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# Poly (amic acid) Salt-stabilized Au-Ag Alloy Nanoparticles as Efficient and Recyclable Quasi-homogeneous Catalysts for the Imines Synthesis from Alcohols and Amines in Water

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Water-soluble Au–Ag bimetallic nanoparticles with different Au/Ag molar ratios stabilized by poly (amic acid) salt (PAAS) were synthesized by a one-pot method and characterized by ultraviolet-visible spectrophotometer (UV-vis), X-ray diffractometer (XRD), X-ray photoelectron spectroscope (XPS) and High-Angle Annular Dark Field scanning transmission electron microscope (HAADF-STEM). The Au–Ag/PAAS catalysts displayed high activity for the aerobic oxidative coupling reaction of alcohols and amines in water. Attributing to the synergistic effect between Au and Ag, the activity of the bimetallic catalysts was superior to that of the corresponding monometallic catalysts. The catalyst with an Au/Ag molar ratio of 6/1 showed the best catalytic performance, which could be easily recovered and reused without significant loss of activity for over 5 times due to the pH response of PAAS.

## Introduction

Imines, which own reactive C═N bonds, are common intermediates for the synthesis of pharmaceutically and biologically active compounds and fine chemicals.[1] Conventionally, carbonyl compounds, especially unstable aldehydes are usually required in the condensation with amines to produce imines. The necessity of dehydrating agents and Lewis acid make the reaction suffer from various drawbacks such as energy consumption and complicated operation.[2] Therefore ecological friendly synthesis of imines remains a challenge and developing an efficient and durable catalyst is highly desirable.[3] Recently, the direct synthesis of imines via oxidative coupling of alcohols with amines has received much attention as it meets the requirements of green chemistry for the following advantages: i) the starting materials are readily available; ii) molecular oxygen or air can serve as the terminal oxidant; iii) the only byproduct is water and iv) various imines can be easily obtained by choosing different starting substrates.[4] The reaction of synthesis of imines from amines and alcohols was normally thought to be divided into two steps shown in Scheme 1.[5] During the transformations, a molecular of alcohol is oxidized to corresponding aldehyde as the intermediate. Then the cross-coupling reaction occurred between amine and aldehyde to form imine, amide or other product during which selectivity depends on the nature of catalysts and reaction condition.[6]

$$R_2CH_2OH + 1/2\ O_2 \longrightarrow R_2CHO + H_2O$$

$$R_1NH_2 + R_2CHO \longrightarrow R_1{-}N{=}CHR_2 + H_2O$$

**Scheme 1.** Two step synthesis of imines from amines and alcohols.

Many homogeneous transition-metal complexes have been reported in the application of the cross-coupling of alcohols with amines. However, some problems, such as recycling, reusing strict reaction conditions and high cost of ligands, have not been well solved.[7] In contrast, owing to inherent advantages of heterogeneous systems such as high activity, convenience of handling and recovery, diverse heterogeneous transition-metal catalysts were designed to prepare imines from alcohols and amines. Among them noble metals like Pd,[8] Pt,[9] Ru,[10] and Au[11] are usually selected as the active species of catalysts. However, sometimes a high temperature is still required, while in most cases the coupling of amines with alcohols is carried out in organic solvent. Great efforts have been made for the utilization of water as solvent in the reaction by researchers. Zhang et al. reported an Au–Pd/resin catalyst which can catalyze the aerobic oxidative coupling of alcohols with amines in water phase,[3] however, low yield of imines was obtained. To improve the yield of imines in aqueous phase, Wang et al. developed an Au/HT catalyst and the highest yield of imines reached 99% under mild conditions.[12] But a drawback is that the yield of imines decreased dramatically when the catalyst was put into use for the second run.

