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Evaluating the potential of chitin extracted from shrimp shell wastes as support material of gold nanoclusters (AuNCs) for catalysis

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Abstract. Thiolate-protected gold nanoclusters (AuNCs) have been intensively studied due to their appealing physicochemical properties that can be used in various applications, especially catalysis. However, thiolate-protected AuNCs in a free suspension form, tend to aggregate during catalytic reaction due to the high surface reactivity of its ultrasmall size, hence, reducing the rate of their catalytic reaction. Their recovery and reusability are also difficult. Therefore, several support materials have been studied to immobilize the thiolate-protected AuNCs for a better recovery, reusability and stability in solution and during a catalytic reaction. Herein, chitin extracted from shrimp shell waste was used as support material for the immobilization of the AuNCs protected by *p*-mercaptobenzoic acid ligands, using deposition-precipitation method. The free chitin and chitin immobilized with thiolate-protected AuNCs (abbreviated as AuNCs/Chitin) were characterized using FTIR. The catalytic properties of the AuNCs/Chitin were then evaluated in the hydrogenation of 4-nitrophenol in solution as the model reaction. It was found that the chitin extracted from SSW has a good potential to be support materials of thiolate-protected AuNCs because the shorter reaction time it took (12 minutes) as compared to the reaction without catalyst (60 minutes) and it can be recovered and reused twice.

1. Introduction

Gold nanoclusters (AuNCs) have received increasing attention due to their intriguing physicochemical properties which offer a myriad of applications (e.g., catalysis [1-4], and biomedical applications [5-10]). Unlike plasmon gold nanoparticles (Au NPs) which have continuous or semi-continuous energy levels [11], Au NCs have higher surface area-to-volume ratio, distinctive discrete electronic structure and redox behavior [12-15]. These different properties could cause better or different catalytic properties of AuNCs as compared to AuNPs. However, due to ultrasmall size, protecting ligands are compulsory in the synthesis of AuNCs to prevent their aggregation and maintain their monodispersity and ultrasmall size. Among various ligands, thiolates with sulfhydryl (-SH) functional group are commonly used to synthesize AuNCs due to the strong bonding between sulfur and gold (Au-S bond) [16].



Nevertheless, a study by Nasaruddin, et. al. (2018) AuNCs reported that the thiolate-protected AuNCs in a free suspension form, were still unstable and easily aggregated during a catalytic reaction (i.e., 4-nitrophenol hydrogenation in solution) [16]. Therefore, it is crucial to immobilize the thiolate-protected AuNCs to improve their stability during a catalytic reaction and to increase its recovery and reusability potential in catalysis.

The immobilization of thiolate-protected AuNCs is usually done using solid support materials (e.g., carbon-based materials, water-soluble and insoluble polymers, mesoporous silica, and metal oxide [17]). Natural biopolymer such as cellulose, chitosan and chitin could also be used as support material. We selected chitin in this study because it is the most abundant natural nitrogen-containing biopolymer and it has been used for various applications such as health supplements [18-20], agricultural [21, 22] and water treatment [23-25]. It's potential as support material of metal nanocatalysts is still rarely reported. Interestingly, chitin can be extracted from crustacean shells (e.g., crab shell and shrimp shell wastes), hence, it can be a sustainable support material for metal nanocatalysts and could further overcome the environmental concerns caused by the wastes [26].

In this study, we investigated the immobilization of AuNCs on chitin extracted from shrimp shell wastes (abbreviated as SSW) and evaluated their catalytic activity, recovery and reusability in the hydrogenation of 4-nitrophenol in solution, as the model reaction.

2. Experimental Section

2.1. Preparation of chemicals and materials

The grey shrimp was bought from the local supermarket (AEON Big at Wangsa Maju). The other chemicals such as hydrochloric acid (HCl), sodium hydroxide (NaOH) and 4-nitrophenol were obtained from the Department of Biotechnology Engineering (BTED), Kulliyah of Engineering, International Islamic University Malaysia while gold precursor, tetrachloroauric(III) acid (HAuCl_4) and sodium borohydride (NaBH_4) were purchased from Sigma Aldrich. All the glasswares were rinsed with ultrapure water before use.

2.2. Chitin extraction from SSW

The extraction of chitin from the SSW was done based on the conventional method reported in Yang et. al., (2019) [4]. Briefly, the SSW was dried under sunlight for 10 hours to decrease its moisture content. After drying under the sunlight, the SSW was blended to be in a powder form and then was left to dry again. The dried SSW powder was then weighted to identify its moisture content. For the extraction of the chitin from the SSW, deproteinization was done by stirring one gram (1 g) of SSW powder with 20 mL of NaOH aqueous solution (5 wt%) at $80.0 \pm 5^\circ\text{C}$ for 2 hours. The sample was then washed using distilled water, dried and weighted. Next, the dried deproteinized sample was stirred with 10 mL HCl aqueous solution (5 wt%) at room temperature for 1 hour for the demineralization process. The demineralized sample (extracted chitin) was then washed using distilled water, dried and weighted. The extracted chitin was then characterized using FTIR.

