

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 H₂, and were used to catalyze the three-component coupling reaction of aldehyde, alkyne, and amine with good to excellent yields in one pot.

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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]. Unsuspectingly 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 activation 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 activation 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 AgNO₃ was added into 20 ml PEG (400 Da) and the mixture were stirred with bubbling of H₂ 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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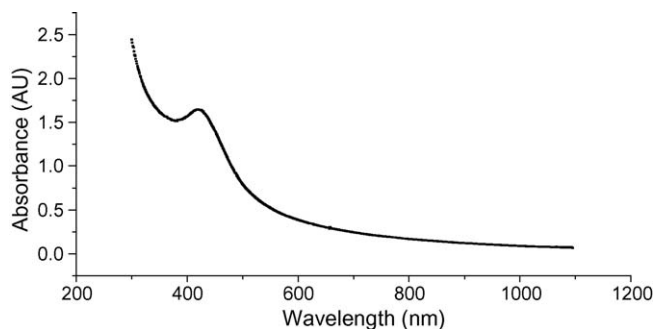


Fig. 1. The UV–vis absorption spectrum of Ag nanoparticles in PEG.

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 electron diffraction 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 ¹³C NMR spectra were measured on a Bruker Am 300M (NMR in CDCl₃ with TMS as an internal standard) spectrom-

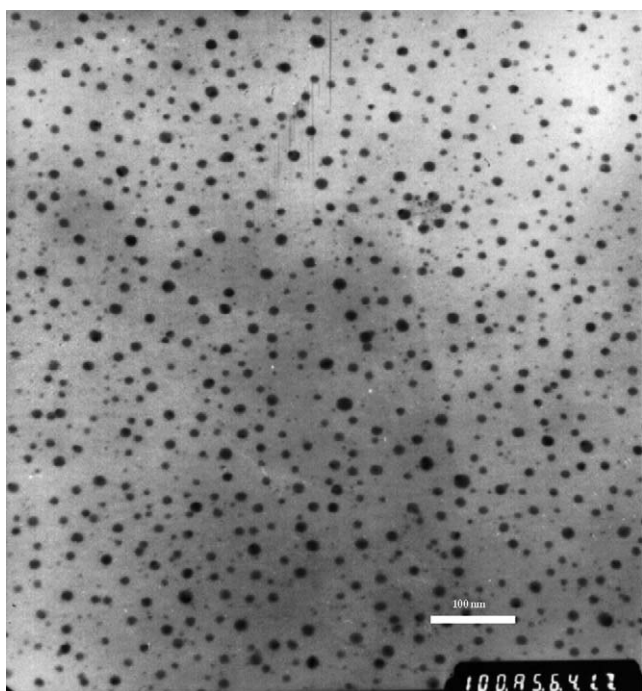


Fig. 2. Transmission electron micrograph of silver nanoparticles, the scale bar: 100 nm.

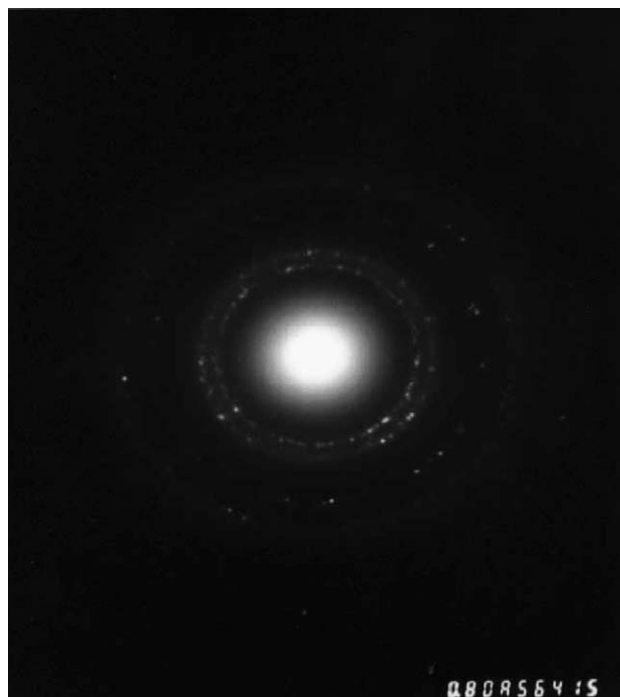


Fig. 3. The corresponding electron diffraction pattern.

eter. IR spectra were obtained on a Nicolet Avatar 360 FT-IR spectrometer. MS data were obtained by a HP 5890 and ZAB-HS apparatus.

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 Na₂SO₄. 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

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