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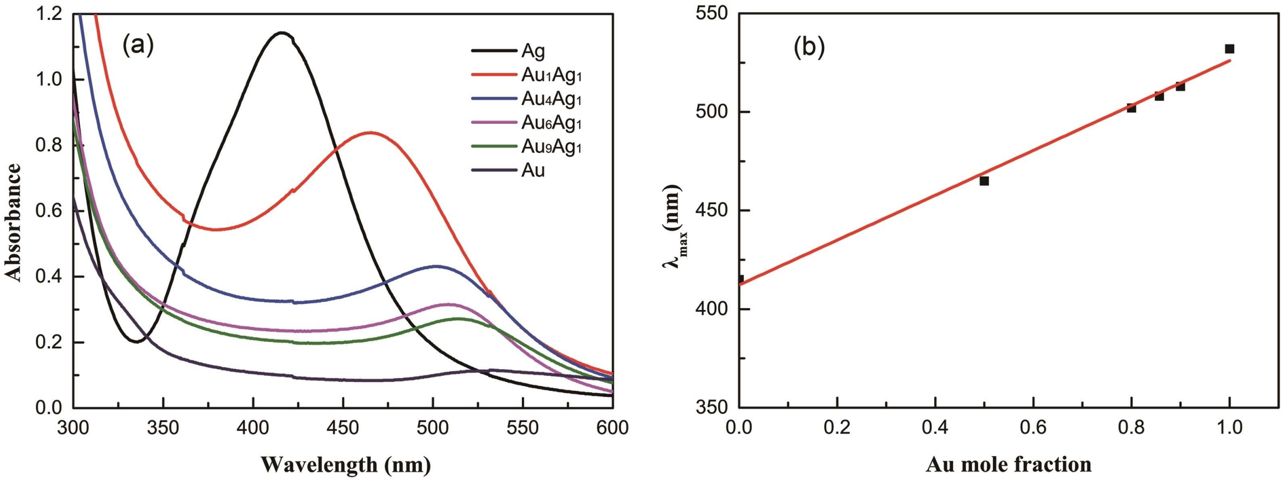


**Figure 1.** (a) UV-visible absorption spectra of Au–Ag alloy nanoparticles, (b) A linear plot of surface plasmon bands against the mole fractions of Au atoms in alloy nanoparticles.

During the past decades, bimetallic nanomaterials have attracted considerable attention due to their improved catalytic activity, selectivity, and stability derived from synergistic effects.[13] Among all the bimetallic systems, Au–Ag alloy nanostructure have a great potential in the synthesis of fine chemicals,[14] especially in catalytic oxidation reactions. In addition, the activity and selectivity of Au–Ag bimetallic nanocatalysts can be controlled via varying the Au/Ag molar ratio. Huang et al. reported selective oxidation of alcohols catalyzed by P123-stabilized Au–Ag alloy nanoparticles and the catalyst with a composition of $Au_{0.95}Ag_{0.05}$ showed the best catalytic activity and selectivity of alcohols.[15] However, to the best of our knowledge, no research of applying Au–Ag bimetallic nanocatalysts to direct synthesis of imines from alcohols and amines has been reported.

Nowadays, novel quasi-homogeneous catalysts combining the efficiency of homogeneous catalysts and the durability of heterogeneous catalysts offer the possibility of designing an efficient and durable catalyst which can catalyze the synthesis of imines under mild conditions in aqueous media. In prior work, Ag nanoparticles stabilized by pH-responsive poly (amic acid) salt (Ag/PAAS) were prepared successfully via a one-pot method.[16] The Ag/PAAS was found to have high activity for the catalytic hydration of various nitriles in aqueous medium and could be recycled and reused easily by adjusting pH of the system. In this paper, we present a one-pot synthesis of Au–Ag alloy nanoparticles stabilized by poly (amic acid) salt (Au–Ag/PAAS). The nanoparticles were applied in catalyzing the synthesis of imines via oxidative coupling of alcohols with amines under mild condition in water. The catalyst with a composition of $Au_6Ag_1$ demonstrated the highest activity and selectivity. Ascribing to its pH response, the catalyst was able to be easily recycled for 5 times at least without apparent decrease of activity after the reaction.

