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Dendrimer-like core cross-linked micelle stabilized ultra-small gold nanocluster as robust catalyst for aerobic oxidation of α -hydroxy ketones in water

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As one of the most general and promising stabilizers, dendrimers have been widely used to prepare ultra-small gold nanoclusters. However, the complex synthesis of dendrimers hinders the further application of protected nanoclusters. Here we report a facile strategy to prepare an alternative material via core cross-linking of self-assembled micelles. The resulting dendrimer-like core cross-linked micelles (DCCMs) keep the main characteristic of dendrimers and avoid complex chemical synthesis. As expected, the DCCMs could easily encapsulate gold nanoparticles within their cores. The ultra-small clusters of Au₅ were prepared without the participation of external reductants. Importantly, the DCCM stabilized noble gold clusters furnish excellent catalytic activity and perfect reusability for aerobic oxidation of α -hydroxy ketones in water. Only under open air the oxidation could be repeated up to 48 times with negligible turn-over frequency change. The total turnover number (TON) of the reaction reached unexpected >48,000, a highest TON for metal catalysed oxidation of hydroxy ketones so far. The further mechanism study hints that the carboxylic group of substrate might be involved in the catalytic process. The simple catalyst preparation, the environmentally benign reaction condition, and the excellent catalytic performance and durability make the novel DCCM protected gold nanoculster a green catalyst.

Introduction

Ultra-small noble-metal nanoclusters (NCs), for example Au, are of fundamental interest and technological importance in the field of catalysis due to their size dependent catalytic activity.¹ The syntheses to these particles usually include chemical or electrochemical reduction of metal salts in the presence of stabilizers.² The purpose of the stabilizers is to control particle size and enhance resistance to agglomeration and deactivation. In past years, some innovative stabilizers such as dendrimers,³ thiols,⁴ polymers,⁵ peptide complexes,⁶ surfactants⁷ and supported matrix⁸ have been developed for preparation of ultra-small gold nanoclusters. Among them, dendrimers probably stand as the most general and promising ones. Indeed, the fairly spherical dendrimer features controllable size, functionalized exterior, and highly chemical stability, which make it particularly well-suited hosting metal nanoparticles for catalysis.⁹ Nevertheless, the dendrimer

stabilizers suffer from drawbacks. For example, most dendrimers require complex chemical synthesis, especially for high-generation compounds; even the increase of one generation, one has to pay much more efforts than that of lower ones. The high cost largely hinders their industrialization and commercialization.¹⁰ In this regard, development of new stabilizers with dendrimer-like characteristic but much easier preparation method would be highly desirable.

The self-assembly utilizes non-covalent interactions to build varied nanostructures and avoids the complex chemical synthesis,¹¹ which might be a good protocol to develop new stabilizers of metal nanoclusters. For instance, the surfactant micelles driven by amphiphilic interaction represent a dendrimer-like spherical structure and have been served as template for metal nanoparticles.¹² However, this kind of particles could hardly be used in catalysis since the rapid dissociation equilibrium of the noncovalent structure would tend to precipitate the metal catalyst out during the reaction process and, the hard separation between the stabilizer and product would also make the catalyst's reusability difficult.¹³ These drawbacks are fatal in modern catalysis because the development of sustainable catalysts is becoming more urgent than ever in face of the stringent environmental standards and economic pressures.¹⁴

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Electronic Supplementary Information (ESI) available: Synthetic procedures of chemicals, Measurement of critical micelle concentrations of **1b-d**, additional Figures, Tables, NMR and MS data. See DOI: 10.1039/x0xx00000x

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Scheme 1. Preparation of DCCMs by thiol-ene addition and synthesis of ultra-small gold nanoclusters.

