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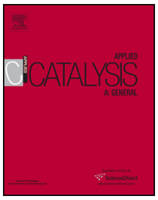

AuFeAg hybrid nanoparticles as an efficient recyclable catalyst for the synthesis of α,β- and β,β-dichloroenones

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ABSTRACT

A facile and green pioneer approach for the synthesis of stable trimetallic AuFeAg hybrid nanoparticles is described. This synthetic method is green-chemistry compatible and totally free of additives. The particle shape and size, surface chemistry, crystallinity, elemental composition, thermal and magnetic properties were investigated. The catalytic performance of the synthesized nanoparticles is also described. The hybrid nanocatalyst exhibited strong catalytic activity for the synthesis of α,β- and β,β-dichloroenones, which are important synthetic intermediates in the preparation of natural products. The reason behind the catalytic performance of nano sized hybrid particles was attributed to their high specific surface area. In addition, the nanocatalyst was easy to separate from the reaction mixture using an external magnet and could be reused for five consecutive reactions without any significant loss of activity. Using the present method, the trimetallic hybrid combination can be designed for similar types of catalytic reactions.

1. Introduction

Hybrid nanoparticles with multifunctional materials accommodate a wide range of nanoscale domains into a single system that can exhibit enhanced properties, which are not available from their individual components. Heterogeneous hybrid nanoparticles with multiple domains in an epitaxial arrangement possess unique catalytic [1], magnetic [2], electronics [3], and optical properties [4]. Owing to its intrinsic robustness and potential feasibility, hybrid nanoparticles (NPs) have been developed and applied extensively in different technological fields. To synthesize these hybrid nanoparticles, one particle nucleates directly on the surface of another particle [5,6].

Many attempts have been made to synthesize multimetallic NPs because of their multiple advantages, including high selectivity and chemical/physical stability, compared to its monometallic components [7–10]. The properties of multimetallic NPs are affected entirely by their shape, similar to that of monometallic NPs. Moreover, the particle shape can determine the overall catalytic properties of NPs due to the different forms of exposed planes on their surfaces [11–13].

The authors' interest in developing a mild and efficient methodology to synthesize a variety of α, β-dihaloenones prompted the present study to search for more convenient and safer catalysts. To the best of the authors' knowledge, there are no reports on the phytosynthesis of AuFeAg hybrid nanoparticles and its catalytic application to synthesize α,β- and β,β-dichloroenones. Here the author's have used *Astragalus membranaceus* root extract for the synthesis of hybrid nanoparticles.

A. membranaceus (Fabaceae) is a perennial plant distributed widely in China and Korea and roots of it used mostly for immune stimulators and as a traditional medicine for anti-diabetic. The root of *A. membranaceus* contains several electron-rich molecules including saponins, polysaccharides, flavonoids, isoflavonoids, and sterols [14,15].

Molecules bearing α- and β-haloenones exist in nature and have potent biological activities [16–18]. They are important synthetic intermediates because a range of substituents can be installed at their α- and β-positions to synthesize biologically active natural products [19,20]. Because of their importance and utility, a range of synthetic methods have been developed for α- and β-haloenones [21,22]. The synthetic procedures for α-haloenones generally utilize halogenation–dehydrohalogenation [23], an addition–elimination [24], or halohydrin dehydration [25]. Recently, a number of synthetic approaches have been reported for β-haloenones, such as the Brønsted acid-promoted cyclization of 1-siloxy-1,5-diynes [26] and the halogen-induced 1,2-silyl migration reaction [27]. In addition, the 3-step synthetic route to α, β-dihaloenones from cyclohexane-1,3-dione has been reported [28]. Many methods for the synthesis of β-dichloroenones and α,

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β-dichloroenones have been well discussed, but these approaches have several shortcomings, such as the mixtures of products, low yields, low regioselectivity, and long reaction times.

Recently, to develop a protocol, we have reported on the synthesis of α,β- and β,β-dichloroenones by Ru(II)-catalyzed reactions of diazodicarbonyl compounds [29]. However, there is still a demand for novel and enhanced synthetic routes involving readily available and environmentally benign recyclable catalysts that efficiently provide a variety of α,β- and β,β-dichloroenones.This paper reports a facile and green approach for the synthesis of AuFeAg hybrid nanoparticles using *A. membranaceus* root extract as both the reductant and capping agent. The synthesized nanoparticles were used as catalysts for the synthesis of α,β- and β,β-dichloroenones from a diazodicarbonyl compound and oxalyl chloride.

2. Experimental

2.1. Materials and methods

Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%), iron (III) oxide (Fe_2O_3, 99%), and silver nitrate ($AgNO_3$, 99%) were obtained from Sigma-Aldrich. Oxalyl chloride and fluorobenzene were purchased from Tokyo Chemical Industries Co. Ltd. All chemicals were used as received. The air dried roots of *A. membranaceus* was obtained at a market in Yeongchon, South Korea. The *A. membranaceus* root extract was prepared using a previous method [30]. 6 g of the powdered roots was added to 300 mL of deionized Milli-Q water, boiled for 10 min and filtered.