## Results and Discussion

### Characterization of the Ag/PAAS, Au/PAAS and Au-Ag/PAAS materials

UV-vis spectroscopy has been proved to be helpful to distinguish the structure of bimetallic particles. In case of a physical mixture of monometallic Ag and Au nanoparticles as well as system with a core-shell structure, there should appear two surface plasmon resonance (SPR) bands while exclusive peak to an alloy structure, whose position fall in between monometallic nanoparticles.[17] As shown in Figure 1(a), plasmon absorption peaks of monometallic Au and Ag nanoparticles were observed at 532 nm and 413 nm, respectively. Single absorption peaks were observed for each alloy cases. Meanwhile, the peaks in Figure 1(b) showed a red-shift linearly with the increasing of Au content. These results helped to deduce that the obtained Au-AgNPs are alloy structure.[18]

TEM image displayed in Figure S1 showed that Au–Ag bimetallic nanoparticles were typically spherical and highly dispersed in the PAAS solution proving the protective effect of PAAS chains. Clearly, all of bimetallic nanoparticles have relatively smaller sizes than monometallic ones. The sizes of $Au_6Ag_1$NPs in Figure 2(a) were collected and the statistic was displayed in Figure 2(b) with a counted diameter of 10 ± 5 nm. HAADF-STEM was employed to characterize Au–Ag bimetallic nanoparticles. It is well-known that HAADF imaging is particularly sensitive to atomic number, which could distinguish the structure of bimetal through the degree of light and shade.[19] Therefore, an alloy structure could be deduced clearly from uniform intensity distribution in the particle region in Figure 2(c).[20]

The XRD patterns for the monometallic Ag, Au and their bimetallic nanoparticles were given in Figure 3. The four peaks appearing at $2\theta =$ 38.60°, 44.22°, 64.92°, 77.72° were assigned to the (111), (200), (220) and (311) planes of the face centered cubic Ag (or Au) particles.[21] Since gold and silver have the

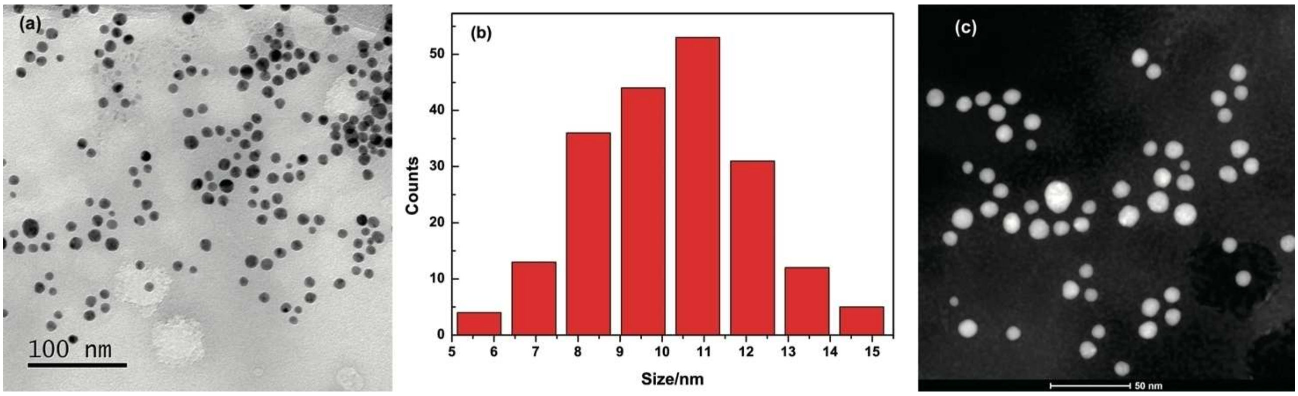


**Figure 2.** (a) TEM micrographs, (b) size distribution of $Au_6Ag_1$ nanoparticles and (c) HAADF-STEM images of $Au_6Ag_1$NPs.

