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# A novel, practical and green synthesis of Ag nanoparticles catalyst and its application in three-component coupling of aldehyde, alkyne, and amine

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**Abstract**

Ag nanoparticles were synthesized in PEG with simple bubbling of $H_2$, and were used to catalyze the three-component coupling reaction of aldehyde, alkyne, and amine with good to excellent yields in one pot.


*Keywords:* Ag nanoparticles; PEG; Three-component coupling reaction; One pot synthesis

## 1. Introduction

As compared to bulk materials, nanoscale materials exhibit large surface areas and size-dependent quantum confinement effects. They often have distinct electronic, optical, magnetic, chemical, and thermal properties [1–3]. The literature is rich with examples where metallic nanoparticles exhibit excellent catalytic activities. For example, Pd nanoparticles show very high catalytic activities in some reactions [4–9]. Unsuspiciously nanoparticles can be employed as heterogeneous catalyst and be recycled [10]. Silver nanoparticles which can be employed as building units for the "bottom-up" assembly and construction of architectures [11–14] and can be used to transform chemisorbed allyl into allene [15]. So it is important to develop new methods for synthesizing this nanosilver particles and find new reactions which can be applied.

PEG has been widely applied in the pharmaceutical and biomedical industries as prodrugs. Ethylene glycol and diols can be used as a reducing agent to prepare metal particles through the so-called polyol process [16–17]. Compared with the major reducing agents reported to date for the preparation of metal nanoparticles such as hydrazine, sodium borohydride, and DMF, ethylene glycol is an environmentally benign material. Recent reports show that PEG is an efficient, recyclable reaction medium for the Heck reaction, catalytic hydrogenations and asymmetric dihydroxylation reactions [18–21].

Three-component coupling of aldehyde, alkyne, and amine (A3 coupling) via C–H activition in water has been developed by several groups [22]. Generally these reactions are catalyzed by Cu(I) [23], Ag(I) [24] and Au(I) [25], showing very high yields. Li et al. also reported A3 coupling via C–H activition in ionic liquid catalyzed by Ag(I) [26]. However, aromatic aldehydes were not suitable for the A3 coupling in ionic liquid.

Here we wish to report the development of a novel, practical and green A3 coupling using silver nanoparticles in PEG the synthesis of Ag nanoparticles and reaction was finished in one pot. Furthermore, we demonstrate the possibility of recycling and reuse of catalyst and PEG.

## 2. Experimental

### 2.1. Preparation of silver nanoparticles

The preparation of silver nanoparticles was quite straightforward. In a typical preparation, 17 mg $AgNO_3$ was added into 20 ml PEG (400 Da) and the mixture were stirred with bubbling of $H_2$ at room temperature. The resulting solution was stirred at room temperature for 10 h. The transparent solution converted to the characteristic pale pink or gray-black color, which indicated

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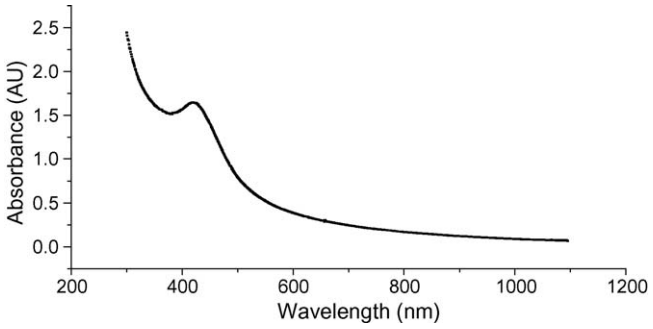



Fig. 1. The UV–vis absorption spectrum of Ag nanoparticles in PEG.

the formation of silver nanoparticles. The UV–vis absorption spectrum of the sample after 20 h, shows the plasmon absorption of these Ag(0) particles in 419 nm [27] and no clearly absorption of $Ag^+$ [28] (Fig. 1).

