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Polydimethylsiloxane Sponge Supported Nanometer Gold: Highly Efficient Recyclable Catalyst for Cross-Dehydrogenative Coupling in Water

Weiwei Liang,‡ Teng Zhang,‡ Yufei Liu, Yuxing Huang, Zhipeng Liu, Yizhen Liu, Bo Yang, Xuechang Zhou and Junmin Zhang*[a]

Abstract: The successfully developed polydimethylsiloxane (PDMS, a stable hydrophobic polymer material) sponge supported nanometer gold can be used as a highly efficient recyclable catalyst for cross-dehydrogenative coupling of tertiary amines with various nucleophiles in water. This PDMS sponge nanometer gold can provide much better catalytic activity than free nanometer gold in water. Through an easy-to-build continuous flow reactor, the sponge nanometer gold catalyzed reaction can be facilely scaled up. It should be believed that this porous hydrophobic PDMS sponge material will be a promising carrier of highly efficient recyclable catalysts in water.

Gold is generally considered inactive, however, its form of nano-size particles possesses a higher surface to volume ratio that leads to its high catalytic activity.[1] In last few years, zero-valent gold catalysis have received considerable attentions.[2] In this regard, several types of gold (0), such as gold nanoparticles (AuNPs),[3] gold nanopores (AuNPore)[4] and gold nanoclusters,[5] have been well developed as catalysts for various organic transformations. Despite these elegant pioneering studies, conventional filtration or centrifugation is still required for the recycle of these kinds of gold catalysts as they are generally nano-size solid particles. The extra separation process greatly limited their reusability and practical application in industry. The recovery and reuse of catalysts is a very important and eternal subject in green chemical synthesis,[6] water is the greenest and cheapest reaction medium,[7] therefore, the development of green, highly efficient and reusable catalyst in water is highly anticipated. Recently we have found that a hydrophobic polydimethylsiloxane (PDMS) sponge[8] material can be successfully applied to the immobilization of organic photocatalyst and has achieved excellent results.[9] In addition to its convenient separation and purification due to its sponge-type, it is more interesting that this hydrophobic porous sponge material supported catalyst has the distinct highly effective catalytic activity in the water.[9b] Taking into consideration of the remarkable catalytic activity of gold nanoparticles together with the hydrophobicity of PDMS sponge, which should be beneficial for organic reactions in water, we reasoned that the PDMS sponge supported gold nanoparticles should be a promising heterogeneous catalyst for efficient organic transformations in water. With our continual interests on PDMS sponge supported catalysts[9] and nanometal catalysts[10c], in this paper, we demonstrate for the first time that a hydrophobic PDMS sponge supported nanometer gold can act as a highly efficient recyclable catalyst for cross-dehydrogenative coupling (CDC)[11] of tertiary amines with various nucleophiles in water. We have found out that PDMS sponge nano-gold can provide much better catalytic activity than free nano gold in water. Therefore, it should be believed that this porous hydrophobic PDMS sponge material will be a promising carrier for the development of highly efficient recyclable catalysts in water.

Here we adopt a facile approach to synthesize the supported gold nanoparticles on PDMS sponge. The procedure involves the functionalization of sponge with propylamine groups and then reductive deposition of nanometer gold particles using the readily available $HAuCl_4$ precursor, as is represented schematically in Fig. 1A. Due to long-chain functional groups are helpful for immobilizing stable and robust metal nanoparticles on polymer surface,[12] in the above process, propylamine groups were covalently grafted on the surface of porous PDMS sponge, which not only promote the interaction between sponge and