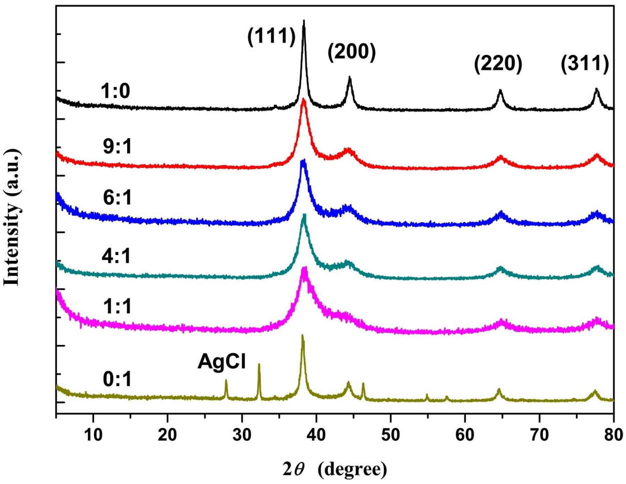


**Figure 3.** X-ray diffraction patterns of the catalysts with different composition.

same face-centered cubic (fcc) structure and almost the same lattice constant, thus, it is difficult to distinguish Au–Ag alloy from a mixture of the monometallic phases by XRD pattern. The result matches with the earlier reports.[22] Broader bands appeared for bimetallic combinations than monometallic nanoparticles, which is in accordance with the sizes comparison from TEM images. The appearance of diffraction peaks belonging to fcc AgCl species (the values of 27.90°,32.30°,46.30° and 54.99° corresponding to the (111), (200), (220) and (311) planes of AgCl in the XRD pattern of Ag/PAAS) indicated that silver ions could not be reduced completely by using piperidine as reducing agent. The phenomenon disappeared after Au ions was added simultaneously, and it could be assumed that the addition of Au catalyzed the reduction of the other kind of ions.

XPS was applied in order to evaluate the surface composition and chemical states of metal atoms in the composites. The XPS trace of Au–Ag alloy shown in Figure S2 containing peaks of both Au 4f and Ag 3d confirmed the bimetallic nature of alloy nanoparticles.[23] The binding energy (BE) values for the bimetallic Au–Ag and monometallic Au or Ag nanoparticles shown in Table 1 were in good agreement with reported literatures.[24] Firstly, zero valent state of Au and Ag atoms in alloy was actually proved. The minute shift of BE values was another indication that the Au and Ag metals have formed alloy nanoparticles rather than monometallic nanoparticles.[25] Besides, for bimetallic core-shell structure, the surface atomic composition should be exclusive. As displayed in Table 1, the surface composition analyzed by XPS changed with the different addition of Au and Ag, further indicating the formation of Au–Ag alloy rather than core-shell structure.[26] The weak peak at 200 eV only appearing on monometallic AgNPs (Figure S2) indicated the traces of AgCl, which is in accord with XRD results. The analysis of XPS spectra also confirmed the presence of polymer (C1s) as stabilizing agents of the Au–Ag alloy nanoparticles.

**Table 1.** Positions of XPS peaks and surface compositions for Au–Ag nanoparticles with different composition

| Catalysts | Au:Ag(by XPS) | Binding energy (eV) | | | |
|---|---|---|---|---|---|
| | | Au | | Ag | |
| | | $4f_{7/2}$ | $4f_{5/2}$ | $3d_{5/2}$ | $3d_{3/2}$ |
| Au | 1:0 | 84.26 | 87.86 | - | - |
| $Au_9Ag_1$ | 9.25:1 | 84.11 | 87.75 | 367.73 | 373.66 |
| $Au_6Ag_1$ | 6.22:1 | 84.06 | 87.73 | 367.71 | 373.72 |
| $Au_4Ag_1$ | 4:1 | 84.11 | 87.78 | 367.74 | 373.75 |
| $Au_1Ag_1$ | 1:1 | 83.96 | 87.60 | 367.77 | 373.80 |
| Ag | 0:1 | - | - | 368.26 | 374.29 |

## Catalytic applications for the oxidative cross-coupling of amines and alcohols

The catalytic performance of Ag/PAAS, Au/PAAS and Au–Ag/PAAS were explored by selecting the synthesis of imines via oxidative coupling of alcohols with amines under aqueous conditions as the model reaction. Firstly, the effect of the Au/Ag ratio was investigated with aniline and benzyl alcohol as substrates and the results were listed in Table 2. The reaction