A typical transmission electron microscope (TEM) image and the corresponding electrondiffraction pattern of the nanoparticles on a carbon-coated copper TEM grid are presented in Figs. 2 and 3, respectively. In general, the particles are sphere in shape. These figures demonstrate the formation of Ag nanoparticles through reduction inside the PEG.

### 2.2. Catalyst characterization

All reactions were carried out under argon. Reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel. All aldehydes and alkene were purchased from Acros or Fluka. $^1H$ and $^{13}C$ NMR spectra were measured on a Bruker Am 300M (NMR in $CDCl_3$ with TMS as an internal standard) spectrometer. IR spectra were obtained on a Nicolet Avatar 360 FT-IR spectrometer. MS data were obtained by a HP 5890 and ZAB-HS apparatus.

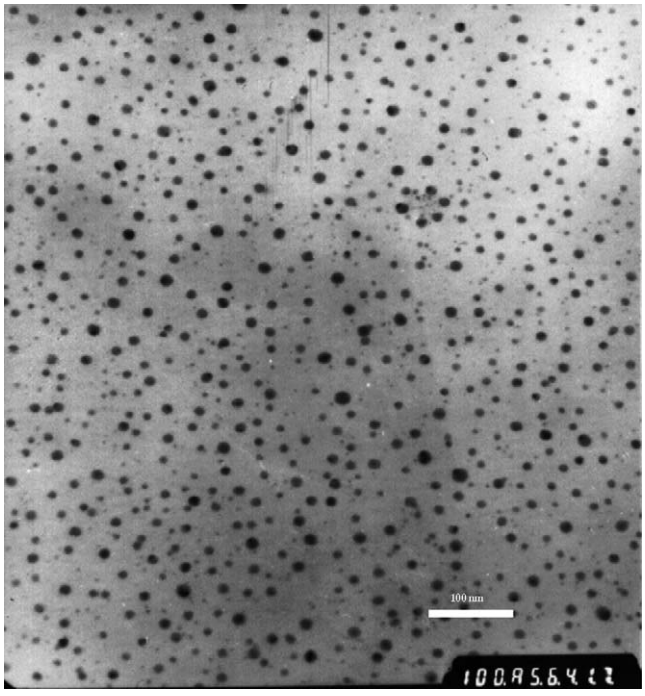



Fig. 2. Transmission electron micrograph of silver nanoparticles, the scale bar: 100 nm.

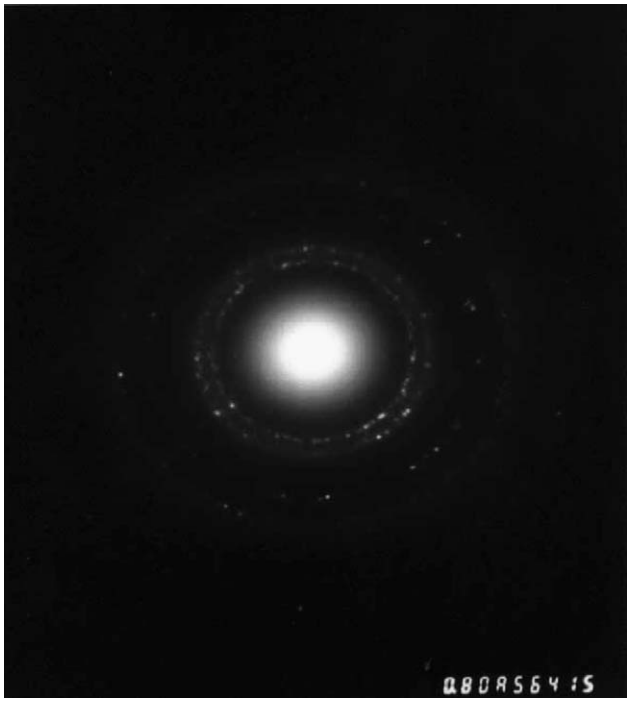


Fig. 3. The corresponding electron diffraction pattern.

