SYNTHESIS AND CHARACTERISATION OF CUO/HNT NANO-PARTICLES THROUGH IN-SITU GLYCINE NITRATE PROCESS

HUI-HUI LIM, PHEY-NEE CHUA, HANG PUI MUN, BAHMAN AMINI HORRI, BABAK SALAMATINIA

1Discipline of Chemical Engineering, School of Engineering, Monash University Malaysia
E-mail: babak.salamatinia@monash.edu

Abstract - Transition metal oxides have various interesting properties, especially nanostructures of the Copper (II) Oxides (CuO) have special magnetic properties and larger surface area which enhance the applications of the CuO in various fields. In this study, CuO nanoparticles supported on Halloysite Nanotubes (HNTs) via an in-situ glycine nitrate process was successfully synthesized by templating on chitosan. Effects of calcination time and temperature are fully elaborated by detail characterizations including, FESEM, FTIR, TGA, EDX, BET and Raman Spectroscopy. The best calcination condition was found to be at 600°C for 5 h of calcination duration. Characterizations confirmed the presence of both HNT and CuO within the particles confirming that the in-situ synthesis of metal-oxides by supporting them on HNTs is very much feasible.

Keywords - Chitosan, Copper (II) Oxide, Nanoparticles, Glycine Nitrate Process, Halloysite Nanotube

I. INTRODUCTION

Nanosized transition metal oxides have successfully drawn major attentions in material science and technology in recent years due to their special properties that consequently escalate the demand in various industries such as pharmaceuticals [1], cosmetics manufacturing, construction, food packaging[2], catalysis[3], Solid Oxide Fuel Cells [4] etc. Among the aforementioned applications, catalysis is the current highlight to researchers since presence of catalysts enables almost 80% of the chemical reactions to work effectively [5]. For instance, metal oxides have been widely applied in reactions such as Fischer – Tropsch (F – T) process [6], alkylation [7]; transesterification[8], catalytic oxidation of volatile organic compounds (VOCs)[3], and catalytic reduction of nitrogen oxides [8].

Copper (II) oxide (CuO), considered as a transition metal oxide, is a p-type, narrow band semiconductor that has a monolcnic structure with multiple interesting properties, such as high stability, superthermal conductivity, antimicrobial activity and photovoltaic property [1]. Despite catalytic reactions, CuOcan as well be applied in some technological fields, for example, optoelectronics, solar cells, high efficiency thermal conducting material, or magnetic recording media. CuO nanostructures possess superior hydrophobic and unique magnetic properties, which allow it to be a promising heterogeneous catalyst in reactions like conversion of hydrocarbons into carbon dioxide, anodes of lithium ions battery, nanoenergetic material, or to enhance thermal conductivity of nanofluids.

Of all these applications, morphologies, size and surface area of the CuO nanoparticles are the main determinant of the catalytic performance [2]. However, it is also theoretically proven that adequate support allows greater dispersion of active phase that subsequently leads to better performance of catalysts compared to that of a bulk catalyst [9]. There are various supports available in the current market, which include titanium oxide [10], Gadolinium doped Ceria [11], carbon nanotubes [12] and nanocrystalline cellulose [3]. However, these supports can decompose easily at high temperature, for instance, carbon nanotubes will decompose at a temperature of 600°C. Moreover, the surface areas of the CuO nanoparticles supported on these supports were found to be ranging from 7m²/g to 15m²/g. To date, research on synthesizing CuO nanoparticles with larger surface area is still a challenge to researches.

Simple hydrolysis electrochemical [5], hydrothermal [13], sonochemical[5], impregnation method [14], sol-gel method [15] or combustion synthesis [16] are commonly employed as the synthesis methods of both supported and non-supported CuO nanoparticles. Combustion synthesis and sol-gel methods are comparably simple, inexpensive and require shorter reaction time, therefore are more widely applied. Three types of combustion synthesis involve different physical nature of initial reaction medium, mainly solid, liquid and gaseous states. Glycine nitrate combustion synthesis is a type of solution combustion synthesis, which involves an oxidant (normally metal nitrate solutions) and glycine as a fuel.

