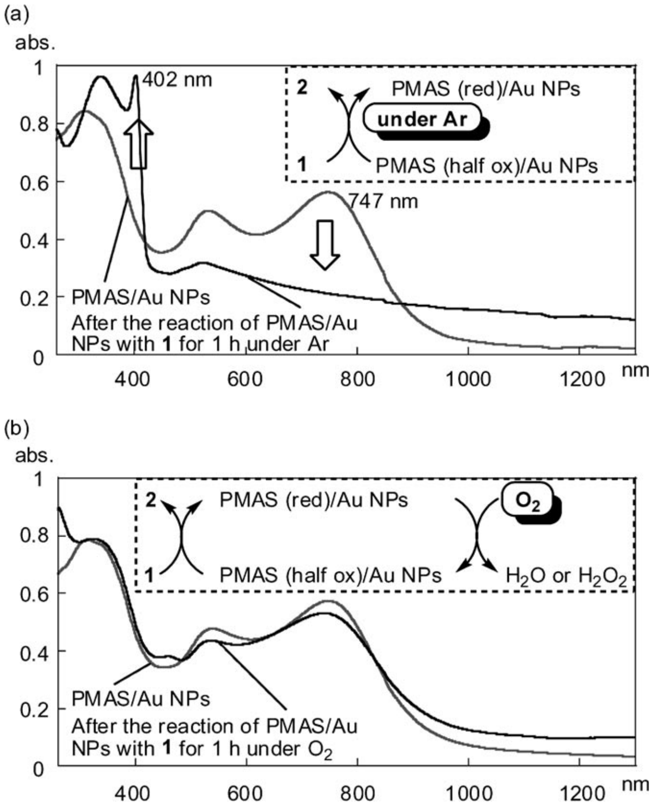


Figure 3. UV-vis-NIR spectra of (**a**) PMAS/Au NPs solid line) and after the reaction of PMAS/Au NPs with **1** for 1 h under Ar (dotted line), and (**b**) PMAS/Au NPs (solid line) and after the reaction of PMAS/Au NPs with **1** for 1 h under O_2 (dotted line) (1.0×10^{-4}M based on the aniline monomer unit, pH 9.0 buffer solution, 25 °C).

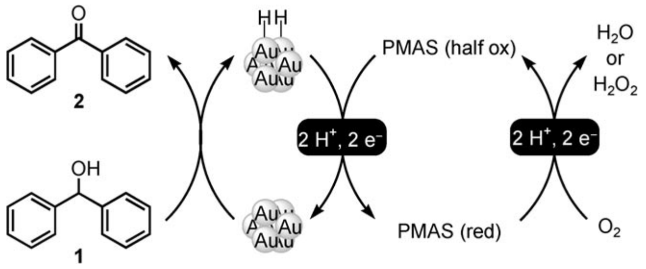


Figure 4. Proposed multi-catalytic cycles for aerobic alcohol oxidation with PMAS as a redox mediator in the presence of Au NPs.

face is known to be low,[11] which often reduces the catalytic activity. Therefore, the redox-mediating effect by PMAS is likely to accelerate the reaction.

The utility of the PMAS/Au NPs prepared according to the process in Figure 2, a was examined for the oxidation of a wide variety of alcohols as summarized in Table 2. Secondary alcohols were oxidized to give the corresponding ketones in high yields (entries 1–5). In the case of α-cyclopropylbenzyl alcohol, the oxidation of the hydroxy group occurred without cleavage of the cyclopropyl ring (entry 1). When the catalyst was reused, there was no loss of the activity, at least for four times reuse (Supporting Information, Table S1). Furthermore, its oxidation could be carried out under organic-solvent-free conditions in all process with 81% isolated yield (Supporting Information, Scheme S1). It is possible to synthesize dicarbonyl compounds, which are important building blocks for the synthesis of heterocyclic compounds, as exemplified by the oxidation of benzoin (entry 2). In the oxidation of an α,β-unsaturated alcohol, the C=C bond remained intact (entry 5). Several benzyl alcohols were transformed into the corresponding aldehydes, carboxylic acids, and esters with high conversion yields (entries 6–8). 1-Adamantaneethanol as a primary alcohol was found to be oxidized to the corresponding aldehyde in 70% yield in spite of the need for a longer reaction time (entry 9). Furthermore, the aerobic oxidation of a non-activated aliphatic primary alcohol proceeded although 10 mol% PMAS/Au NPs and 72 h reaction time were required (entries 10 and 11). 1,10-Decanedicarboxylic acid was obtained in 54% yield (entry 10). The oxidation of 1-decanol to the corresponding carboxylic acid was perfomed in the presence of 300 mol% K_2CO_3 (74% yield, entry 11).

In conclusion, we have demonstrated that the redox-active PMAS can work in a multi-catalytic process as both a stabilizer of Au NPs and redox mediator for aerobic alcohol oxidation in water. This design concept provides a new type of redox catalyst system for transferring protons and electrons.