### 2.3. A representative procedure for A3 reactions

PEG nanosilver colloid (2 ml), drew out using an injector, was mixed with aldehyde, alkyne, and amine. The mixture was cooled to room temperature after stirring for 10 h at 100 °C and the product was isolated by extraction with ether (5 × 10 ml). The organic layers were combined, and washed with a small amount of brine, and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent and purification of the crude product by column chromatography yielded the desired product.

## 3. Results and discussion

The TEM images of nanoAg prepared at room temperatures using PEG 400 for 10 h demonstrated that the Ag nanoparticles were separated widely and did not agglomerate. Relatively narrow size distributions were also apparent for the products. The average size of silver nanoparticles was in the range from 8 to 10 nm.

PEG nanosilver colloid (2 ml) was mixed with cyclohexanecarboxaldehyde, phenylacetylene, and pyrrolidine. Stirring 10 h at 100 °C gave the corresponding propargylamine in 95% yield. The recycling of the mother liquor and the catalyst was examined (Table 1). Five millimole scope aldehyde, 1% catalyst and 10 ml PEG were used, and the coupling reaction was repeated three times. Each time after the extraction, the mother liquor was dried at 100 °C for 1 h under reduced pressure. The result showed that every time the yield was excellent while the

Table 1
The recycling of the mother liquor and the catalyst

| | Run 1 | Run 2 | Run 3 |
|---|---|---|---|
| Reaction time (h) | 10 | 12 | 15 |
| Isolated yield (%) | 95 | 96 | 94 |

Isolated yield is based on aldehyde; reactions were carried out on a 5 mmol scale with aldehyde/amine/alkyne = 1:1.1:1.2 and 1% catalyst, 100 °C, 10 ml of PEG.

reaction time was delayed. We supposed that this result was induced by the conglomeration of silver nanoparticles which was size-dependent. The TEM images of silver nanoparticles after three times repeated reactions are presented in Figs. 4–6. Clearly there were conglomeration of silver nanoparticles after repeated reactions and self-assembled belts appeared (Fig. 6, Scheme 1).

Various aldehydes, alkynes, and dialkylamines were similarly coupled and the results are summarized in Table 2. Both aromatic and aliphatic aldehydes were able to undergo addition to afford the corresponding propargylicamines effectively. While no products were obtained with crotonaldehyde (entries 11 and 12), aromatic and aliphatic aldehydes, cyclic secondary amines and two terminal alkynes reacted efficiently in these conditions. However, the reaction was found to be highly affected by the

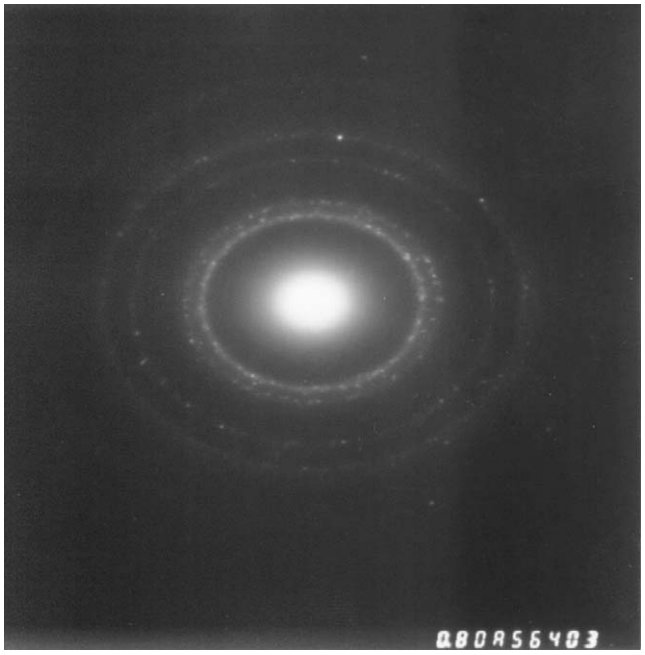


Fig. 5. The corresponding electrondiffraction pattern.