Glycine nitrate process is an easy and simple process that is able to produce products of any desired morphology and stable metal phases by using simple equipment[15]. This study focuses on in-situ synthesis of CuO nanoparticles supported on Halloysite Nanotubes (HNT) via glycine nitrate process by templating on chitosan. The effects of temperature and calcination time are elaborated by analyzing the samples using various techniques.
II. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

Chitosan was used as the intermediate supports for synthesizing nanoCuO supported on Halloysite Nanotubes (HNTs) via in-situ nitrate glycine process. Chitosan flakes and copper nitrate trihydrate were purchased from Sigma – Aldrich having properties of deacetylation degree of 75 ~ 85% and a molecular weight of 241.60 g/mol, respectively. Glacial acetic acid with a purity of 98% was used for aqueous acetic acid preparation. Similarly, HNT was reported to have surface area of 0.12 cm²/g, was also purchased from Sigma – Aldrich.

Chitosan powder (1wt%) was dissolved in an aqueous acetic acid prepared by adding the glacial acetic acid (1wt%) into water. Then, HNT powder with a ratio of 1:1 to the copper ions was added into the prepared chitosan solution. Next, 100 ppm copper solution was prepared by dissolving the copper nitrate trihydrate into water. Stoichiometric ratio of glycine was weighed and added to the copper solution. Two solutions were then being mixed by using a mechanical stirrer (IKA – RW 20, IKA Works, Malaysia) at 600 rpm for 24 hunder ambient conditions to produce a homogenous mixture. Sonication mixing using an ultrasonic probe (QSONICA, 700W, USA) with a pulse cycle of 5 s on and 5 s off for 5 min was employed to ensure thorough mixing of the solution.

The mixed solution was then transferred to a crucible and was dried in an oven at a temperature of 60 °C for 24 h to remove excessive water and other impurities. The dried products were then calcined in a carbonate furnace. The calcination temperature was varied from 500°C to 700°C whereas the calcination duration was manipulated from 3 h to 5 h with a constant ramping rate of 100°C/ h. Characterization test such as Fourier Transform Infrared Spectroscopy (FT-IR), Raman Spectroscopy, Brunauer-Emmett-Teller (BET) Surface Area were done on all the calcined sample while Thermal Gravimetric Analysis (TGA) was performed on the precursor to identify the calcination range and thermal behavior of the solution.

III. RESULTS AND DISCUSSION

3.1. Thermal Stability (TGA)

The degradation curve obtained through thermal gravimetric analysis (TGA) is presented in Fig.1. The degradation curve shows four steps of degradation, where the first weight loss of 10% started approximately from 30°C to 120°C was concluded to be due to the evaporation of adsorbed water in the samples. The degradation temperature of carbonates formed in the sample was determined to start from 120°C to 200°C, resulting in another 10% weight loss of the sample. The next step consists of the largest weight loss of 20% and was attributed to the degradation of the chitosan in the samples. The last weight loss was attributed to the dehydroxylation of the alumino groups of HNTsand was observed within the range of 400°C to 550°C. This at the end allows the copper to deposit on the surface of the HNT and allow the formation of CuO with the occurrence of oxidation as both the TGA and calcination were carried out with the presence of air.

Therefore, based on TGA results, one of the manipulating parameters, which is the calcination temperature, was decided to be varied from a temperature of 500°C to 700°C, with an interval of 100°C to assure the full decomposition of unwanted substances.

![Fig.1Degradation curves of chitosan as intermediate support for the synthesis of nano-CuO supported on HNTs via in-situ glycine process](image)

3.2. Optimal Calcination Conditions for In-Situ Glycine Nitrate Process for the Synthesis of Copper Oxide Nanoparticles

3.2.1. Effects of Calcination Time

Fig.2a, Fig.2b and Fig.2c present the FESEM results of the sample synthesized at a fixed calcination temperature of 600°C at varying time elapse of 3 h, 4 h and 5 h, respectively. It is observed that at 5 h of calcination time a better morphology, in terms of size and shape distribution is achieved. Fig.2c clearly demonstrates lesser agglomerations as compared to the other two samples. This indicates a complete combustion of all carbonaceous components, leaving behind the CuO and HNT. Besides, the shape distribution of the nanoparticles of CuO synthesized at such condition, a uniform spherical shape is also observed. Particle size of around 22-28 nm can be observed at the calcination duration of 5 h which shows smaller size distribution at lower contact hours showing a range of 30 to 41 nm and 33-60 nm for samples calcined at 3 h and 4 h, respectively. It is also observed that 4 h of contact time leads to the largely agglomerated particles of CuO.
Synthesis and Characterisation of CuO/HNT Nano-Particles through In-situ Glycine Nitrate Process

3.2.2. Effects of variation of calcination temperature with calcination duration being constant

Fig. 3 presents the FESEM images for the samples obtained at varying calcination temperatures at fixed contact time of 5 h. The results for the temperatures of 500 °C, 600 °C and 700 °C of calcination time could be observed in Fig. 3a, Fig. 3b and Fig. 3c, respectively.

