Preparation of Bimetallic Catalyst: Gold-Copper (Au-Cu) Nanoparticles for Catalytic Reduction of p-Nitrophenol

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Abstract. The combination of gold (Au) and copper (Cu) nanoparticles can enhance their chemical and physical characteristics for the application in catalysis. This combination of Au and Cu reduce the cost of Au and improve the stability of Cu towards oxidation. This study involves the preparation of Au-Cu NPs for the application in the reduction of p-nitrophenol (p-NP). The Au-Cu NPs catalyst was synthesized with different Au:Cu ratio and addition hexadecylamine (HDA). The highest rate constant (k) of 8.2 x 10⁻³ s⁻¹ was obtained over 1.5 Au-Cu HDA2 catalyst. UV-Vis spectrophotometer and Transmission Electron Microscope were used to characterize the prepared sample.

1 Introduction

In recent years, there has been an increasing interest in the application of gold nanoparticles (Au NPs) as a catalyst for reduction of p-nitrophenol (p-NP) [1; 2] and p-nitroaniline [3]. The Au NPs was widely studied either as monometallic or bimetallic NPs. Wang et al. (2013) mentioned that the performance of monometallic Au NPs is limited by its particles size and the preparation procedure, while an additional of second metal reduced these limitations [4]. The combination of Au NPs with other transition metals such as Au-Pt, Au-Cu, Au-Pd, and Au-Ag has better catalytic activities than monometallic Au NPs. Specifically for Au-Cu NPs, Rout et al. (2017) emphasized that it is a good bimetallic alloy since it has better resistance toward oxidation, thus extended the catalyst’s lifetime [5].

Therefore, this work proposes the preparation of Au-Cu NPs for catalytic reduction of p-NP. Several parameters such as the Au/Cu ratio and capping agent, HDA were varied to optimally produce Au-Cu catalyst of high activity towards reduction of p-NP.

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2 Methodology

2.1 Synthesis of Au-Cu

Au-Cu NPs were synthesized based on the chemical reduction technique. An aqueous solution of CuCl$_2$·2H$_2$O (50 mM) was mixed with 0.3 mL HAuCl$_4$·3H$_2$O (50 mM) and 0.28 mL of glucose (0.5 M) in a glass vial containing the HDA solution of 22.5 mg in 2 mL distilled water [6]. The vial was magnetically stirred at room temperature overnight followed by heating treatment at 100 °C for 10 mins. This sample is denoted as 0.3 Au-Cu HDA. Similar procedures were repeated for 1.5 Au-Cu HDA and 1.5 Au-Cu HDA2 but using 1.5 mL of HAuCl$_4$·3H$_2$O precursor and addition of 15 mg of HDA after heating, respectively. The detail preparation parameters were summarized in Table 1.

Table 1. Summarized parameters for synthesis of Au-Cu.

| Sample notation | Parameters |
|-----------------|------------|
|                 | 0.5 M glucose | 50 mM CuCl$_2$ | 50 mM HAuCl$_4$ (0.3 or 1.5 mL) | 22.5 mg HDA | Stirred (rt, overnight) | Heating time at 100 °C | 15.0 mg HDA |
| 0.3 Au-Cu HDA   | √ | √ | 0.3 mL | √ | √ | x |
| 1.5 Au-Cu HDA   | √ | √ | 1.5 mL | √ | √ | x |
| 1.5 Au-Cu HDA2  | √ | √ | 1.5 mL | √ | √ | √ |

2.2 Catalytic reduction of $p$-nitrophenol

Accurately, 20 µL of Au-Cu HDA catalyst was put into a cuvette containing freshly prepared NaBH$_4$ (1.5 mL, 1.5 x 10$^{-2}$ M) and $p$-nitrophenol (1.5 mL, 0.05 mM) solution. The reduction of $p$-NP was monitored by using UV-Vis spectrophotometer (Lambda 25, Perkin Elmer) at 400 nm based on a pseudo first-order model. The rate constant ($k$) value was then calculated.