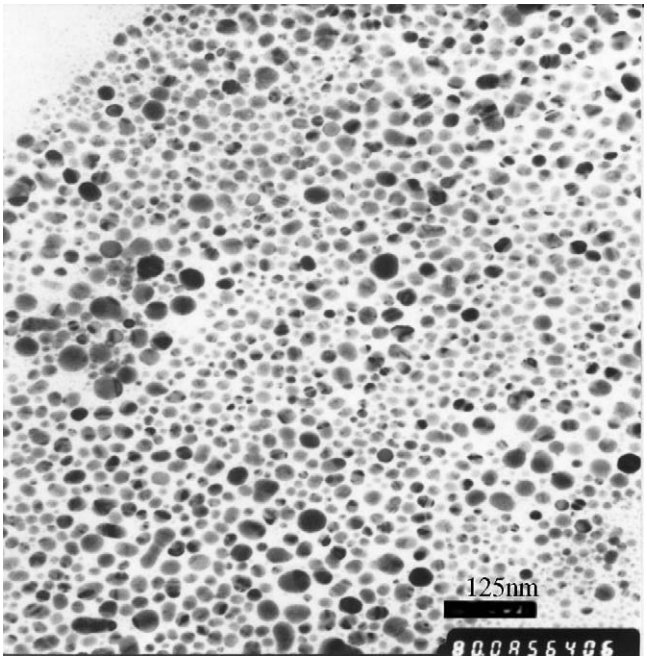



Fig. 4. Transmission electron micrographs of silver nanoparticles, after three times repeated runs the scale bar: 125 nm.

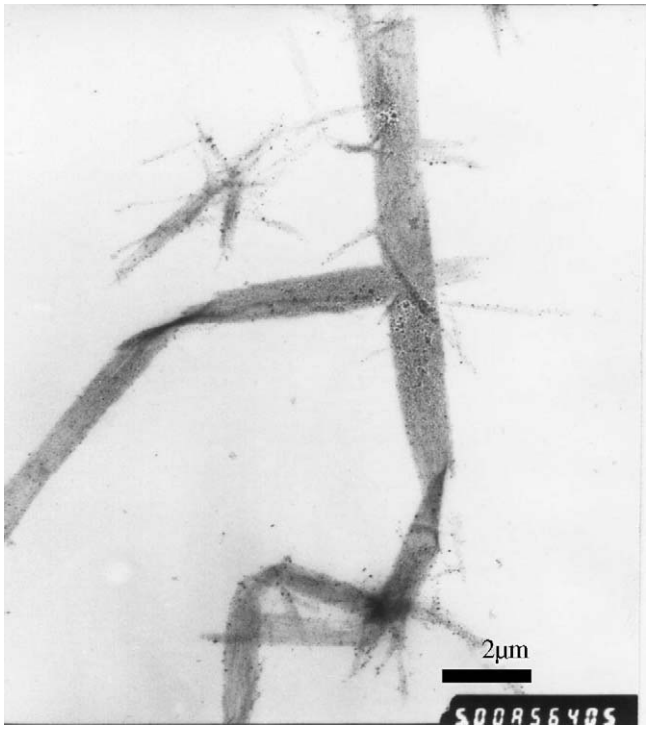
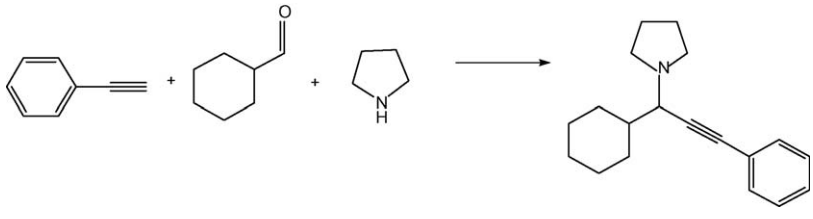
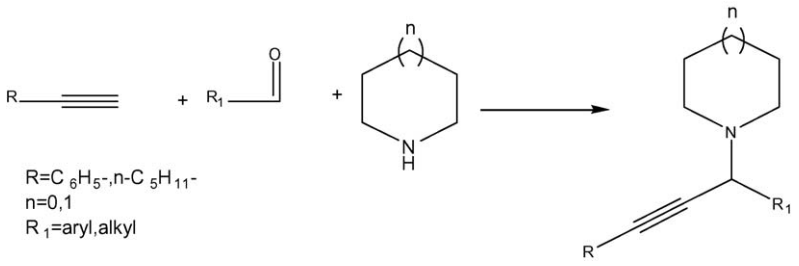



Fig. 6. Transmission electron micrographs of silver nanoparticles, after three times repeated runs the scale bar: 2 μm).