Inspired by our long-term effort in developing stable materials from various self-assemblies,^{7,15} we hypothesized that the dynamic micelles might be covalently captured to get a solid media for metal catalysts. Although cross-linking of surfactant micelles has been reported as early as in the 1970s, there is no mention of their application in stabilizing metal nanoparticles for catalysis.¹⁶ In this contribution, we employ for the first time the highly efficient thiol-ene "click" reaction to cross-link the core of neutral micelles formed by readily available surfactants 1a-1d (Scheme 1).17 The resulting core cross-linked micelle demonstrates dendrimer-like properties such as spherical shape, controllable size, hydrophobic interior and highly chemical stability, and is proved to be outstanding template for gold nanoparticles. The ultra-small clusters of Au₅ were prepared without the participation of any external reducing reagents. Importantly, the novel dendrimer-like core cross-linked micelle (DCCM) protected gold nanocluster (Au@DCCM) was found to be excellent catalyst for aerobic oxidation of α -hydroxy ketones in water. The oxidation of alcohols to corresponding carbonyl compounds is ubiquitous importance in production of fine chemicals and intermediates.¹⁸ Traditional methods based on the use of a stoichiometric amount of oxidants are often toxic and release considerable by-products.¹⁹ As a consequence of the evergrowing concerns over green chemistry and chemical processes, the gold particle catalyst combined with molecular oxygen represents an emerging alternative to the traditional procedures.¹ However, the previous gold particle based catalytic systems need additionally bubbled air or oxygen to push the reaction,²⁰ which increases the economic burden to some extent. Besides, most of the reported systems suffer from the harsh synthesis and cumbersome reusability of catalyst.^{20,21} In contrast, the colloidal Au@DCCM system reported here features the easy catalyst preparation, the environmentally benign and economic reaction condition (open air as oxygen source, water as the sole solvent, and as low as 0.1% catalyst loading), the excellent reaction performance, and the outstanding catalyst reusability (cycle up to 48 time!). It thus would be severed as a real "green" catalyst for oxidation of α -hydroxy ketones.

Results and discussion

respectively (Fig. 1S).

DOI: 10.1039/C6GC00010J Design, synthesis and characterization of dendrimer-like core cross-linked micelles. Compounds 1a-d were simply prepared in four steps by alkylation of methyl gallate with 6-bromohexene, reduction of the ester with lithium aluminium hydride, bromination of the resulting alcohol with phosphorus tribromide, and nucleophilic displacement of the bromide with polyethylene glycol (PEG) (See Supporting Information for details). With a hydrophobic alkyl head and a hydrophilic PEG tail, these neutral surfactants were expected to form micelles in water. However, as compound 1a was added into deionized water, a white suspension, which would further precipitate out of solution over time, was obtained. This phenomenon happened possibly because the hydrophilic tail of 1a could be not long enough to protect the relatively large hydrophobic head, consequently leading to the formation of meta-stable molecular aggregates rather than micellar self-assemblies. Indeed, compounds 1b-d with longer hydrophilic parts were readily soluble in water and gave rise to the stable pale blue emulsions at room temperature, which is characteristic of the

self-assembly taking place. The initial dynamic light scattering (DLS) measurement of aqueous emulsion from **1b** revealed nanoparticles with a hydrodynamic diameter of ~9.0 nm formed. With continuously increasing the hydrophilic chain to PEG-1000 and PEG-2000 (**1c** and **1d**), larger nanoparticles with sizes of ~28.0 and ~75.0 nm were obtained (Fig. 1). Further analysis indicated that the critical micelle concentrations (CMC) of **1b-1d** were approximately 1.60, 1.18 and 0.60 µmol/L,



Fig. 1 Distribution of the hydrodynamic diameters of micelles (black line) and DCCMs (red line) formed by **1b-1d** in aqueous solution determined by DLS ([**1**] = 2.6 mM).

The design of surfactants puts numerous alkenyl groups at the core of micelles, which are readily cross-linked by UV irradiation in the presence of dithiothreitol (DTT) –a cross-linker and 2,2'-dimethoxy-2-phenylacetophenone (DMPA) –a photoinitiator to form a covalent captured 3D spherical material (Scheme 1 and see Experimental for details). The cross-linking process could be easily monitored by ¹H NMR spectroscopy. Taking **1d** as example, upon core cross-linking, the sharp ¹H NMR signals of the surfactant were replaced by broad peaks and the protons belonging to alkenyl groups disappeared almost (Fig. 2S). The successful cross-linking was Published on 22 March 2016. Downloaded by Gazi Universitesi on 31/03/2016 10:08:15.

