Nickel nanoparticles-chitosan composite coated cellulose filter paper: An efficient and easily recoverable dip-catalyst for pollutants degradation☆

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ABSTRACT

In this report, we used cellulose filter paper (FP) as high surface area catalyst supporting green substrate for the synthesis of nickel (Ni) nanoparticles in thin chitosan (CS) coating layer and their easy separation was demonstrated for next use. In this work, FP was coated with a 1 wt% CS solution onto cellulose FP to prepare CS-FP as an economical and environment friendly host material. CS-FP was put into 0.2 M NiCl$_2$ aqueous solution for the adsorption of Ni^{2+} ions by CS coating layer. The Ni^{2+} adsorbed CS-FP was treated with 0.1 M NaBH$_4$ aqueous solution to convert the ions into nanoparticles. Thus, we achieved Ni nanoparticles-CS composite through water based in-situ preparation process. Successful Ni nanoparticles formations was assessed by FESEM and EDX analyses. FTIR used to track the interactions between nanoparticles and host material. Furthermore, we demonstrated that the nanocomposite displays an excellent catalytic activity and reusability in three reduction reactions of toxic compounds *i.e.* conversion of 4-nitrophenol to 4-aminophenol, 2-nitrophenol to 2-aminophenol, and methyl orange dye reduction by NaBH$_4$. Such a fabrication process of Ni/CS-FP may be applicable for the immobilization of other metal nanoparticles onto FP for various applications in catalysis, sensing, and environmental sciences.

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1. Introduction

Sustainable alternatives for high-performance and functional materials based on renewable resources are intensely needed as future alternatives for currently available fossil-based materials. Nanomaterials display a variety of certain specific useful properties that are usually different from the bulk state of the same material. Therefore, they show potential applications in catalysis (Noh et al., 2016), controlled release technology (Jayakumar et al., 2010; Xiao et al., 2015), electronics (Zhang and Zhu, 2015), photonics (Dyachenko et al., 2011) and sensor fields (Rithesh Raj et al., 2016). Particularly, metal nanoparticles are found to be very efficient catalytic entities for catalyzing a large number of chemical reactions (Zhang and Xie, 2016; Yan et al., 2013). This is because of their sizes in the range of 2–100 nm imparting them high surface area to volume ratio (Kao et al., 2013). For instance, numerous reports certify the high catalytic activity of Au, Pd, Pt, and Ag nanoparticles in various chemical reactions such as C–C coupling reactions (Wang et al., 2009), alcohols oxidation (Mao et al., 2016; Yan et al., 2014), CO oxidation (Miao et al., 2015), dopamine and ascorbic acid electro-oxidation (Oko et al., 2015), and others (Zhang et al., 2014; Ji et al., 2015). Owing to the high surface energy and van der Walls forces, the above mentioned noble metal nanoparticles readily tend to aggregate (Xu and Sun, 2011). This aggregation results in the lowering of their catalytic activity. In order to use them effectively, various chemical based methods were applied to keep them separate from one another without forming aggregates. For instance, Ag-Au bimetallic nanoparticles aggregated more rapidly then the triblock copolymer stabilized nanoparticles which were stable for a time period of several weeks (Holden et al., 2014). Other famous methods used the block copolymer micelles (Ray et al., 2011), dendrimers (Niu and Crooks, 2003), surfactants (Drinkel et al., 2014), polymer single crystals (Dong et al., 2012), functionalized carbon nanotubes and graphene (Xie et al., 2012; Yan et al., 2015), and hydrogels (Hu et al., 2014a) which stabilized the metal nanoparticles. Besides aggregation problem, noble metals carry

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high cost which is another hurdle in their commercialization. Transition metal nanoparticles were considered as cost effective alternatives to the noble metal nanoparticles (Bulut et al., 2016). They show similar catalytic activities in various chemical reactions. However, they are less stable in ambient air and rapidly adopt their oxidized states (Falcaro et al., 2016). For example, in an attempt to synthesize copper nanoparticles, CuO and Cu_2O were also formed when reaction medium had dissolved oxygen (Zhou et al., 2013). Therefore, stabilization of transition metal nanoparticles is utmost important to help prevent them from not only aggregation but also from oxidation.

Amongst various stabilization systems, hydrogels are comparatively easy to use as immobilizing hosts for the metal nanoparticles (Zinchenko et al., 2014). Hydrogels are composed of polymer network structure which holds high volume of water (Becht et al., 2011). In the past decade, several synthetic polymers were crosslinked and hydrogels were prepared such as polyvinyl alcohol (Gonzalez et al., 2014), polyacrylamide (Hu et al., 2014a), polyacrylic acid (Kim and Lee, 2007) and etc., which has either $-OH$ or $-NH_2$ functional moiety in a single chain. Besides, synthetic routes to preparation of hydrogels, chitosan (CS) is a naturally available and derivative polymer of second most abundant material (chitin) on the earth which upon crosslinking readily makes hydrogel when incorporated in acidic water (Xia et al., 2012). It bears both the $-OH$ and $-NH_2$ functional groups in the polymer chains which impart them to interact with various species including metals ions and fix them in the matrix by electrostatic and dipole-ion attractions (Kumar-Krishnan et al., 2015; Zeng et al., 2015; Kandile and Nasr, 2009).

