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Full Length Article

Polymer supported gold nanoparticles: Synthesis and characterization of functionalized polystyrene-supported gold nanoparticles and their application in catalytic oxidation of alcohols in water

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ABSTRACT

Sulfonated polystyrene microsphere were functionalized using ethylene diamine to introduce amine groups to the polymer chains. The amine functionalized polymers were used as a support for gold nanoparticles. A thorough structural characterization has been carried out by means of transmission electron microscopy (TEM), scanning electron microscopy (SEM) images, EDS, CHN and atomic absorption spectroscopy. The polymer supported gold nanoparticles was found to be an efficient catalyst for the oxidation of alcohols in water.

1. Introduction

Hybrid composites of colloidal microsperes with metal nanoparticles have attracted much attention due to their uses in photonic crystal, surface-enhanced Raman scattering and plasmon resonance [1–5]. Amongst the various microsperes that are used for the immobilization of metal nanoparticles, polymeric supports have attracted much attention [6–8]. These supports can be easily functionalized with organic groups such as thiols, phosphines, carboxylic acids and amines [9,10]. In addition to the aforementioned advantages, the facile preparation in desired shape and size make the polymers as a promising support for the immobilization of metal nanoparticles for catalytic application, fluorescent probes for visualizing biological processes, immobilization of cells and enzymes, magnetic resonance imaging and thermotherapy agents for the diagnosis of many diseases [11–15]. Polystyrene is one of the most used polymers due to its easy availability, affordable price, chemical inertness and ability to be functionalized easily. Gold nanoparticles have been in focus of both academic and industrial research in the past few decades due to their unique properties in various fields ranging from catalysis, electrocatalysis and optical kits for cancer therapy and drug delivery [16–20]. Moreover studies have shown that gold nanoparticles stabilized on polymeric supports have more catalytic activity compared to other supports [21]. The fabrication of gold nanoparticles on colloidal microsphere polymers can be achieved in a number of various methods which a chemical reduction is most commonly and convenient.

In contrast to the widely studied gold nanoparticles coated on various functionalized polymers [22–25], relatively few papers have been reported on the preparation of controlled size of nano gold particles on simple functionaolized polymer micospheres [26], although there is evidence that these nanocomposites are applicable in oxidation reaction of alcohols [27–30]. Recently, Wang et al. reported preparation and applications of gold nanoparticles on silver seed coated sulfonated polystyrene microsphers for SERS application [6]. Most recently, Ritcey et al. reported a novel method for the coating of gold nanoparticles on thiol-terminated polystyrene chains at air-water interface [31].

In this study, we report preparation and characterization of a novel polystyrene microsphere supported gold nanoparticles. The polymer supported gold nanoparticles was also applied as a catalyst for the aerobic oxidation of benzyl alcohol in water.

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2. Materials and methods

2.1. Preparation of monodispersed polystyrene (PS) microspheres

Polystyrene (PS) beads were obtained according to reported method by Wang etal. [6] with slight modification. Styrene (5 mL) was added to a mixture of H_2O/EtOH (1:9 v/v, 25 mL) in three necked flask. Then PVP (0.21 gr) and AIBN (0.0517 gr) were added and the mixture was deoxygenated with bubbling with N_2 for 10 min. The mixture was kept at 70 °C for 8 h under N_2 atmosphere with continuous stirring. Finally obtained particles were separated from reaction mixture by centrifuging at 6000 rpm for 10 min and washed repeatedly with ethanol and water.

2.2. Preparation of chlorosulfonated PS (CS-PS)

CS-PS beads were obtained by treatment of PS with chlorosulfonic acid according to reported method by Bicak etal. [32].

2.3. Amination of chlorulfonated PS

Chlorosulfonated PS (0.2 gr) were dispersed in 20 mL of NaOH solution (5%) by ultrasonic. Ethylenediamine (1.2 mL) was added to the reaction mixture and the mixture was allowed to take place at ambient temperature for 12 h under magnetic stirring. Finally amine functionalized PS ($PSNH_2$) particles were separated by centrifuging (6000 rpm, 10 min) and washed three times with water.

2.4. Preparation of gold nanoparticles coated on $PSNH_2$ microspheres (AuNPs@$PSNH_2$)

AuNPs@$PSNH_2$ were preapred by in-situ reduction method [33]. $PSNH_2$ (0.2 gr) in distilled water (20 mL) was dispersed for 5 min by ultrasonic. $HAuCl_4{\cdot}3H_2O$ aqueous solution (1.5×10^{-2} M, 5 mL) was added dropwise into the mixture and the mixture was stirred for 12 h at room temperature. The ice-cooled $NaBH_4$ solution (5 mL, 4.7×10^{-2} M) was added dropwise to the reaction mixture with vigorous stirring for 1 h to reduce gold ions. The resulting AuNPs@$PSNH_2$ were purified by centrifuging (6000 rpm, 10 min) and washed three times with deionized water.