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also confirmed by DLS measurement except a little bit size increase from prior to cross-linking ~9.0, 28.0 and 75.0 nm to after cross-linking ~12.0, 40.0 and 90.0 nm, respectively (Fig. 1). In addition, the resulting DCCMs were further characterized by transmission electron microscopy (TEM). As shown in Fig. 2a, a micrograph obtained from the DCCM of **1b** very clearly revealed the formation of distinct spherical aggregates with a uniform diameter of around 20.0 nm. Further analysis revealed that the particles increased in size with the increase of hydrophilic fraction, which is consistent with the trend observed in DLS assays. For example, the DCCM from **1c** gives a larger size in the micrograph, averaging about 35.0 nm in diameter (Fig. 2b); the particles from **1d** are much larger, with their sizes mostly ranging from 80.0 to 100.0 nm (Fig. 2c).



Fig. 2 TEM micrographs of DCCMs formed by a) **1b**, b) **1c** and c) **1d** in aqueous solution (2.6 mM) on the carbon-coated copper grids. All samples were stained with an aqueous solution of 2% phosphotungstic acid.

As expected, the stability of micelles is highly enhanced via the covalent capture. After dialysis in water and evaporation of the solvent, the DCCMs could not only re-dissolve in water but also in most polar organic solvents (e.g. methanol, chloroform and tetrahydrofuran, etc.) without decomposition of the spherical structure determined by DLS (data not shown). Besides, the cross-linked materials could be stably maintained over a year at ambient temperature with a neglectable size decrease. It is particularly worthy to note that the DCCMs could even tolerate high temperature treatment and survive from a broad range of pH conditions (1-14).

Synthesis of DCCMs stabilized gold nanoparticles and nanoculsters. With the super stable DCCMs in hand, we directed toward the template synthesis of gold nanoparticles (NPs), which are carried out by sequestering AuCl₄- within DCCMs followed by chemical reduction (See Supporting Information for details). Different reducing conditions had an enormous impact on the nanoparticle production. Addition of NaBH₄ to the water solution formed by 0.5 of [AuCl₄-]/[DCCM-1d] immediately turned its colour from light yellow to dark purple. The UV-Vis spectrum shows a plasmon band at 520 nm (Fig. 3, red). This means that the Au NPs formed have a diameter larger than 2.0 nm.²² Surprisingly, when the auratecontaining DCCMs were allowed to sit at room temperature without any NaBH₄ added, the solution also turned from yellow (the distinctive colour of aurate) to light purple in a few hours whereas the surface plasmon absorption band at 520 nm disappeared, indicating the formation of ultra-small (< 1.0 nm) nanoclusters (Fig. 3, blue).²³ This conclusion was confirmed by TEM measurement showing that the Au NPs formed in the presence of NaBH₄ averaged about 4.0 nm in diameter (Fig. 4a,b) and nanoclusters obtained in the absence

of external reductants less than 1.0 nm in size (Fig. 4 cd). Noticeably, from the TEM one can find that the Auc NRS were distributed in the whole DCCM rather than in a special space (Fig. 4b,d). This observation suggests that the PEG chains, which occupy the most space of DCCM, play an important role in stabilizing the Au NPs. The previous reports have shown that the PEG units could protect Au NPs through the multiple but weak interaction between Au and the pseudocrown ethers.²⁴ In the present case, the thick PEG layers of DCCM would likely do the same. It should be noted that although the thioethers existed in the DCCM could also provide weak coordination with gold nanoparticles, this interaction could not be the main factor for the stabilization since all thioethers centred in the core of DCCMs (Scheme 1).²⁵



Fig. 3 UV-Vis spectra of Au@DCCMs formed with and without externally added reducing agent NaBH₄. [AuCl₄·]/[**1d**] = 0.5, [**1d**] = 5.2×10^{-4} M.