Scheme 1.




Scheme 2.

nature of the aldehyde. Aromatic aldehyde showed low reactivity for the reaction, giving lower yields. So longer reaction time and more catalyst were required. Aliphatic aldehydes, on the other hand, displayed high reactivity and high selectivity for the desired product; no by-product was found in these reactions (Scheme 2).

The above experiments shed some light on the cross-coupling mechanism with the Ag nanoparticles catalyst. Although we did not have a detailed mechanistic scheme yet, the mechanism was certainly different from that of $Ag^+$, $Au^+$ proposed by Li [24,25]. A tentative mechanism was proposed involving the absorption of alkyne followed by the insertion of an Ag nanoparticles into the C–H bond (Fig. 7). The alkenyl-Ag intermediate then reacted with the iminium ion generated in situ from aldehydes and secondary amines to give the corresponding propargylamines

Table 2
Coupling of aldehyde, alkyne, and amine by Ag nanoparticles in PEG

| Entry | R | $R_1$ | *n* | Time (h) | Yield% |
|---|---|---|---|---|---|
| 1 |  |  | 0 | 20 | 86[a] |
| 2 |  |  | 1 | 20 | 77[a] |
| 3 |  |  | 0 | 10 | 97 |
| 4 |  |  | 1 | 10 | 95 |
| 5 |  | $n$-$C_7H_{15}$– | 0 | 10 | 88 |
| 6 |  | $n$-$C_7H_{15}$– | 1 | 10 | 86 |
| 7 |  |  | 0 | 10 | 95 |
| 8 |  |  | 1 | 10 | 97 |
| 9 | $n$-$C_5H_{11}$– |  | 0 | 10 | 90 |
| 10 | $n$-$C_5H_{11}$– |  | 1 | 10 | 88 |
| 11 |  |  | 0 | 20 | nr[b] |
| 12 |  |  | 1 | 20 | nr[b] |

Isolated yield is based on aldehyde; reactions were carried out on a 1 mmol scale with aldehyde/amine/alkyne = 1:1.1:1.5 and 1% catalyst, 100 °C, 2 ml of PEG.
[a] 2% catalyst, 4 ml of PEG were employed.
[b] No desired product was obtained.

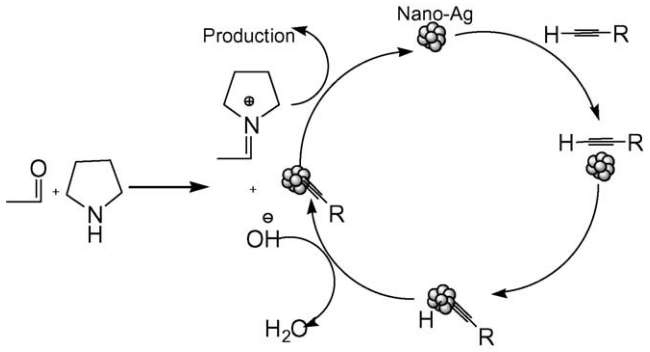



Fig. 7. Probable mechanism of the A3-coupling catalyzed by Ag nanoparticles.

and to regenerate the Ag nanoparticles catalysts for further reactions.

## 4. Conclusion

We have developed a novel, practical, green method for the synthesis of Ag nanoparticles and used them for three-component coupling of aldehyde, alkyne, and amine in one pot. This simple process provided a diverse range of propargylamines in high yields. Investigations of the scope and asymmetric catalysis of this reaction are now in progress in our laboratory.

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