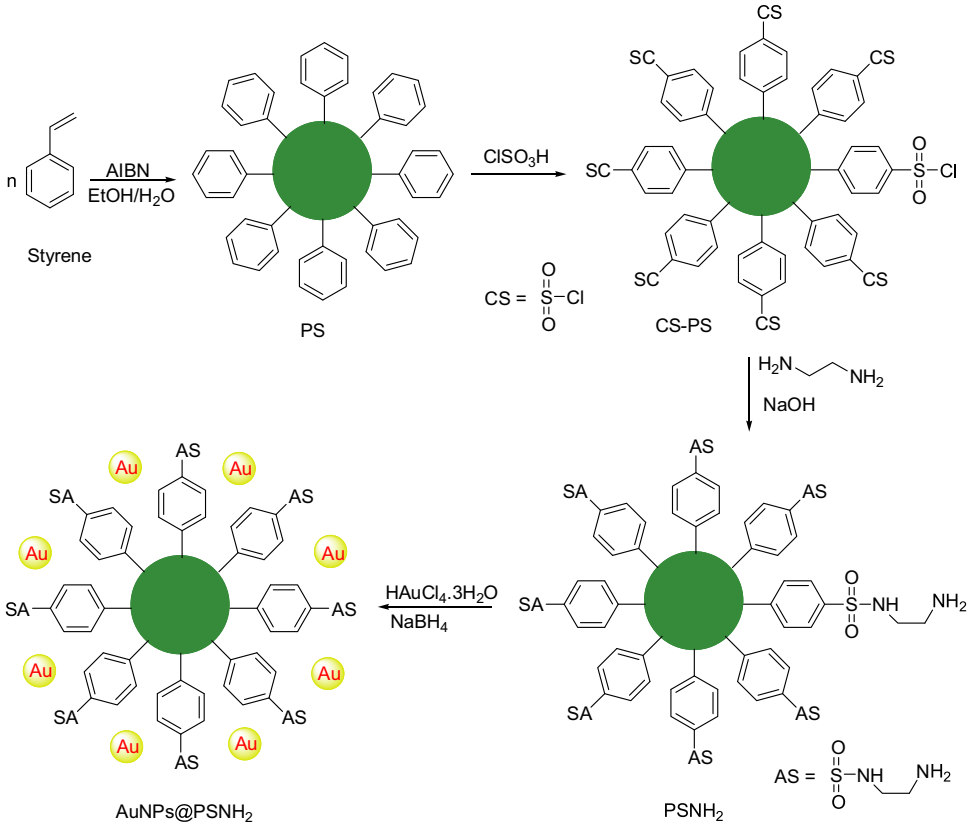
2.5. Oxidation of benzyl alcohol catalysed by AuNPs@$PSNH_2$

AuNPs@$PSNH_2$ (6 mg, 1% mol) in distilled water (2 mL) was dispersed for 5 min by ultrasonic. NaOH (0.008 g, 0.2 mmol) and benzyl alcohol (20 μL, 0.2 mmol) was added into the reaction mixture and the mixture was stirred under an atmospheric of oxygen for 24 h at 50 °C. The catalyst were collected by centrifuging (6000 rpm, 10 min) and washed three times with deionized water. The solution was neutralized with 0.1 M HCl (pH = 3-4) and extracted with AcOEt (3×7 mL). The extracted organic layer was dried over Na_2SO_4 and then analysed by gas chromatography. The GC yield was obtained from the calibration curve.

3. Results and discussion

Amine groups through lone-pair on nitrogen atoms and also benzene ring in polymer chains are ideal stabilizers for gold nanoparticles [34]. Therefore we decided to prepare a simple functionaolized polystyrene micospheres icluding amine groups to synthesize gold nanoparticles on their surface. Scheme 1 shows a schematic illustration of the step-by-step approch for the preparation of AuNPs@$PSNH_2$.

The polystyrene microspheres (PS) with an average diameter in abouts 1.0 μm were prepared by the procedure described in the litreature and were characterized by SEM [6,33] (Fig. 1a). The



Scheme 1. Schematic illustration of the step-by-step approch for the preparation of AuNPs@$PSNH_2$.