2.2. Synthesis of AuFeAg hybrid nanoparticles

A volume of 10 mL of the root extract solution was added to 100 mL of an aqueous solution of 0.5 mmol Fe_2O_3 and sonicated for 1 h. After 1 h, the color of the solution changed to dark brown. To the solution, 5 mL of an aqueous solution of 2.0 mmol $AgNO_3$ was added and sonicated for 1 h. After 1 h, the color of the solution changed to dark blue, indicating the formation of FeAg nanoparticles. Again, 5 mL of an aqueous solution of 1.0 mmol $HAuCl_4$ was added and sonicated for 1 h at 60 °C. The color of the final solution changed to dark purple, indicating the formation of AuFeAg nanoparticles. The synthesized nanoparticles were isolated by centrifugation (10,000 rpm, 4 °C and 20 min) and purified twice by the addition of water, centrifuged and removed the supernatant.

2.3. UV–visible analysis of total phenolic acid present in A. membranaceus

The total phenolic acid present in *A. membranaceus* extract was determined by Folin–Ciocalteu's calorimetric method [31]. 1.5 mL of diluted Folin—Ciocalteu's reagent (2/20) was added in 1.0 mL of root extract, and allowed to stand for 5 min at room temperature. Then 1.5 mL of 7% sodium carbonate (w/v) was added to the mixture to neutralize it and kept in the dark at room temperature for 60 min. The absorbance was taken at 760 nm against a reagent blank. The result was expressed in grams of gallic acid equivalent (GAE)/(100 g dried weight of root).

2.4. Characterization of AuFeAg hybrid nanoparticles

The surface plasmon resonance was monitored using an Optizen 3220 (Double beam) UV–vis spectrophotometer with a quartz cuvette and distilled water as a reference. The Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FTIR spectrometer in transmittance mode over the range of 400 - 4000 cm^{-1} and the samples were prepared by adding ~2 mg of dry powder with 200 mg of KBr to produce pellets for both the extract and nanoparticles. X-ray diffraction (XRD) was performed using powdered samples on a PANalyticalX'PertPRO MPD (operating at 40 kV and 30 mA with Cu Kα as the X-ray source ($\lambda = 1.5406$ Å) over the 2θ angle range, 20–90°, and a scanning rate of 1.2°/min). The size of the nanoparticles was assigned by field emission transmission electron microscopy (FE-TEM, FEI Tecnai F20). The samples were prepared by placing a drop of the nanoparticle solutions on carbon-coated copper grids and allowing the solvent to evaporate in air at ambient temperature. The elemental make-up of the bimetallic nanoparticles was analyzed by high-angle annular dark-field scanning TEM energy-dispersive X-ray spectroscopy (HAADF-STEM-EDS) at 200 kV with a point resolution of 0.24 nm, a Cs and Cc of 1.2 mm each and focal length of 1.7 mm, using a Genesis liquid nitrogen cooled EDS detector with an ultrathin window. The magnetic susceptibility and magnetization were investigated with by quantum design vibrating sample magnetometry (VSM Lake Shore Cryotronics, Inc., Idea-VSM, model 662 with 735 VSM controller) at room temperature in an applied magnetic field sweeping from −10 kOe to 10 kOe. The thermal properties of the nanoparticles were analyzed by thermogravimetric analysis coupled with differential scanning calorimetry (DSC-TGA, SDT-Q600 V20.5 Build 15) and heated under N_2 atmosphere to 700 °C at a heating rate of 10 °C min^{-1}. Atomic force microscopy (AFM, XE-100) has been assigned for sample surface characterization. AFM images were processed at resolution x, y: 0.1 nm and z: 0.01 nm. The composition of the nanoparticles and the chemical state of each element were analyzed by x-ray photoelectron spectroscopy (XPS) using a Thermo scientific, K-Alpha system fitted with an Al Kα X-ray light source. The ion source energy was 100 V to 3 KeV for the survey. Zeta-potential measurements were performed using a Malvern Zetasizer. The sample was equilibrated for 2 min at 25 °C and repeated three times for consistent results.

2.5. Catalytic activity

The resulting AuFeAg hybrid nanoparticles were used as a catalyst for the synthesis of α,β- and β,β-dichloroenones by reactions of diazodicarbonyl compound and oxalyl chloride.

2.5.1. General procedure for the synthesis of α,β- and β,β-dichloroenones

AuFeAg-NPs (3.5 mg, 1.0 mol.%) were added to a solution of cyclic or acyclic diazodicarbonyl compound (1.0 mmol) and oxalyl chloride (1.5 mL) in PhF (5.0 mL) at room temperature. The reaction mixture was stirred at 50 °C for 3 h or at room temperature for 5 h until the reaction was completed, as indicated by TLC. The solvent was evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel with n-hexane/EtOAc (20:1) to give the product.

2.5.2. General procedure for the large scale synthesis of α, β-dichloroenones

AuFeAg-NPs (35 mg, 10.0 mol.%) were added to a solution of diazodicarbonyl compound **1a** (10.0 mmol, 1.660 g) and oxalyl chloride (15 mL) in PhF (10.0 mL) at room temperature. The reaction mixture was stirred at 50 °C for 3 h until the reaction was completed, as indicated by TLC. The solvent was evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel using n-hexane/EtOAc (20:1) to give the product **2a** (1.785 g, 93%).