Fig. 4 TEM images of Au@DCCMs formed with (a, b) and without (c, d) the addition of NaBH₄, ($[HAuCl_4]/[1d] = 1:1$). The gold nanoparticles appear as dark spots due to their high electron density.

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Fig. 5 (a) Photographs of Au nanoclusters prepared in DCCM templates with and without NaBH₄ under a hand-held UV lamp (365 nm). (b) Emission spectra of Au@DCCMs obtained with and without NaBH₄. $\lambda_{ex} = 330$ nm; [AuCl₄⁻]/[**1d**] = 0.5, [**1d**] = 1.3 mM. (c) Comparison of emission spectra of Au nanoclusters formed in DCCM templates with different amphiphiles **1b** ($\lambda_{ex} = 390$ nm), **1c** ($\lambda_{ex} = 380$ nm) and **1d** ($\lambda_{ex} = 330$ nm). [AuCl₄⁻]/[**1**] = 0.5, [**1**] = 1.3 mM. The gold nanoclusters were formed without externally added reducing reagents. (d) Comparison of emission spectra of Au@DCCMs formed with different ratios of [AuCl₄⁻]/[**1d**] (0.02, 0.1 and 0.5 respectively), [**1d**] = 1.3 mM. The gold nanoclusters were formed without externally added reducing reagents.

The ultra-small Au nanoclusters obtained in the absence of external reducing reagents were further investigated by photoluminescence study. As we know, when their size approaches the Fermi wavelength of electrons, gold nanoclusters would display molecule-like emission.²⁶ Indeed, under a hand-held UV lamp, the Au-DCCMs prepared without the external reductant gave a bright blue light but the materials obtained by NaBH₄ reduction showed no signs of luminescence (Fig. 5a). The fluorescence spectroscopy confirmed this trend. As shown in Fig. 5b, the Au@DCCMs prepared by spontaneous reduction demonstrated the intense fluorescence emission while the sample obtained by NaBH₄ reduction kept almost silent. From the excitation/emission spectra peaks of 330 nm (3.76 eV)/387 nm (3.20 eV),²⁷ the gold nanocluster size could be tentatively ascribed to 5 atoms according to the jellium model described by Zheng et al.,²⁸ although the theoretical datum (3.22 eV) is slightly larger than that observed in our experiment (Fig. 3S, \Box). Interestingly, the size of the gold NCs could be further adjusted by the size of DCCMs. For example, in 0.5 of $[AuCl_4]/[1]$ samples, the larger the DCCM size (from 1b to 1c to 1d), the shorter the fluorescence emission, indicating the formation of smaller Au clusters (Fig. 5c). Moreover, the cluster size could also be controlled by the amount of gold precursor loaded in the materials. For instance, in the Au@DCCM samples with [AuCl₄-]/[1d] from 0.02 to 0.1 to 0.5, the excitation/emission wavelengths changed from 300/358 to 309/374 to 330/387 nm, respectively (Fig. 5d).

DCCM protected gold nanoculsters (Au@DCCMs) as "green" catalyst for aerobic oxidation of α -hydroxy ketones in water. As mentioned in the beginning, the catalytic activity of a metal catalyst is highly sensitive to its surface property. The gold catalyst obtained by spontaneous reduction gives smaller particle size compared that by reduction with external reducing reagents, which is expected to afford higher reactivity since the smaller particle size can provide more contacting surface area between catalyst and substrates.^[1a,1g,29] the Additionally, the spontaneous reduction avoids incorporation of exotic impurities and is more in line with the requirements of green synthesis. Based on above considerations, the gold NCs stabilized by DCCM from 1d without the participation of external reducing reagents were chosen to test the catalytic activity of Au@DCCMs. Optimization of catalytic conditions was performed with the aerobic oxidation of benzoin as the model reaction. Firstly, temperatures were examined, and it was found that the complete conversion of benzoin was observed at 50 °C after 14 h (Table 1S, entry 3). With this promising observation, we then turned our attention to the aurate loading in the DCCMs. A number of loadings from 2%-100% were tried and the optimized result was obtained in 50% of [AuCl₄-]/[1d], which gave 33.1% yield within 6 h (Table 1S, entries 4-12).³⁰ An ideal catalysis would also be a system where the catalyst used as little as possible. In this context, we tried to reduce the amount of the catalyst under above optimized reaction

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condition. To our delight, even the catalyst decreased as low as 0.1%, the quantitative yield was still obtained in despite of a little bit longer reaction time needed (Table 1S, entry 15). It should be noted that under the identical condition the reaction run very slowly in the absence of Au (Table 1S, entry 17).