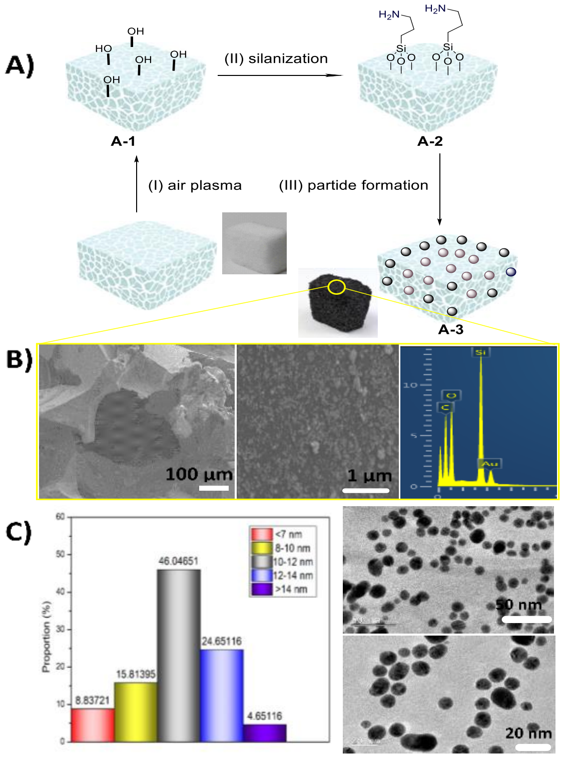

Figure 1. A) Schematic representation of supported gold nanoparticles on PDMS sponge; B) SEM image and EDX spectrum of sponge nano-Au catalyst; C) TEM images for sponge nano-Au catalyst dissolved by trifluoroacetic acid, Particle size distribution of sponge nano-Au catalyst obtained by randomly counting 215 particles in different areas.

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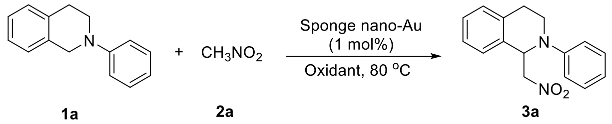
$HAuCl_4$ precursor to enable gold particles enter into the sponge pores, but also help stabilizing the formed particles to prevent their mobility and aggregation. In this manner, the structural properties of PDMS sponge were highly exploited. The morphology of the obtained sponge nano-Au catalyst was characterized by scanning electron microscopy (SEM), which showed that PDMS sponge is a 3D-porous polymer material and gold particles were evenly distribution on the sponge pores (Fig. 1B). The corresponding energy dispersive X-ray spectroscopy (EDX) further proved the homogenous distribution of Si, C, N, O and Au elements throughout the PDMS sponge (see the SI for details). Gold particle sizes were analyzed by transmission electron microscopy (TEM), the histograms showed that 7-14 nm gold particles were found on sponge surface (Fig. 1C). Catalyst loading on PDMS sponge was determined by inductively coupled plasma emission spectrometer (ICP) and the analysis results was 1.34×10^{-5} mmol/g.

In order to investigate the catalytic activity of as-prepared sponge nano-Au catalyst, the CDC reaction between N-phenyl-tetrahydroisoquinoline (N-THIQ) and nitromethane was chosen as the model reaction to study (Table 1). The sponge nano-Au catalyst amount for the model reaction was set for 1 mol% and molecular oxygen was used as oxidant in each reaction. Initially, various solvents were screened to examine their effects in the catalytic system. As our anticipated, a promising result was found when the reaction was carried out in water (66% yield, Table 1, entry 9). After prolong reaction time, the improved yield were obtained (92%, Table 1, entry 10). In addition, by using free gold nanoparticles as catalyst, only 26% yield was detected even after 36 h (Table 1, entry 10). The above results indicated that sponge nano-Au catalyst can provide much better catalytic activity than free gold nanoparticles in water. In order to shorten the reaction time, other oxidants were further examined (Table 1, entries 11 and 12). Both H_2O_2 (30 wt.% in water) and TBHP (70 wt.% in water) were effective oxidants for this CDC reaction in water, with providing 88% and 98% yields after 24 h, respectively. It should be mentioned that the above two aqueous oxidants were generally ineffective for this type of CDC reactions.[11] The result is exciting due to its efficient construction of carbon-carbon bonds in an environmental friendly and efficient manner. In the viewpoint of green and sustainable chemistry, both entries 10 and 12 were chosen as the optimized conditions for CDC reactions catalyzed by sponge nano-Au catalyst.

