Abstract

Hollow and porous nanostructures attracted great attention because of their high surface-to-volume ratio and much improved optical, electrocatalytic and mechanical properties compared to their normal spherical counterparts. The plasmonic response and availability of inner surfaces, facets, and pores of these nanoparticles (NPs) are highly beneficial in the field of modern catalysis. These nanocatalysts (NCs) show higher turnover number (TON), turnover frequency (TOF), and faster reaction rates compared to conventional catalysts and thus superseding them in various chemical reactions. Especially gold and silver NCs are the most popular choice because of their biocompatibility, trivial and reproducible synthesis techniques, and stability. In this regard, galvanic replacement reaction (GRR) is a widely used, robust, and reliable synthesis technique to produce different hollow and porous nanoparticles (HPNPs). In this technique, one sacrificial template metal nanostructures having a lower reduction potential value is allowed to react with a more noble metal salt precursor (having a higher reduction potential value than the sacrificial template metal), and because of the difference in their reduction potential values the more noble metal ions sitting on the surface of the template metal reduced to its elemental form by oxidizing the template to its ionic form. The template ions are continuously diffused out from the core until all the template materials are transformed into ion by the noble metal to form a hollow core with a shell composed of noble metal. In the present work the metalloid As(0) was utilized as an alternative to commonly used metal nano-templates. The most interesting aspect of the GRR is that newly formed HPNPs resemble in size and shape to its parental sacrificial nanostructures. In this work, two different sized As(0) nanoparticles viz., As1 and As2 are prepared by reducing arsenite with sodium borohydride ($NaBH_4$) maintaining the pH range 7-9. These arsenic nanoparticles are further used as templates to synthesize two different-sized homogeneous hollow gold nanoparticles (HGNPs) viz., AuNP1 and AuNP2. These HGNPs i.e. AuNP1 and AuNP2 are further adsolubilized onto cationic surfactant-modified silica (SMS) to produce heterogeneous NCs viz., RG-SMS and BG-SMS, respectively. Two silver NCs, AgNP1 and AgNP2 were synthesized using nano-templates As1 and As2 and then converted to heterogeneous catalysts Ag1-SMS and Ag2-SMS using SMS.

Further, As1 and As2 are utilized to produce two different sized silica-coated HGNPs namely SHGNP1 and SHGNP2, using (3-mercaptopropyl)trimethoxysilane (3-MPTS).

All the abovementioned nanocatalysts are characterized by different techniques and then utilized to reduce 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of $NaBH_4$ to examine the size effect. The effectiveness of individual catalysts is measured in terms of TOF and TON. It is realized that smaller-sized particles show higher catalytic activity compared to larger particles. This phenomenon holds true for homogeneous as well as heterogeneous catalysts. It is also observed that heterogeneous catalysts are less efficient in terms of catalytic efficiency to their homogeneous counterpart but has much longer shelf life. The recyclability of all catalysts for 4-NP reduction has been tested up to the fourth cycle, and the results suggest them as a potential candidate for catalytic application. The studies prove the strong potential of As(0) as a sacrificial template instead of conventionally used metal templates.

Keywords: Arsenic zero nanoparticles; Galvanic replacement reaction; Gold nanoparticles; Silver nanoparticles; Adsolubilization; Silica-coated gold nanoparticles; 4-NP catalytic reduction; Size effect; Homogeneous and heterogeneous catalysis