2.3. Synthesis of AuNCs

The thiolate-protected AuNCs used in this study were protected by thiolate ligands, *p*-mercaptobenzoic acid (*p*-MBA). They were synthesized using a reported carbon dioxide (CO)-reduction method developed by Xie and co-workers [27]. Briefly, 0.25 mL of aqueous solution of *p*-MBA (50 mM in 150 mM NaOH) and 0.25 mL HAuCl_4 (40 mM) were mixed in 9.5 mL ultrapure water under stirring (500 rpm). After 2 hours, the colour of the solution turned to light yellow, indicating that the Au^{3+} ions had been reduced to Au^+ -SR complexes. The pH of the solution was then brought to 11.6 by the addition of NaOH and CO was bubbled through the solution for 2 mins. The flask was sealed airtight and the synthesis reaction was done for 72 hours. The colour of the solutions was gradually turned into dark brown indicating the presence of thiolate-protected AuNCs. The final as-synthesized thiolate-protected

AuNCs with molarity of 0.5 mM (based on the mol of Au in the solution) were analyzed by UV-Vis and further used for the immobilization and catalytic tests.

2.4. Immobilization of AuNCs on extracted chitin

The immobilization of AuNCs was done by using deposition-precipitation method. Appropriate amount of dried chitin and deionized water (0.9 mL) was added simultaneously in a vial. It is important to make sure the pH of the solution is at pH 7.0. Then, 0.1 mL of as-synthesized thiolate-protected AuNCs solution were added afterwards. The mixture was stirred at 600 rpm for 1 hour and at room temperature. The change in colour of the mixture and the presence of precipitate were observed. The mixture was then centrifuged at 1000 rpm and the remaining liquid was taken out for UV-Vis absorption analysis. Meanwhile, the solid precipitates which were the immobilized AuNCs on chitin (abbreviated by AuNCs/Chitin) were then dried at room temperature overnight.

2.5. Hydrogenation of 4-nitrophenol (4-NP) in solution

The AuNCs/Chitin was tested for its catalytic activity through the hydrogenation of 4-nitrophenol in solution. In this experiment, 25 μL of 4-nitrophenol (4 mM) was added into 0.01 g of AuNCs/Chitin. Then 2 mL of NaBH_4 (0.25 M) was added into the solution to start the catalytic reaction. The yellowish colour of deprotonated 4-nitrophenol (i.e., 4-nitrophenolate ions) gradually decreased to colourless, indicating the conversion of 4-nitrophenol to 4-aminophenol. After a catalytic reaction was done, the AuNCs/Chitin was recovered by centrifugation. Then, the recovered AuNCs/Chitin was tested again to study its recoverability and reusability using the same model reaction. The kinetic study was done using UV-Vis spectroscopy under kinetic mode by focusing on the absorbance of 4-nitrophenolate ions at wavelength 400 nm only. The UV-Vis absorption at 400 nm decreased with the time of reaction. According to Nasaruddin et al., (2018) since the high amount of NaBH_4 was added into the solution, the reaction could be regarded as the first order reaction and the slope of the decreasing UV-Vis absorption at 400 nm was taken as the apparent reaction rate constant, k_{app} (s^{-1}) [28].

3. Results and discussion

3.1. Characterisation of the extracted chitin

The average yield of extracted chitin was 38.96 ± 10.86 wt.%. From the FTIR spectra (Figure 1), the characterization peaks of the extracted chitin are at around 1010 cm^{-1} for -CO stretching band, 1428 cm^{-1} for -CH₃ deformation, 1556 cm^{-1} for amide vibrational band II, 1620 cm^{-1} for amide vibrational I with a single H-bond, 1652 cm^{-1} for amide vibrational I with double H-bond, 3256 cm^{-1} for -NH stretching band and 3431 cm^{-1} for -OH stretching band. The decreasing of peak intensity at around 1550 cm^{-1} and 1640 cm^{-1} (belong to amide groups of protein) between the shrimp shell waste sample and the deproteinized sample shows the practical removal of protein from the SSW sample. Moreover, the sharp peak at 872 cm^{-1} and at 1408 cm^{-1} (labelled by orange dashed line) that can be seen on deproteinized sample shows a vibration of carbonate ions ($-\text{CO}_3$) of CaCO_3 mineral. These peaks are more noticeable on the sample after deproteinization process as compared to the raw SSW because the protein matrix has been removed, thus exposing more minerals which further ease the demineralization process [29].