With the established optimal reaction condition, we then managed to investigate the scope of this novel Au@DCCMs catalysed oxidation reaction and the results are summarized in Table 1. To our delight, the aryl α -hydroxy ketones with either electron donating or withdrawing substituting groups on the aromatic ring all performed excellent reactivity (entries 1-8); even the sterically hindered ortho-substituted benzoins likewise got quantitative yields (entries 4, 6, and 8). Heteroaryl groups also afforded the desired oxidised products in excellent yields. The reaction conditions were mild enough to tolerate furan, thiophene and pyridine rings (entries 9-11). Particularly, it was surprising that the same excellent reactivity was obtained for alkyl substituted α -hydroxy ketones as well, although the reactions needed to be carried out at a little bit higher temperature (entries 12,13). The reaction condition used for alkyl substituted α -hydroxy ketones was further employed to try the oxidation of benzylic alcohols. AS shown in Table 2S, the benzylic alcohol with electron withdrawing group on the benzene ring also gave excellent reactivity (Table 2S, entry 1). Unfortunately, the naked benzylic alcohol, or benzylic alcohol with electron donating group, or even benzylic alcohol with electron withdrawing group at the α -position could only get a moderate yield (Table 2S, entries 2-4). Interestingly, once a carbonyl benzylic alcohol was employed to do the oxidation, although the carbonyl groups was located at the β -position, quantitative yield was obtained again (Table 2S, entry 5). This result hints that the carbonyl group might play an important role in the catalytic process.³¹ It needs to point out that the all isolated products were fully characterized from their spectral data and by direct comparison with the reported data.

Table 1. Au@DCCMs catalysed aerobic oxidation of α -hydroxy ketones in water.^a

OH 人	R'Au@DCCM-1d (0	.1%)	
R' Y O	K ₂ CO ₃ , H ₂ O, 50 ^o C, C	Dpen air	R' ∦ O
Entry	α-Hydroxyketone	t (h)	Yield (%) ^b
1	OH OH	48	>98
2	CI CI OH CI	24	>98
3	CH F	8	>98
4	F OH O F	12	>98



^{a)} Reaction conditions: α -hydroxyketone (0.077 mmol), Au@ DCCM-**1d** (0.077 μ mol, for Au), K₂CO₃ (32 mg, 0.23 mmol), H₂O (2 mL), open air, 50 °C. ^{b)} Yields were determined by ¹H NMR analysis. ^{c)} This reaction was performed at 80 °C.



Fig. 6 Recycle of Au@DCCMs in the aerobic oxidation of α -hydroxy ketone (thenoin) in water. The reaction detail was reported in experimental section.

Reusability of the Au@DCCMs catalyst system. The results so far are quite promising whereas the largest superiority of the DCCM stabilized gold catalyst is not reflected in that but its ulta-high reusability. In a typical experiment, substrate 2hydroxy-1,2-di(thiophen-2-yl)ethanone was employed to test the recycle of the gold catalyst (See Supporting Information for details). At the end of each cycle, the catalyst was simply recovered by extracting the aqueous phase with ethyl ether, and the organic layer was concentrated and analyzed by ¹H NMR spectroscopy. To our surprise, the catalyst could be reused as high as 48 times with negligible turn-over frequency (TOF) change (Fig. 6), and even at the 49th cycle the yield still remained quite good (81%). The total turnover number (TON)

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of the reaction reached unexpected over 48,000,32 which constitutes so far, from this point of view, the highest efficient catalytic system in metal catalysed oxidation of hydroxy ketones. It should be mentioned that the reaction mixture stayed completely clear at the end of the reaction, showing no formation of gold black (Fig. 4S). The further spectroscopic study at the molecular lever showed there is no obvious difference before and after reaction, suggesting the recycled catalyst keeping the same property with that before catalysis (Fig. 5S). Considering so many times treatment between the reactions, the gold catalyst was extremely robust when protected in the DCCMs.