Recently various catalyst supports have been prepared like graphene oxide (Yang et al., 2012), Al_2O_3, poly(ε-caprolactone) single crystals (Dong et al., 2012), and cellulose nanocrystals (CNCs) (Wu et al., 2014; Dhar et al., 2015). Cellulose, the most abundant polymer, has been processed for obtaining cellulose nanocrystals which dimensions consist of nanometers thickness and micrometer length. Cu, CuO, Au and other metal nanoparticles were loaded on CNCs supports for the efficient catalysis of organic pollutants (Zhou et al., 2013; Wu et al., 2013, 2014). Similarly, Madhu et al. synthesized CNCs as non-innocent support for loading Ru^0 nanoparticles catalyst for the application of arene hydrogenation (Kaushik et al., 2015). However, a necessary step of centrifugation was required for the metal nanoparticles loaded CNCs separation from the reaction medium. The authors claimed that the homogeneous dispersion of their catalysts loaded on high surface area supports in reaction medium led to the excellent catalytic performance (Zhou et al., 2013). However, longer and special procedures for the preparation of these supports may hinder their practical use. Another shortcoming is the separation of these catalysts from the reaction media. Some researchers have immobilized magnetic nanoparticles on their supports along with original catalysts for easy recovery (Dong et al., 2012). Therefore, researchers are still searching for better supports which should provide high surface area for catalysts, be readily available and economical, and easy preparation and recovery process.

While the field of using synthetic polymer hydrogels as stabilizing host for the catalyst is mature, reports on using naturally available polymer hydrogels is still sparse which needs less efforts for their applications. In this regards, we used filter paper (FP) as cellulose source in the form of high area substrate and a thin CS layer was coated on it. We used our previous method of in-situ metal nanoparticles preparation that involved the metal ions uptake by CS coating layer followed by $NaBH_4$ treatment (Kamal et al., 2016a). Nickel (Ni) was chosen here as it is a famous hydrogenation catalyst. Ni^{2+} ions were entrapped by CS coating layer from an aqueous solution of nickel salt. The Ni^{2+} loaded CS-FP strips were treated with sodium borohydride aqueous solution to convert the metal ions to alloy nanoparticles. Thus, we prepared Ni nanoparticles-CS composite by a simple water based process. The Ni/CS-FP strips were utilized as dip-catalysts in chemical transformation of nitrophenols to aminophenols and an azo dye methyl orange reduction. These nitrophenols and azo dye are highly toxic and many efforts have been made which utilized the efficient catalysts to convert them into non-toxic substances. The prepared catalytic strips were easily recovered from the reaction medium by just pulling them from the reaction vessel and re-used.

## 2. Experimental

2.1. Materials

Chitosan with a degree of deacetylation >75% and high molecular weight (800—2000 cP), 1 wt % in 1% acetic acid (25 °C, Brookfield) was purchased from Sigma Aldrich, Ireland. Sodium borohydride ($NaBH_4$, 99%), nickel chloride hexahydrate ($NiCl_2.6H_2O$, 99%), 4-nitrophenol and 2-nitrophenol were purchased from BDH chemicals, England. Acetic acid was purchased from NTN Ltd, U.K. Cellulose filter papers with dimensions of 12.5 cm and 0.3 mm thickness were purchased from Whatman company. Methyl orange dye was purchased from Koch-lite Laboratories, England. All chemicals were of analytical grade and used without further processing. Water with resistivity of 18.2 MΩ cm was used throughout this work.

2.2. Chitosan coating layer

The yellowish flaked form of chitosan was dissolved in 2% v/v acetic acid solution by stirring overnight. The chitosan solution concentration was 1 wt%. Filter paper was cut into rectangular pieces of 0.6×4.5 cm^2 and dipped into 1 wt% chitosan solution for 1hr. The excess solution was wiped from the filter paper pieces and kept for drying. Higher concentration of chitosan solutions were also used as coating but they formed thick layer over filter paper (Kamal et al., 2015). Such a thick layer formation blocked the micropores of filter paper which was not desirable here. Therefore, we proceeded with further experiments by using 1 wt% chitosan coated filter paper.

2.3. In-situ nanoparticles synthesis

Nickel nanoparticles were prepared inside thin chitosan layer by two steps method. In first step, many strips of CS-FP were kept in 0.2 M $NiCl_2.6H_2O$ aqueous solution for 4 h. This turned the white CS-FP strips to a greenish color due to the Ni^{2+} ions uptake by the CS layer. The strips were washed with DI water several times and dried. In a second step, the dried strips were dipped into 100 mL of 0.1 M $NaBH_4$ solution. As soon as the strips were dipped into $NaBH_4$ solution, they changed the color to black. The strips were kept in $NaBH_4$ solution for 1 h to completely reduce the Ni^{2+} according to the following reaction,

$$2Ni^{2+} + 4\,BH_4^- + 12\,H_2O \rightarrow 2\,Ni^0 + 14\,H_2 + 4\,B(OH)_3$$
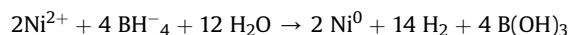
The reduced Ni nanoparticles immobilized in CS layer (Ni/CS-FP) were stored inside water as exposing it to open air oxidizes them with passage of time. The amount of Ni in Ni/CS-FP was determined by TGA.

2.4. Catalytic reactions

Catalytic activity of the Ni/CS-FP was evaluated in three different