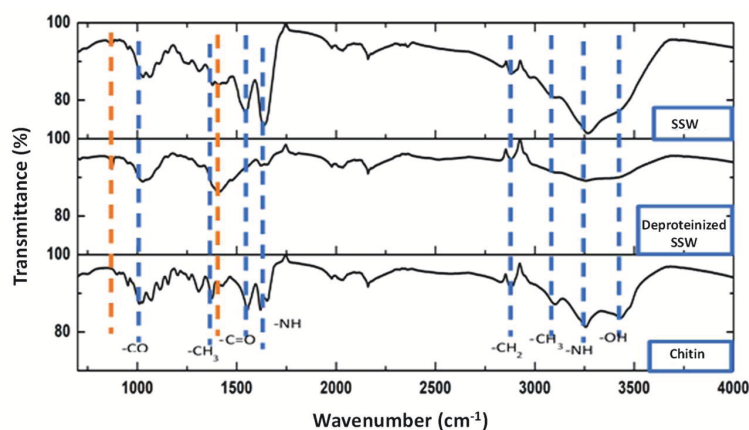


Figure 1. FTIR spectra shows the functional group of shrimp shell waste (SSW), deproteinized SSW and the final chitin after the demineralization of the deproteinized sample.

3.2. Immobilization of AuNCs on extracted chitin

The diluted thiolate-protected AuNCs solution was light brown in colour (refer to the inset image before centrifugation in Figure 2). As shown by the UV-Vis absorption spectra (black line; Figure 2), the thiolate-protected AuNCs shows featureless peak indicating the possibility of several species of AuNCs in the solution. During the stirring, immobilization happened, and AuNCs/Chitin was recovered by centrifugation. The immobilization of the thiolate-protected AuNCs could be seen indirectly when the colour of the remaining solution was colourless (refer to the inset image of after centrifugation in Figure 2). Due to the ultrasmall size of AuNCs, centrifugation of AuNCs solution at 1000 rpm did not result in precipitates and the color of the solution remained brownish. The UV-Vis absorption spectra in Figure 2 indicate that the peak for thiolate-protected Au NCs in the remaining solution almost disappeared after immobilization which could be an indirect evidence for the successful immobilization of thiolate-protected AuNCs on the surface of chitin.

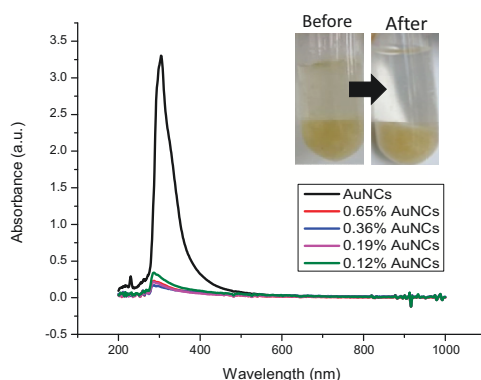


Figure 2. The UV-Vis absorption spectra of the thiolate-protected AuNCs and their remaining solution taken after their immobilization on chitin. Insert shows the image of the thiolate-protected AuNCs and chitin mixture before and after the centrifugation.

3.3. Hydrogenation of 4-nitrophenol by AuNCs/Chitin

The catalytic activity of the AuNCs/Chitin was determined by using hydrogenation of 4-nitrophenol (4-NP) in solution as the model reaction due to the simplicity of the process as the catalytic reaction can be observed by UV-Vis spectroscopy. Figure 3a shows the initial spectrum of 4-NP at 400 nm after the addition of NaBH_4 . The absorption peak at 400 nm gradually decreased and the absorption peak at 296 nm appeared and gradually increased indicating the presence of the product, 4-aminophenol (4-AP).

Based on Figure 3a, the control reaction of hydrogenation of 4-NP (without any catalyst) took about 60 minutes to complete, meanwhile with the presence of Au NCs/Chitin as catalyst (Figure 3b), the reaction only took 12 minutes to complete.

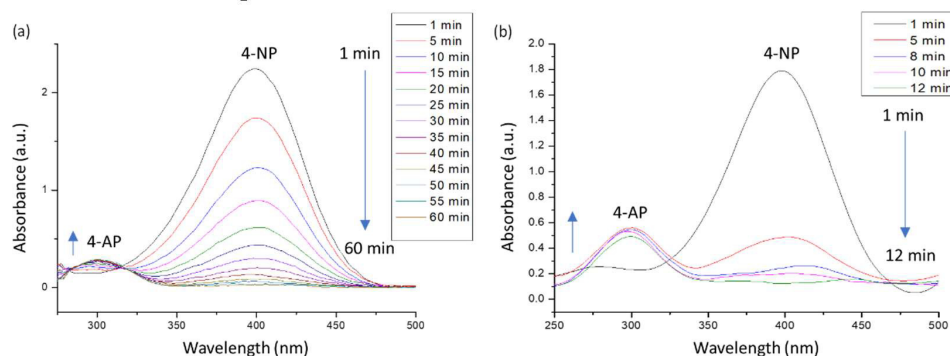


Figure 3. (a) The model reaction of hydrogenation of 4-nitrophenol (4-NP) which takes 60 minutes to complete. (b) The same reaction with the presence of Au NCs/Chitin as catalyst takes 12 minutes to complete. (Reaction conditions: 0.01 g AuNCs/Chitin; 5000:1 molar ratio of NaBH_4 :4-NP; room temperature; in 3 mL cuvette; no stirring)

