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Facile Synthesis of Highly Stable Gold Nanoparticles and Their Unexpected Excellent Catalytic Activity for Suzuki−Miyaura Cross-Coupling Reaction in Water

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The Suzuki−Miyaura cross-coupling reaction of aryl halides with arylboronic acids is one of the most powerful and convenient synthetic protocols for the generation of biaryl in organic chemistry.[1−5] In general, the catalysts of choice for Suzuki−Miyaura reaction is almost invariably palladium, although nickel[6] and copper[7] catalysts have been reported but with relatively low yields. In particular, gold(I) complexes can also be used as efficient catalysts for such reactions.[8] Recently, the interest in palladium catalyst has shifted from palladium complexes to supported palladium nanoparticles, considering the simple separation and reusability of the catalyst.[9−12] In addition, palladium nanoparticles usually show enhanced reactivity under mild conditions because of their large surface area.[13,14]

Gold nanoparticles for catalytic applications in various organic reactions have aroused considerable attention in recent years.[15−17] Nevertheless, to the best of our knowledge, their application as catalysts for the Suzuki−Miyaura cross-coupling reaction has yet not been discovered. Here, we demonstrate that gold nanoparticles can also be used as efficient catalysts for Suzuki−Miyaura cross-coupling reaction of aryl halides with arylboronic acids for the first time. The gold nanoparticles used were synthesized by a simple one-step strategy through chemical redox reaction between $HAuCl_4$ and 2-aminothiophenol, which act as gold nanoparticles and polymer stabilizer resources, respectively. The redox reaction between aniline (or its derivative) and $HAuCl_4$ for the preparation of conducting polymer and gold nanoparticles has aroused increasing interest in the past few years.[18−21] However, well-defined polymer-stabilized gold nanoparticles are seldom seen. The choice of 2-aminothiophenol as the reductant is based on the fact that its polymerized polymer poly(2-aminothiophenol) (PATP) can act as an effective capping agent for gold nanoparticles, as conjugated π electrons of benzene rings and thiol groups coexist in PATP chains which can significantly control and stabilize gold nanoparticles.[22,23] Figure 1 shows the typical transmission electron microscopy (TEM) image of PATP-stabilized gold nanoparticles, where the gold nanoparticles are estimated to be 1.0 nm in size and in narrow size distribution. Characterizations of X-ray diffraction, X-ray photoelectron, UV−vis, and Fourier transform infrared spectroscopies indicate the successful synthesis of PATP-supported gold nanoapritcles (Supporting Information, Figure S1). The synthesized PATP-stabilized gold nanoparticles can be stable without obvious aggregation for more than 6 months, which undoubtedly evidence their high stability.

It is accepted that more economical aryl chlorides are less reactive than aryl bromides and iodides.[13] Therefore, we first examined the catalytic activity of synthesized PAPT-stabilized gold nanoparticles toward cross-coupling of phenylboronic acid and chlorobenzene to give biphenyl as a test reaction (Table 1). The reaction media is chosen as water instead of organic solvent in consideration of the green-chemistry processes and low cost.[24,25] With relatively low gold catalysts loading (0.05 mol %), the yield of biphenyl can reach as high as 87% (Figures S2, S3). Biphenyl that may come from homocoupling of phenylboronic acid[26] has been eliminated as supported by the fact that no biphenyl product is observed under the same experimental conditions except for the absence of chlorobenzene. Repeated experiments confirm that the results are reproducible, and more importantly, the same yield can also be attained when the gold catalysts are used after aging as long as 6 months. The recyclability of gold catalyst is also investigated and results show that the gold catalyst is recovered by simple filtration and reused without significant loss of catalytic activity (yield loss within 3% for six cycles, Table 1). Besides, the gold nanoparticles remain the same size, and the aggregation phenomenon is not observed after six cycles, together with similar kinetic curves for each run (Figure S5), which prove their excellent catalytic activity, reusability, and again high stability. The mechanism of gold nanoparticle catalysts involved in a cross-coupling reaction may follow a homogeneous path, as the leaching of gold is observed in the first half-hour of the reaction (0.27 ppm, 5.5% of the initial catalyst charge).[27]

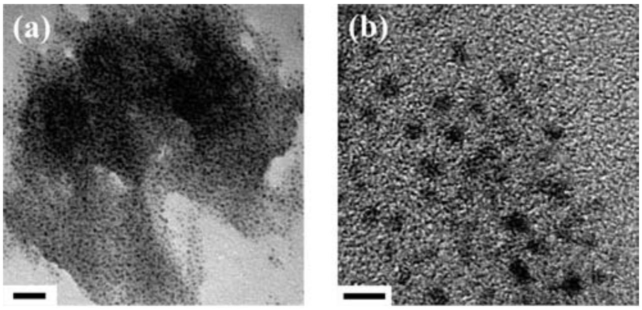
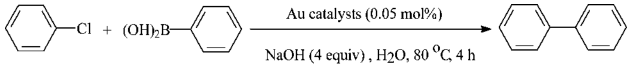


Figure 1. (a) TEM and (b) HR-TEM images of PAPT-stablized gold nanoparticles. Scale bar: (a) 20 nm, (b) 4 nm.