3 Findings

3.1 Au-Cu HDA

The aqueous phase synthesis of bimetallic Au-Cu involves CuCl$_2$ and HAuCl$_4$ as the precursors while glucose and hexadecylamine (HDA) as the reducing and capping agent, respectively. The colour of the aqueous mixture (0.3 Au-Cu HDA) turns from kelly green to black after heating at 100 °C (Fig. 1.). Meanwhile, for 1.5 Au-Cu HDA formulation (Refer to Table 1), the colour change from kelly green to dark brown (Fig. 2.). Figure 3 shows the UV-Vis spectra of 0.3 and 1.5 Au-Cu HDA with the surface plasmon resonance (SPR) band at 520 nm and 565 nm, respectively. According to Pal et al., monometallic Au NPs has the SPR band around 521 nm while monometallic Cu NPs is at 573 nm. The bimetallic Au/Cu of 1:1 ratio shows a peak at 548 nm [7]. Therefore, the 1.5 Au-Cu HDA with Au/Cu ratio of 2.5:1 shows positive confirmation of producing Au/Cu as the appearance at 565 nm. Besides, the colour change from kelly green to dark brown was also an indication of Au/Cu [6].
3.2 Effect of addition HDA

The addition of HDA into the sample solution gives an important impact on the size of Au-Cu NPs [6]. Fig. 4 shows the photograph of 1.5 Au-Cu HDA2 before and after addition of HDA. Positive indication of Au/Cu was observed as the solution turn to deep brown (Fig. 4b). Fig. 5 shows UV-Vis spectra of 1.5 Au-Cu HDA2 at 552 nm, shifted towards shorter wavelength compared to 1.5 Au-Cu HDA formulation discussed above. The finding indicates the formation of a smaller diameter of bimetallic Au/Cu. According to the previous report of spherical gold-copper nanocubes (NCs), the nanocubes highly depends on its size in which increasing size of NCs will cause red shift of the SPR band wavelength [8]. The TEM image in Fig. 6 depicts Au/Cu nanocubes of 116 ± 29 nm.
3.3 Catalytic reduction of \( p \)-nitrophenol

The reduction of \( p \)-nitrophenol (\( p \)-NP) to \( p \)-aminophenol (\( p \)-AP) in the presence of NaBH\(_4\) was used as a model reaction to evaluate the catalytic activity of the prepared catalysts [3]. This method is easy to be monitored by a simple spectroscopic technique that is UV-Vis spectroscopy [9]. In all catalytic runs, the experimental conditions at a molar ratio of NaBH\(_4\) : \( p \)-NP at 300:1 were kept constant. From the observations, after the addition of a fresh aqueous solution of NaBH\(_4\) into an aqueous solution of \( p \)-NP, the absorption peak of \( p \)-NP shifted from 317 to 400 nm due to the formation of \( p \)-nitrophenolate ions [10]. The significant change of solution colour has occurred from light yellow to dark yellow. Fig. 7 shows the UV-Vis spectra of catalytic reduction of \( p \)-NP over 0.3, 1.5 Au-Cu HDA and 1.5 Au-Cu HDA2. The incomplete reduction was obtained for 0.3 Au-Cu HDA while 1.5 Au-Cu HDA and 1.5 Au-Cu HDA2 has the \( k \) value of \( 3.0 \times 10^{-3} \) and \( 8.2 \times 10^{-3} \) s\(^{-1}\), respectively. Plot ln (\( A \) - \( A_\infty \)) vs time shows linear correlation inconsistent with pseudo first-order kinetic reaction (Fig. 8). The 1.5 Au-Cu HDA2 requires only 6 mins to completely reduce \( p \)-NP which,
illustrates a highly active catalyst for this reaction. Overall $k$ values are summarized in Table 2.

**Fig. 7**: UV-Vis spectra of catalytic reduction of $p$-NP over different formulation of Au-Cu (a) 0.3 Au-Cu HDA, (b) 1.5 Au-Cu HDA and (c) 1.5 Au-Cu HDA2.
Fig. 8. Plot Plot ln A/A₀ vs time of 1.5 Au-Cu HDA and 1.5 Au-Cu HDA2.

Table 2: Comparison of the catalytic reduction of p-NP by using Au-Cu HDA catalysts.

| Samples          | Time for reduction of p-NP to complete (min) | Rate constant (k) value (s⁻¹) | R²   |
|------------------|---------------------------------------------|--------------------------------|------|
| 1.5 Au-Cu HDA    | 24                                          | 3.0 x 10⁻³                     | 0.8378 |
| 1.5 Au-Cu HDA 2  | 6                                           | 8.2 x 10⁻³                     | 0.9599 |

4 Conclusions

The Au-Cu nanocubes shape of 116 ± 29 nm size was successfully prepared by using chemical reduction technique. The highest k value of rate constant (k) is 8.2 x 10⁻³ s⁻¹. The efficiency of this prepared catalyst might be due to the addition of HDA as the capping agent and Au:Cu of 2.5:1 ratio.

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