Proposed mechanism for the aerobic oxidation of alcohols by Au@DCCMs. Based on the previous studies^{1g,21a,33} and the catalytic performance, a mechanism of O_2 activated by anionic Au cores is suggested (Fig. 7). As we above-mentioned, the gold clusters were encapsulated in the cavities formed by the thick and constrained pseudocrown ethers of PEG coils (Fig. 7, I). During the catalysis, parts of the weakly coordinated pseudocrown ethers were "pushed away" from the Au NCs and replaced by the substrate with stronger coordination sites (carbonyl group and oxy anion here) (Fig. 7, II).³⁴ This replacement on one hand exposed more portions of the cluster surfaces, on the other hand enhanced the cluster's surface charges further. Both of them would facilitate the attraction of O_2 on Au NPs in the form of superoxo or peroxo species (Fig. 7, III). The resulting O_2^{n-} species finally abstract hydrogen from alcohol to squeeze out the ketone product and the Au NPs were quickly reprotected by the surrounding PEG chains to complete the catalytic cycle. From the mechanism, the substrate's carbonyl group is involved in the coordination with Au clusters in such a way that the substrate molecule could push away the thick PEG layers around the Au surface easier. This involvement might partially explain the high reactivity of carbonyl group-containing substrates. Although the thick PEG layers of DCCMs hindered the contact between the substrate and Au surface to some extent, it is on the other hand, that the tight arrangement of PEG layers could avoid the possible aggregation of Au clusters during catalysis, which would be responsible for the excellent reusability of the catalyst.



Fig. 7 Proposed mechanism for aerobic oxidation of α -hydroxy ketones by Au@DCCMs based on activation of molecular oxygen.

Conclusions

In summary, a very simple method to prepare dendrimeralike materials has been developed via core erdss linking of oseffi assembled surfactant micelles. The resulting dendrimer-like core cross-linked micelle keeps the main characteristic of dendrimers such as fairly spherical structure, functionalized exterior, size regulation and especially highly chemical stability. Similar to dendrimers, the DCCMs were proved to be excellent templates for the synthesis of gold nanoparticles. Different reducing conditions had an enormous impact on the nanoparticle production. The ultra-small gold clusters of Au₅ were prepared by spontaneous reduction without the participation of any external reducing reagents. The size of gold clusters could be further adjusted by simply using DCCMs with different sizes or the amount of gold precursor loaded in the materials.

Importantly, the DCCM protected gold nanocluster is an outstanding catalyst for aerobic oxidation of α -hydroxy ketones in water. The mechanism study suggests that the carboxylic groups of substrates are involved in the catalytic process. In particular, the gold catalyst system is highly reusable and could be reused as high as 48 times with negligible TOF change. The total turn-over number of the reaction attained unexpected >48,000, a highest TON for metal catalysed oxidation of hydroxy ketones so far. By the way, the DCCM stabilized gold catalyst system reported here is totally environmentally benign and economic, as it uses readily available stabilizer, it avoids the participation of external reducing reagents during its synthesis, it uses water as the sole solvent in catalysis, it utilizes open air as the oxygen resource without bubbled air or oxygen, it needs only 0.1% for efficiently catalytic results, it tolerates a wide range of substrates, it separates easily with products, and it reuses so many times. The next work is following the attractive direction to investigate the applicable scope of other metal particles and nanoalloys stabilized by the novel DCCMs, and some interesting outcomes have actually been obtained and will be reported in due course.