Table 1. Recovery and Reuse of PATP-Stabilized Gold Nanoparticle Catalysts for Suzuki−Miyaura Coupling of Chlorobenzene and Phenylboronic Acid at Reaction Time of 4 h[a]



use	1st	2nd	3rd	4th	5th	6th[c]
yield (%)[b]	87	86	85	85	84	84

[a] Chlorobenzene (2 mmol), phenylboronic acid (2.4 mmol), Au catalyst (0.05 mol %), NaOH (8 mmol). [b] GC yield. [c] Isolated yield.

The size of gold nanoparticles and the amount of PATP stabilizer are found to play important roles in determining the catalytic activity of gold nanoparticles for cross-coupling of phenylboronic acid and

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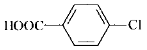
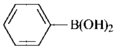
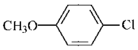
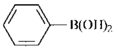
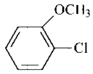
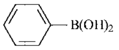
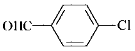
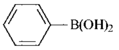
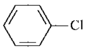
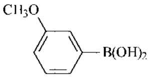
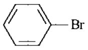
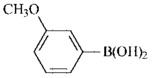
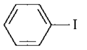
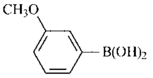
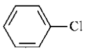
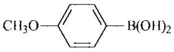
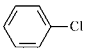
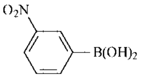
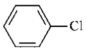
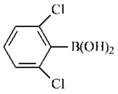
chlorobenzene. When the sizes of gold nanoparticles increase from 1.0 to 2.0 and 5.0 nm by altering the molar ratio of $HAuCl_4$ to 2-aminothiophenol, the yield decreases from 87% to 76% and 10%, respectively. On the other hand, when the size of gold nanoparticles is maintained at 1.0 nm but with considerably more stablizer, the yield is trace (Figure S4, Table S1). It is known that smaller size of gold nanoparticles will lead to higher catalytic activity, while the effect of polymer amount on the gold reactivity may be ascribed to the fact that PAPT polymer may function as a catalyst inhibitor.[28] The results revealed that precise control over the size of gold nanoparticles and thickness of stabilizer is crucial for improving the catalytic activities of gold nanoparticles for the Suzuki−Miyaura cross-coupling reaction of phenylboronic acid and chlorobenzene.

As expected, when the halides of phenyl chlorides change from chlorides to bromides and then iodides, the reactivity of phenyl halides increases and so does the yield of biphenyl. More importantly, the yield can reach 99%, as for the cross-coupling reaction between phenyl iodides and phenylboronic acids. In addition, 5 mmol scale-up reactions for phenyl halides and phenylboronic acids are also conducted, and similar yields can be given (Table S2).

Table 2. Suzuki−Miyaura Coupling of Aryl Halides and Arylboronic Acids[a]

Entry	Aryl Halide	Arylboronic Acid	Yield (%)[b]
1			95
2			92
3			91
4			95
5			74
6			82
7			90
8			81
9			79
10			56

[a] Aryl chloride (2 mmol), arylboronic acid (2.4 mmol), Au catalyst (0.05 mol %), NaOH (8 mmol). [b] Isolated yield.

Further investigations demonstrated that high yields could be obtained with aryl chlorides and arylboronic acids bearing a variety of substituents (Table 2). When hydrophilic −COOH substituent was introduced to phenyl chloride, it was expected that a high yield would be obtained as the reaction conducted in water medium (entry 1, Table 2). As for hydrophobic $-OCH_3$ substituent, high yield could also be obtained (entries 2, 3, Table 2), which might be ascribed to a combination of the hydrophobic effect of water and an interaction with the polymer support.[29,30] Besides, when activated aryl chloride was used, the yield was the highest (entry 4, Table 2) as compared with deactivated ones (entries 2, 3, Table 2). Besides substituted aryl chlorides, high yields could also be obtained with arylboronic acids bearing a variety of substituents (entries 5−9, Table 2). Furthermore, it was observed that when more than one ortho substituent were occupied, relatively low yield was obtained due to the hindering effect (entry 10, Table 2).[31]

In conclusion, we have shown that PATP polymer-stabilized gold nanoparticles are active catalysts for Suzuki−Miyaura cross-coupling reaction of aryl halides with arylboronic acids in water and air for the first time. In contrast with commonly used palladium catalyst in Suzuki−Miyaura cross-coupling reaction, comparable catalytic activity can also be achieved when using gold catalyst. This new finding will undoubtedly broaden the application of gold nanoparticles in organic catalytic reactions. Our further efforts will be devoted to evaluating the catalytic performances of the novel polymer-stabilized gold nanoparticles in other Suzuki−Miyaura cross-coupling reactions.

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Supporting Information Available: Detailed synthetic procedures for polymer-stabilized gold catalysts and Suzuki−Miyaura cross-coupling reactions, characterization for polymer-stabilized gold catalysts, et al. This material is available free of charge via the Internet at http://pubs.acs.org.

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