Kinetic mode analysis under UV-Vis absorption spectroscopy at 400 nm was done to show clear differences between the AuNCs/Chitin and the control experiments (i.e., reaction with the free suspension of thiolate-protected AuNCs, chitin only and without any catalyst). Based on the results in Figure 4a, the UV-Vis absorption peak of the reactant decreased with the reaction time. At the beginning of the catalytic reaction, the slope of the absorbance at 400 nm was steeper, showing a fast conversion of 4-NP to 4-AP. The Au NCs/Chitin shows a faster reaction rate compared to the control reaction without catalyst (inside the vial has 4-NP, NaBH_4 and ultrapure water only). However, the free suspension of thiolate-protected Au NCs only (labelled by AuNCs) had a faster reaction rate than AuNCs/Chitin. This result is expected because Au NCs solution is more reactive and has more active site exposure compared to Au NCs/Chitin. The immobilization may hinder some of the active sites due to the interface interaction between the thiolate-protected AuNCs and the surface of chitin. Nonetheless, the free suspension of thiolate-protected Au NCs cannot be recovered and reused, thus making it unfavourable for catalysis.

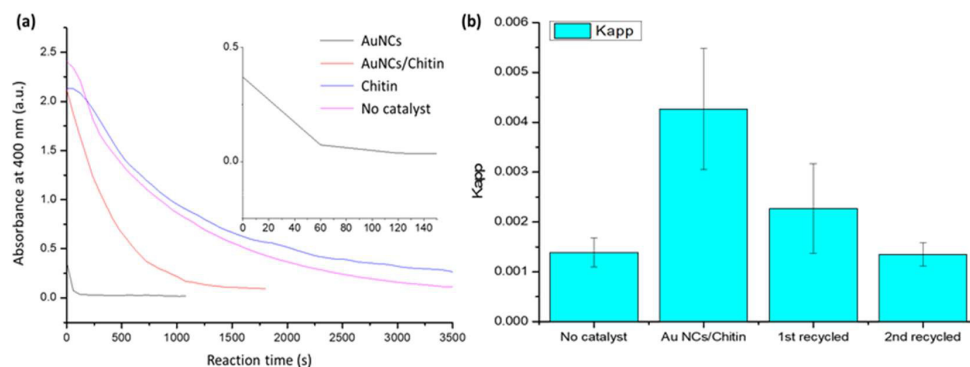


Figure 4. (a) Kinetic mode UV-Vis absorption spectra of 4-nitrophenol hydrogenation catalysed by AuNCs/Chitin, free suspension of thiolate-protected Au NCs, chitin and control experiment with no catalyst. (b) The k_{app} of hydrogenation of 4-nitrophenol of AuNCs/Chitin and the recovered Au NCs/Chitin.

Under kinetic mode, the apparent reaction rate constant (k_{app}) can also be determined by measuring the slope of the decreasing absorbance. From the graph in Figure 4b, the k_{app} for Au NCs/Chitin is about 3 times higher than that from the control reaction. The immobilized Au NCs/Chitin was recovered after being tested for the catalytic reaction to see the recoverability and reusability of the catalyst. Figure 4b also shows the k_{app} of the recovered and reused Au NCs/Chitin. The k_{app} of AuNCs/Chitin decreased from 0.0042 s^{-1} to 0.0022 s^{-1} in the first recycle and to 0.0014 s^{-1} in the second recycle which similar to the k_{app} of the reaction without any catalyst. The decreasing catalytic activity was probably due to some thiolate Au NCs that leached out during the catalytic activity and the recovery process [30].

4. Conclusion

Chitin extracted from shrimp shell wastes has shown a good potential as supporting materials for the immobilization of thiolate-protected Au NC for catalysis. The immobilization of thiolate-protected AuNCs on chitin allowed their recovery and they can be reused for 3 times in the hydrogenation of 4-nitrophenol with acceptable catalytic activity as compared to control condition (no catalyst at all). Overall, this project shows potential to use low cost chitin from shrimp shell waste as support materials to immobilize nanocatalysts. The study has significant impact for adding values to the shrimp shell waste and can be a solution for the solid waste management. The immobilization will also help to reduce wastage of gold nanocatalysts during catalytic reaction because it can be recovered and reused.

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