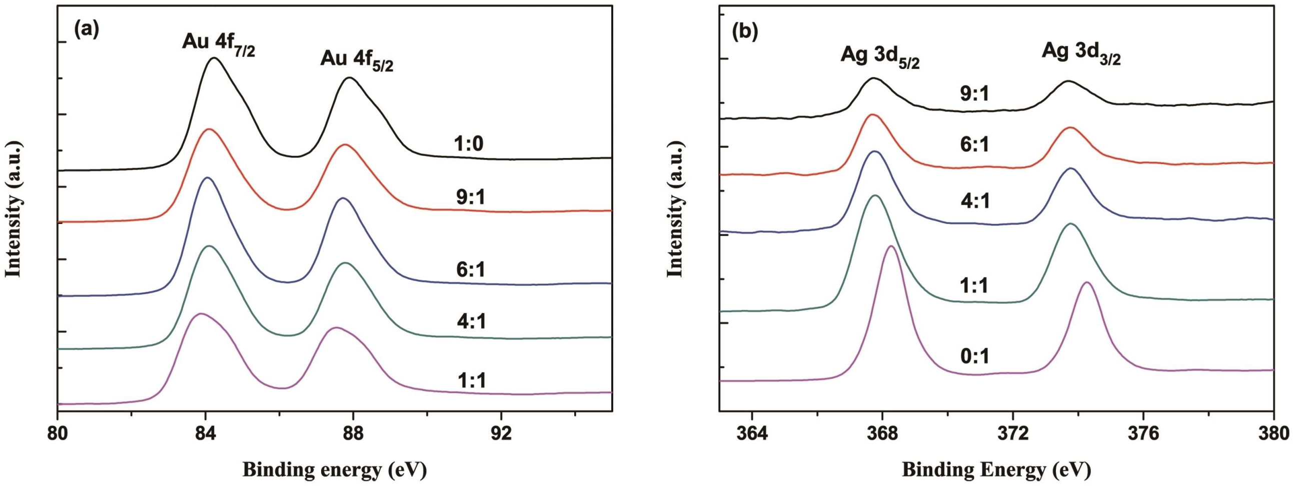
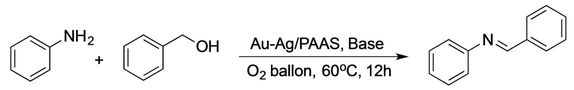


**Figure 4.** (a) and (b) XPS analysis of Au–Ag nanoparticles with different composition.

**Table 2.** Catalytic performance of Au–Ag/ PAAS on the cross-coupling of aniline and benzyl alcohol[a]



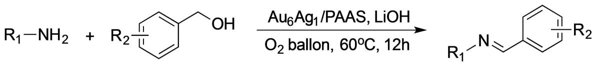
| Entry | Catalysts | Base(equiv.) | Yield %[b] |
|---|---|---|---|
| 1 | PAAS | LiOH(1.1) | <2 |
| 2 | Au/PAAS | LiOH(1.1) | 64 |
| 3 | $Au_9Ag_1$/PAAS | LiOH(1.1) | 80 |
| 4 | $Au_6Ag_1$/PAAS | LiOH(1.1) | 90 |
| 5 | $Au_4Ag_1$/PAAS | LiOH(1.1) | 52 |
| 6 | $Au_1Ag_1$/PAAS | LiOH(1.1) | 16 |
| 7 | Ag/PAAS | LiOH(1.1) | 2 |
| 8 | $Au_6Ag_1$/PAAS | KOH(1.1) | 58 |
| 9 | $Au_6Ag_1$/PAAS | NaOH(1.1) | 62 |
| 10 | $Au_6Ag_1$/PAAS | $K_2CO_3$(1.1) | 4 |
| 11 | $Au_6Ag_1$/PAAS | LiOH(0.5) | 32 |
| 12 | $Au_6Ag_1$/PAAS | LiOH(2.0) | 56 |
| 13 | $Au_6Ag_1$/PAAS | None | <1 |