Table 1. Optimization of reaction conditions.[a]



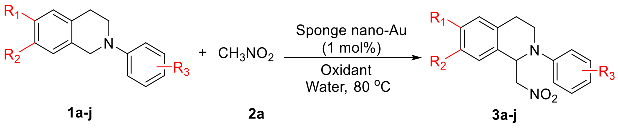
Entry	Solvent	Oxidant	Time	Yield[b]
1	EtOH	O_2	18	10%
2	MeOH	O_2	18	trace
3	CH_2Cl_2	O_2	18	44%
4	CH_3CN	O_2	18	9%
5	Toluene	O_2	18	trace
6	DMF	O_2	18	53%
7	DMSO	O_2	18	24%
8	i-PrOH	O_2	18	trace
9	H_2O	O_2	18	66%
10	**H_2O**	**O_2**	**36**	**92%[c], 26%[d]**
11	H_2O	H_2O_2[e]	24	88%
12	**H_2O**	**TBHP[f]**	**24**	**98%[c]**

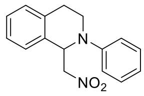
[a] Reactions were performed using **1a** (20.9 mg, 0.1 mmol), **2a** (54 µL, 1.0 mmol) and oxidant (1 atm for O_2 or 2 equiv. for others) in 1.5 mL H_2O, and were catalyzed by 1 mol% sponge nano-Au catalyst at 80 °C for 18-36 h; [b] Yield was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard; [c] Isolated yield; [d] Free nano-gold particles as catalyst; [e] H_2O_2 (30 wt.% in water, 2 equiv.); [f] TBHP (70 wt.% in water, 2 equiv.).

Having identified the optimal conditions, we next explored the substrate scope of the sponge gold catalytic system in water. In order to afford the best yield, the reactions were carried out regardless of the optimized condition A and B. Generally, as shown in Table 2, the different N-THIQ derivatives containing electron-donating or electron-withdrawing groups reacted with nitromethane very well in the condition A; While in the condition B, compounds **3b-d** and **3f-h** were obtained with moderate yields, this could be due to molecular oxygen less reactive than TBHP in the catalytic system. More specifically, only low yield was obtained for compounds **3h** in the condition B, which may contribute to its increasing electron-withdrawing ability of Cl-group on the phenyl ring. In addition, the substrates bearing a methoxyl group on the aryl ring of the THIQ also provided the corresponding products with satisfied yield (Table 2, **3i** and **3j**).

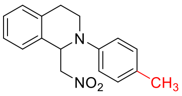
The substrate scope was further investigated by a variety of nucleophiles, as shown in Table 3. Both nitroalkanes and 1, 3-diketones derivatives were active nucleophiles, which could give the corresponding products in good yields (Table 3, **3k-n**). It was

Table 2. Reaction scope with varying N-THIQs.[a]