Experimental Section

Preparation of PMAS/Au NPs

Poly(2-methoxyaniline-5-sulfonic acid) (PMAS), which was kindly provided by Mitsubishi Rayon Co., was deionized through cation-exchange resins before use. Other reagents were used as recieved. The water used in the present study is of a MilliQ grade.

PMAS/Au NPs: An aqueous solution (1 mL) of PMAS (0.06 mmol based on the aniline monomer unit, 12 mg) was mixed with 3 mL of 0.5 M $B(OH)_3$-NaOH buffer (pH 9.0) solution. An aqueous solution (1 mL) of $N_2H_4{\cdot}H_2O$ (0.06 mmol, 3 μL) was added to the PMAS solution, which was stirred at room temperature under air for 24 h. Then, an aqueous solution (1 mL) of $NaAuCl_4{\cdot}H_2O$ (0.06 mmol, 24 mg) was added to the stirring solution at 0 °C. The mixture was stirred at room temperature under air for 24 h. The thus-obtained aqueous solution of PMAS/Au NPs was analyzed by UV-vis-NIR spectroscopy (λ_{max} = 537, 747 nm) (Hitachi U-3500). The aqueous solution of PMAS/Au NPs was dropped on copper TEM grids coated with a carbon mesh (Nissin EM Co., Ltd. Tokyo) for TEM analysis (Hitachi H-8100).

Table 2. Oxidation of various alcohols.[a]

$$\text{Substrate} \xrightarrow[\text{pH 9.0 buffer solution, 80 °C}]{\text{5 mol\% PMAS/Au NPs}} \text{Product}$$

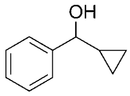
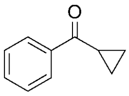
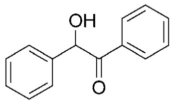
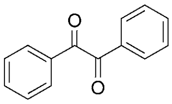
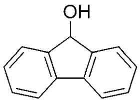
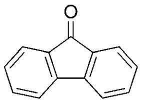
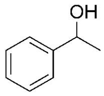
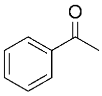
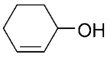
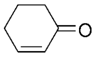
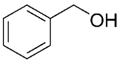
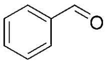
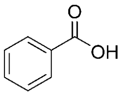
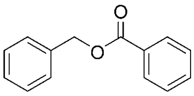
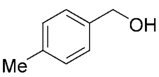
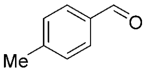
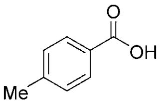
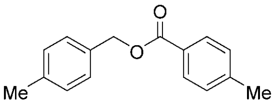
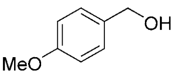
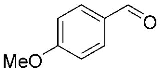
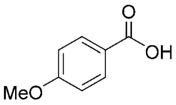
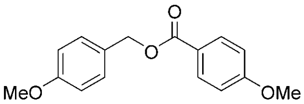
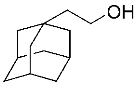
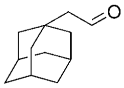
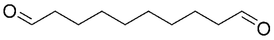
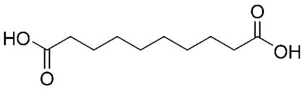
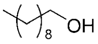
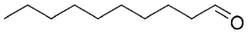
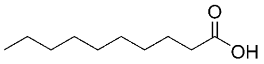
Entry	Substrate	Time [h]	Product	Yield [%][b]
1		3		quant (81)[c]
2		3		quant
3		4		quant
4		8		quant
5		8		80
6		4		15
				43
				38
7		4		60
				17
				17
8		4		64
				23
				13
9		72		70
10[d]		72		trace
				54

Table 2. (Continued)

Entry	Substrate	Time [h]	Product	Yield [%][b]
11[d,e]		72		trace
				74

[a] *Reaction conditions:* substrate (0.2 mmol), 5 mol% PMAS/Au NPs (Au: 0.01 mmol), 0.25 M $B(OH)_3$-NaOH buffer solution pH 9.0 (1 mL), 80 °C.

[b] Determined by ^1H NMR.

[c] Isolated yield through organic solvent-free conditions.

[d] 10 mol% PMAS/Au NPs, 0.25 M $B(OH)_3$-NaOH buffer solution pH 9.0 (2 mL).

[e] 300 mol% K_2CO_3.

General Procedure for Catalytic Aerobic Oxidation

The general procedure for the catalytic aerobic oxidation of alcohols in water is as follows: a 5-mL two-necked flask was evacuated and backfilled with atmospheric oxygen. Then, alcohol (0.2 mmol) and 1 mL of PMAS/Au NPs solution (Au: 0.01 mmol, 5 mol%) were added at room temperature. The mixture was stirred at 80 °C under molecular oxygen. The reaction mixture was extracted with ethyl acetate. The organic layer was evaporated and examined by ^1H NMR analysis (Varian Mercury 300 MHz) with 1,1,2,2-tetrabromoethane as an internal standard.

Supporting Information

Supporting experimental data are presented in the Supporting Information.

Acknowledgements

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