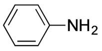
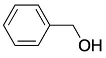
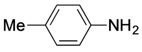
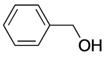
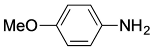
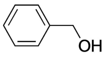
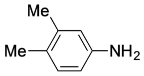
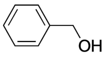
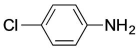
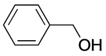
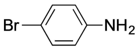
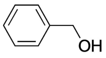
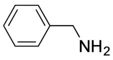
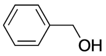
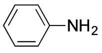
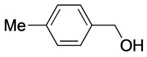
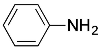
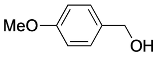
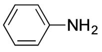
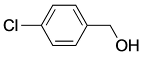
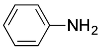
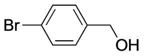
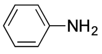
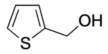
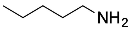
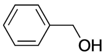
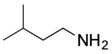
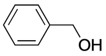
[a] aniline (0.25 mmol), benzyl alcohol (0.5 mmol), catalyst (2 mol%), $H_2O$ (2 mL). [b] The yield was detected by GC-FID according to the peak area.

did not proceed at 60 °C even after 20 h in blank PAAS solutions (entry 1), ensuring that the reaction was not catalyzed by PAAS and LiOH. When using Ag/PAAS, Au/PAAS and Au–Ag/PAAS as catalysts, the only product was N-Benzylideneaniline. The result indicated that the PAAS stabilized Au monometallic, Ag monometallic and Au–Ag bimetallic nanoparticles had a high selectivity towards imines in the oxidative coupling of alcohols with amines in aqueous phase, which is different from the results reported by other groups.[3,12] It was also found that the activity changed remarkably along with varying the composition of Au–Ag nanocatalysts. For monometallic silver and silver-rich alloy catalysts(Ag/Au≧1, entries 6 and 7), the catalyst did not perform well with a conversion less than 20%. On the other hand, for monometallic gold and gold-rich alloy catalysts (Au/Ag≧4, entrie2-5), pretty better conversion was obtained, and the best result with a 90% conversion was achieved by using the $Au_6Ag_1$/PAAS as catalyst (entry 4). In this way, a new method is provided to control the activity of the cross-coupling of amines and alcohols in water phase by tuning the Au/Ag molar ratios. Clearly, the bimetallic catalysts earned more outstanding conversion than corresponding monometallic catalysts and the result should to be attributed to the synergistic effect between Au and Ag.[14g,27] It was also found that gold-rich catalysts were much more active than silver-rich catalysts, hence Au atoms should be considered as the active species in the reaction. It is because of adding Ag to form alloy structure with Au dramatically increased the catalytic activity. In addition to the composition of metal, base is another important factor in comparison of entries 8–12 that affected reaction process as a kind of co-catalyst for the hydrolysis of imine can be inhibited to some extent by base.[11d] However, different base afforded various results and among LiOH, NaOH, KOH and $K_2CO_3$, LiOH displayed best performance with an optimal amount of 1.1 equivalent. Too much base gained lower yield of N-Benzylideneaniline but resulted more N-benzyl aniline which seemed to be more suitable to excess base in the final product.

With the adjusted optimum catalyst, the application scope of the $Au_6Ag_1$/PAAS catalyst was then examined with various combinations of amines and alcohols (Table 3). As expected, the anilines with various substituents were successfully converted to the corresponding imines by condensation with benzyl alcohol (entries1-6). The halide-substituted anilines were successfully cross-coupled with benzyl alcohol and earned a moderate conversion without dehalogenation (entries 5–6). Besides, the electron-donating substituents on the aromatic ring were more suitable for the imidization reaction than the electron-withdrawing substituents through comparing entries 2–3 with entries 5–6. The low water-solubility of halogen-substituted aniline was speculated as the reason of only 67% conversion was obtained when 4-bromoaniline was used as the started material (entry 6). Almost a full conversion was gotten when benzylamine was coupled with benzyl alcohol (entry 7).