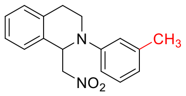




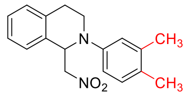
3a A: 98%
B: 92%



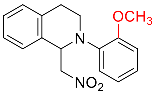
3b A: 94%
B: 75%



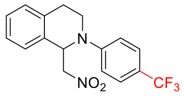
3c A: 92%
B: 65%



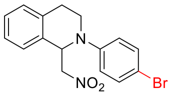
3d A: 91%
B: 44%



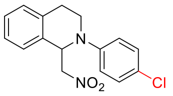
3e A: 92%
B: 91%



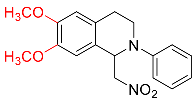
3f A: 93%
B: 49%



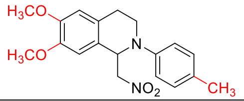
3g A: 66%
B: 46%



3h A: 86%
B: 27%



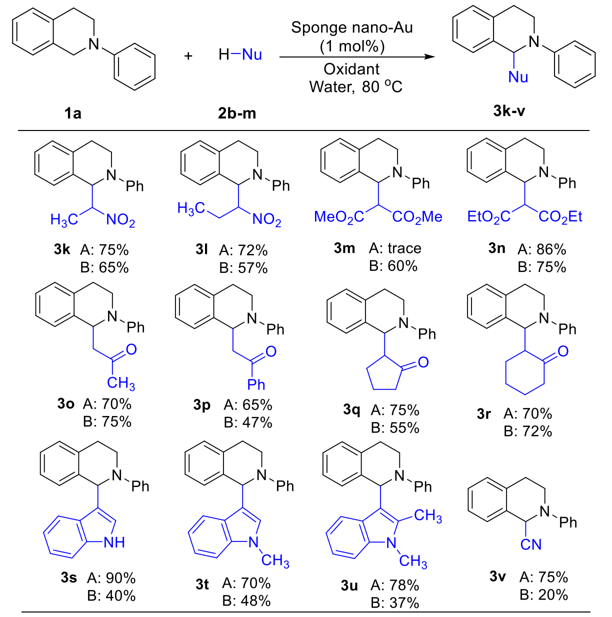
3i A: 85%
B: 75%



3j A: 75%
B: 60%

[a] Method A: **1a-j** (0.5 mmol), nitroalkane **2a** (270 µL, 5.0 mmol), sponge nano-Au catalyst (1 mol%), TBHP in water (70 wt.%, 2 equiv.), 80 ℃, in 3 mL H_2O for 24 h; Method B: **1a-j** (0.5 mmol), nitroalkane **2a** (5.0 mmol), sponge nano-Au catalyst (1 mol%), O_2 (1 atm), 80 ℃, in 3 mL H_2O for 36 h; The yields are isolated yields.

Table 3. Reaction scope with varying nucleophiles.[a]

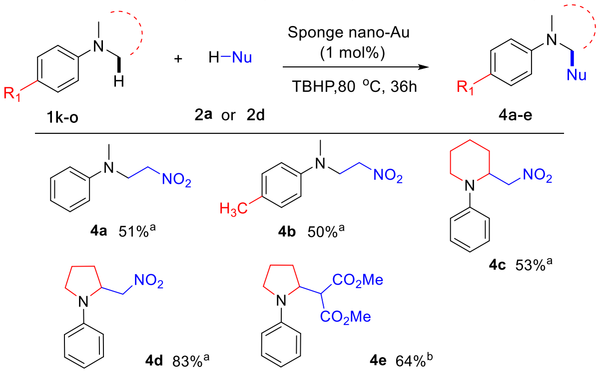


[a] Method A: **1a** (104.5mg, 0.5 mmol), nucleophiles **2b-m** (5.0 mmol), sponge nano-Au catalyst (1 mol%), TBHP in water (70 wt.%, 2 equiv.), 80 ℃, in 3 mL H_2O for 24 h; Method B: **1a** (0.5 mmol), nucleophiles **2b-m** (5.0 mmol), sponge nano-Au catalyst (1 mol%), O_2 (1 atm), 80 ℃, in 3 mL H_2O for 36 h; The yields are isolated yields.

noted that the compound **3m**, there is no desired product formed and only the oxidized by-product was detected under method A. In addition, aliphatic ketone is another promising nucleophiles, which generally resulted higher yields than aromatic ketones (Table 3, **3o** and **3p**), because of the latter conjugation effects between aromatic ring and carbonyl group. To our satisfaction, better yields were also observed when performing the coupling with cyclic ketones at the standard conditions (Table 3, **3q** and **3r**). Furthermore, although indole derivatives showed a lower reactivity under method B (Table 3, **3s-u**, 37-48%), the improved yields of corresponding products were obtained when conducted with TBHP as oxidant (Table 3, **3s-u**, method A, 70-90%). In addition, the corresponding cyanation product **3v** was also obtained with satisfactory yield in the condition A.

Due to the chemical inertness of α C-H, it is hard for simple tertiary amines to react with active nucleophiles. We therefore extended the current gold catalytic system to the simple tertiary amines using TBHP as an oxidant at 80°C (Table 4). The reactions of N-aryl tertiary amines, such as 4-methly-N, N-dimethylaniline and N, N,-dimethylaniline, reacted with excess amounts of nitromethane efficiently to produce the corresponding products in moderate yields (Table 4, **4a** and **4b**). Cyclic tertiary amines, such as 1-phenylpiperidine and 1-phenylpyrrolidine were examined to be suitable substrates, to give the corresponding coupling products in good to excellent yields (Table 4, **4c** and **4d**). Phenylpyrrolidine was also reacted with dimethyl malonate to give the corresponding substituted amine **4e** in 64% yield using acetonitrile as solvent. The mechanism of this sponge nano-Au catalyzed CDC reaction should be consistent with the formation of the iminium intermediate on gold particles, as proposed by Jin et al.[4h]

Table 4. Reaction scope of simple tertiary amines with nucleophiles.[a]



[a] Reaction condition: **1k-o** (0.4 mmol), TBHP in decane (5.5 M, 2 equiv.), sponge nano-Au catalyst (1 mol%), Nitromethane **2a** (3 mL) as solvent, 80 ℃ for 36h. Isolated yields are shown; [b] Dimethyl malonate **2d** (4 mmol) as reagent and MeCN (3 mL) as solvent.