Experimental

General Method. Routine NMR spectra were obtained on a Bruker AV II-400. The ¹H NMR chemical shifts were measured relative to CDCl₃ or D_2O-d_2 as the internal reference (CDCl₃: δ = 7.26 ppm; D_2O-d_2 : δ = 4.79 ppm). The ¹³C NMR chemical shifts were given using CDCl₃ as the internal standard (CDCl₃: δ = 77.16 ppm). Mass spectrometry was performed on a Waters premier instrument. UV-Vis spectrometry Q-Tof was monitored on a Puxin TU-1901 instrument. Fluorescence spectra were obtained using a Hitachi F-7000 fluorescence spectrometer. DLS experiments were recorded using a Malvern Zetasizer Nano ZS particle analyser instrument. TEM studies were carried out using a Tecnai G2F20S-TWIN instrument, operating at 120 kV. The TEM specimens were prepared by gently placing a carbon-coated copper grid on the surface of the sample.

Chemicals. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further

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purification. All solvents for reactions were freshly distilled prior to use. Millipore water was used in all aqueous experiments.

Typical preparation of dendrimer-like core cross-linked micelles. The cross-linker DL-Dithiothreitol (DTT, 20 mg, 0.13 mmol) and photoinitiator dimethylolbutanoic acid (DMPA, 170 μ L of 0.01 mg/mL MeOH solution, 1.72 μ mol) were added to a micellar solution of surfactant 1d (96 mg, 0.043 mmol) in millipore water (4 mL). The reaction mixture was stirred slowly and under UV light irradiation. After 4 h, the mixture was dialyzed against deionized water using a 5000 Da molecular weight cut-off tubing.

Typical preparation of Au@DCCMs with NaBH₄ as the reducing agent. A 10 mM aqueous solution of HAuCl₄ (0.5 mL) was added to a 10 mM solution of DCCM from 1d in H₂O (1 mL). A freshly prepared aqueous solution of sodium borohydride (50 mM, 0.2 mL) was slowly added to the vigorously stirred reaction mixture, and a dark purple solution of gold nanoparticles was thus obtained with seconds.

Typical preparation of Au@DCCMs without externally added reducing agents. A 10 mM aqueous solution of HAuCl₄ (0.5 mL) was added to a 10 mM solution of DCCM from 1d in H₂O (1 mL) under stirring. Upon sitting at room temperature overnight, a light purple solution of gold nanoclusters was obtained.

Typical procedure for aerobic oxidation of α -hydroxy ketones in water. The appropriate amounts of catalyst Au@DCCMs, benzoin, K₂CO₃, and water were added into a 20 mL glass vial at room temperature. The reaction mixture was then heated at 50 °C under the open air condition. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with diethyl ether (3 × 10 mL), The organic layers were combined and concentrated in vacuo. The yields of the reactions were determined by ¹H NMR spectroscopy.

Recycling experiment. The oxidation of thenoin was performed as above. After each cycle of reaction, the aqueous phase (3 mL), where the catalyst was, was extracted with diethyl ether (3×3 mL) and left standing at 50 °C for 2 min to evaporate the residual diethyl ether. Another batch of thenoin was added and the next cycle of the oxidation was performed. Extraction and solvent evaporation were performed in air without special protection.

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- 31. For more detailed discussion about the substrate reactivity, see the part of "Proposed mechanism".
- 32. The TON was calculated by the following formula: TON = $n_{\text{substrate}}/n_{\text{catalyst}}$, where $n_{\text{substrate}}$ represents the total moles of substrate converted to product, n_{catalyst} represents the moles of catalyst used in the recycle.
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- 34. Since the substrate needs first penetrate the thick PEG layers before coordinating with Au clusters, the weak hydrogen bond between the substrate and the coating of gold clusters might play certain role in accelerating the replacement of pseudocrown ethers by the substrate.

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Dendrimer-like core cross-linked micelle stabilized ultra-small gold nanoclusters as robust catalyst for aerobic oxidation of α -hydroxy ketones in water

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Graphical Abstract. Dendrimer-like core cross-linked micelle stabilized gold clusters furnish excellent activity and reusability for aerobic oxidation of α -hydroxy ketones in water.

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Au@DCCMs

· Very simple catalyst preparation

- Water as the sole reaction solvent
- Open air as oxygen source
- As low as 0.1% catalyst loading
- Recyle up to 48 times!