**Table 3.** Synthesis of imines from different alcohols and amines[a]



| Entry | Amine | Alcohol | Yield %[b] |
|---|---|---|---|
| 1 |  |  | 90 |
| 2 |  |  | 91 |
| 3 |  |  | 94 |
| 4 |  |  | 95 |
| 5 |  |  | 87 |
| 6 |  |  | 67 |
| 7 |  |  | 99 |
| 8 |  |  | 92 |
| 9 |  |  | 92 |
| 10 |  |  | 94 |
| 11 |  |  | 84 |
| 12 |  |  | 89 |
| 13 |  |  | 98 |
| 14 |  |  | 99 |

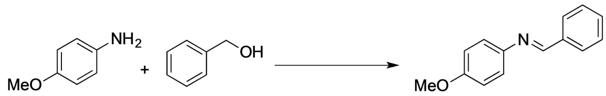
[a] alcohol (0.5 mmol), amine (0.25 mmol), catalyst (2 mol%), LiOH (0.275 mmol), $H_2O$ (2 mL). [b] The yield was detected by GC-FID according to the peak area.

Further, the reactions of anilines with different benzyl alcohols were also studied and surprising performances (entries 8–11) were shown. Excellent yields of 84–94% were recorded in the case of methyl-, methoxy-, chloro-, and bromo-substituted benzyl alcohols. The reaction between aniline and heterocyclic alcohol like 2-thiopheneethanol (entry 12) also gained good result. In addition, two kinds of aliphatic amine reacted with benzyl alcohol successfully (entries 13–14), which might provide a feasible approach for further development of imines with aliphatic groups.

Because the pH-induced precipitation-redispersion process of PAAS is highly reversible, the recycle of the Au–Ag/PAAS can be easily investigated. After the product was extracted by ethyl acetate, the optimal $Au_6Ag_1$/PAAS catalyst was separated by adjusting the pH of solution to ~2. The precipitate was collected and redissolved in 2 mL of water by increasing the pH to ~9.0 with NaOH. The catalytic activity of the recycled catalysts was examined for the imidization of benzylamine and benzyl alcohol which has earned the best yield as listed in Table 3. As shown in Figure 5a, the $Au_6Ag_1$/PAAS catalyst could be reused for five times with no significant loss of activity, indicating that the catalyst was still highly stabilized by the PAAS polymer. The 5 times recycled $Au_6Ag_1$/PAAS catalyst was characterized by TEM and the result was exhibited in Figure 5b. As TEM image illustrated, an increasement of particles sizes and the slight aggregation should be responsible for the little decline of activity in the last few recycles.

To manifest the superiority of our catalytic system, a contrastive list was shown in Table 4 to compare with other analogous reaction system. Apparently, the shortcomings of high temperature and organic solvent that goes against green chemistry were firstly spurned. Besides, that the stabilizer of nanoparticles is more accessible, and the yield is higher could be more adaptive to rapid and economic industry. To sum up, the gold and silver alloy nanoparticles supported on PAAS are a decent system deserved to develop further.

**Table 4.** Comparison of catalytic activity of the Au–Ag/PAAS catalyst in the imination with previously reported systems



| Catalysts | Temp.(°C) | Solvent | Time (h) | Yield (%) | Ref. |
|---|---|---|---|---|---|
| Pd/AlO(OH) | 90 | Heptane | 24 | 91 | [8] |
| Pt–Sn/g-$Al_2O_3$ | 138 | Ethyl benzene | 30 | 99 | [9] |
| Ru(OH)x/$TiO_2$ | 100 | Toluene | 2 | 91 | [10] |
| Au/HAP | 60 | Toluene | 2.5 | 99 | [11a] |
| Au/$Mg_2$Al-HT | 60 | Toluene | 6 | 97 | [11b] |
| Au–Pd/resin | 40 | $H_2O$ | 12 | 65 | [3] |
| Au/HT | 40 | $H_2O$ | 24 | 63 | [12] |
| **$Au_6Ag_1$/ PAAS** | **60** | **$H_2O$** | **12** | **94** | **This work** |