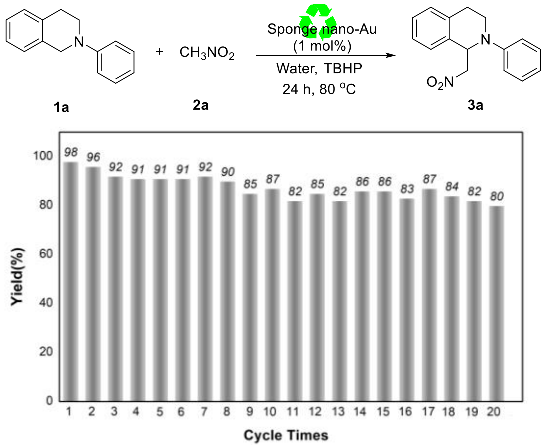


Figure 2. Recycling experiments for sponge nano-Au catalyst.

The reusability of sponge nano-Au catalyst was investigated by the model reaction under the optimal condition (Table 1, entry 12). The yield was measured after 24 h in each cycle and the separated sponge nano-Au catalyst was washed with alcohol and dried for the next cycle directly. According to these observations, the sponge nano-Au catalyst can be recycled more than twenty times, giving consistently high isolated yields and maintaining the size and distribution of gold particles on PDMS sponge (Fig. 2, see the SI for details).

In order to demonstrate the scalability and practicability of sponge nano-Au catalysis in industrial application, a gram scale of the model reaction was performed using an easy-to-build continuous flow reactor, as described in our previous work.7b The product was obtained with 90% of isolated yield after 24 h (see the SI for details).

In conclusion, we have developed a novel PDMS sponge supported nano-Au catalyst. This sponge nano-Au catalyst combined the advantages of high catalytic activity of nano gold and the hydrophobic function of PDMS sponge, which can facilitate the efficient CDC reactions of tertiary amines with various nucleophiles in water. In addition, through an easy-to-build continuous flow reactor, the sponge nano-Au catalyzed reaction can be facilely scaled up. All results indicated that the porous hydrophobic PDMS sponge material will be a promising carrier for the development of highly efficient recyclable catalysts in water. Efforts toward immobilizing other nanometal catalysts on the PDMS sponge and the related more interesting transformations in water is currently underway in our lab and will be reported in due course.

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Keywords: polydimethylsiloxane sponge • supported gold nanoparticles • recyclable catalyst • cross-dehydrogenative coupling • in water

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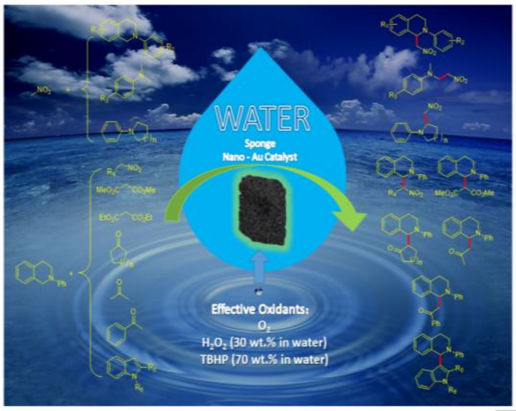
Entry for the Table of Contents

COMMUNICATION

The PDMS sponge supported nano-gold can be used as a highly efficient recyclable catalyst for cross-dehydrogenative coupling of tertiary amines with various nucleophiles in water. This sponge nano-gold can provide much better catalytic activity than free nanometer gold in water. Through an easy-to-build continuous flow reactor, the sponge nanometer gold catalyzed reaction can be facilely scaled up.



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