## Conclusions

In conclusion, PAAS stabilized Au–Ag bimetallic nanocatalysts were developed successfully. The catalysts demonstrated high and tunable activities, a wide substrate scope and good reusability for oxidative coupling of alcohols and amines to synthesize imines in water phase. The $Au_6Ag_1$/PAAS catalyst showed the best catalytic performance. Moreover, the pH sensitivity of PAAS afforded a reversible precipitation–redispersion switch, allowing efficient recovery and recycling of the nanoparticles. The catalyst could be reused for five runs without significant loss of catalytic activity. The synergistic interplay between Au and Ag revealed in this work may offer a new guide in the green synthesis of fine chemicals.

### Supporting Information Summary

The experimental details, TEM images and XPS survey scan of all the prepared Au–Ag nanoparticles, GC-MS spectra for the imines products.

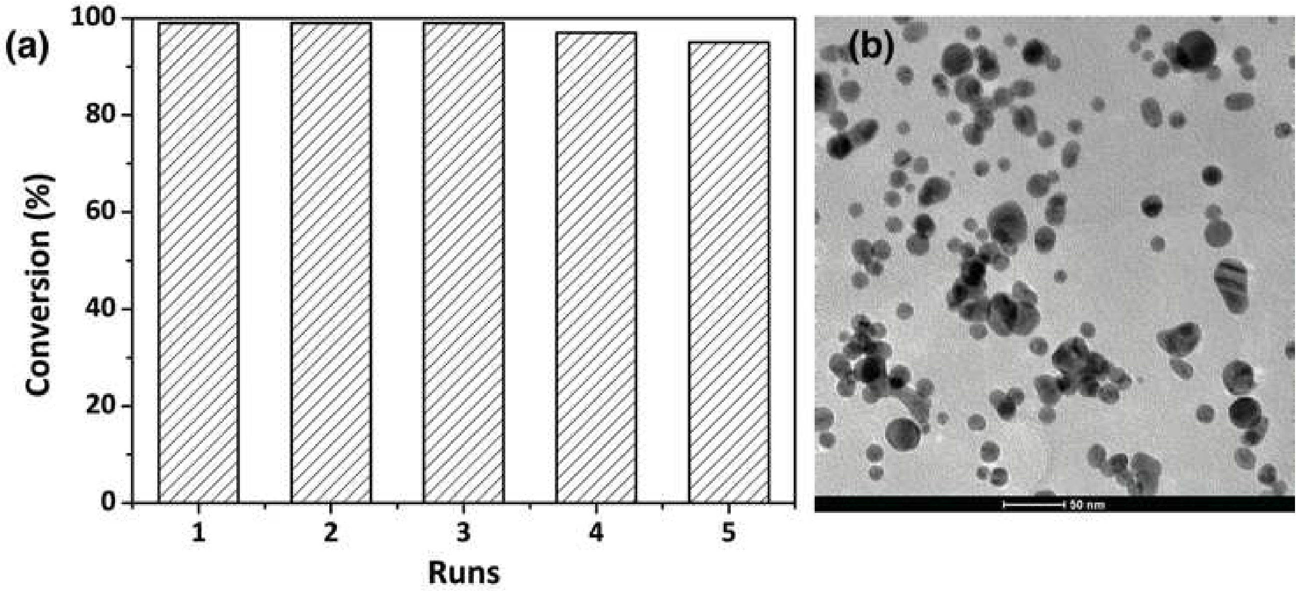


**Figure 5.** (a) Reuse of the $Au_6Ag_1$/PAAS catalyst for the condensation of benzylamine and benzyl alcohol, (b) TEM image of $Au_6Ag_1$/PAAS catalyst after 5 times recycling. Reaction conditions were identical to those indicated in Table 3 (12 h reaction time in each cycle).

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## *Conflict of Interest*

The authors declare no conflict of interest.

**Keywords:** alloy · imines · nanoparticles · poly(amic acid) salt · quasi-homogenous

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