Looking into the images it could be noticed that the sample calcined at 600 °C for 5 h forms the best morphology, size and shape distribution. Clearly, less agglomeration is observed as compared to that of calcined at 700 °C. As seen in Fig. 3c the particles have started to merge in each other which is due to sintering effect at elevated temperatures [15]. In addition to that as observed in Fig. 3a, the particle sizes are bigger in size, which is due to incomplete combustion of the precursor. The nanoparticles synthesized at these conditions had an average size of 23 nm based on 50 random particle measurements using ImageJ software. Therefore, the sample calcined at 600 °C for 5 h was found to be the most suitable sample among all.

3.3. Fourier Transform Infrared Spectroscopy (FT-IR)

Fig. 4 presents the FTIR image of CuO-HNT particle after calcination at 600 °C for 5 h. This graph indicates the existence of halloysite nanotubes by confirming the presence of the stretching or broad bands for the deformation of Al–O–Si, deformation of Si–O–Si, and the presence of Si–O groups. The deformation of Al–O–Si was determined by the stretching observed at wavelength of 532 cm⁻¹. The broad band obtained approximately at the wavelength of 1030 cm⁻¹ was confirmed to be due to the presence of Si–O and Si–O–Si groups in the samples. The deformation of CuO particle was observed at the wavelength of 462 cm⁻¹ through the sharp peak. This results enabled the conclusion that halloysite nanotubes were present in the CuO nanoparticles samples.

Comparing the FTIR image in Fig. 4 with the spectrogram presented in Fig. 5 for the pure HNT; it is noticed that some peaks have been omitted from the HNT after calcination. The bands at wavelength between 3500 cm⁻¹ and 4000 cm⁻¹ were determined to
be the absorption bands of Al2OH groups. These bands were omitted in all the samples, which was mainly due to the absence of the –OH groups in the Al2OH molecules since chitosans tended to form hydrogen bonding with the –OH group during surface immobilization of the halloysite nanotubes before allowing copper oxide nanoparticles to deposit on the halloysite nanotubes. Also elevated temperatures will decompose all the organic parts of the samples [17].

Fig. 4 FTIR spectra of the synthesis of supported on HNTs via in-situ glycine process at 600°C for 5 h

3.4. Raman Spectroscopy

Raman scattering is not only useful in detecting the structure, bonds of materials and also unintended phases such as Cu2O or Cu(OH)2, but also gives the information about the crystallinity of the samples. The zone center Raman normal active modes of CuO are $\Gamma_{RA} = 4A_u + 5B_u + A_g + 2B_g$ since CuO has a space group of $C_{2h}$ with two molecules per primitive cell. These modes consist of three acoustic modes ($A_u + 2B_u$), three Raman active modes ($A_g + 2B_g$) and six infrared active modes ($3A_u + 3B_u$).

Fig.6 Raman Spectroscopy Graph of Sample Contained only Chitosan (Set A7).

In order to determine the presence of halloysite nanotubes in the samples, pure halloysite nanotubes was tested using Raman spectroscopy as well. Similarly, three main Raman active modes were obtained, at 122 cm$^{-1}$, 459 cm$^{-1}$, 733 cm$^{-1}$ as shown in Fig.7. By comparing Fig.7 with Fig.6, the presence of halloysite nanotubes in all samples can be concluded to be due to the peaks detected at the similar Raman shifts as that of the pure HNT curve. Therefore, in this experiment, the samples showed their crystallinity by giving relatively sharp peaks, and essentially showed the existence of both copper oxide and halloysite nanotubes.

Fig. 6 Raman Spectroscopy Curve of Pure HNT

3.5. Energy Dispersive X-ray Spectroscopy (EDX)

EDX was performed on the samples and the results for the sample at 600°C and 5 h of calcination conditions are presented in Table 1. Based on the results, it can be seen that the samples contained both copper oxide nanoparticles and halloysite nanotubes. The presence of halloysite nanotubes can be confirmed with weight percentage of silicon element and aluminium element detected. The oxygen element detected can be due to the presence of copper oxide nanoparticles or due to the presence of halloysite nanotubes.

Fig. 7 Raman Spectroscopy Curve of Pure HNT
3.6 Brunauer-Emmett-Teller (BET) Analysis

The BET test was on the sample calcined at 600°C for 5 h, as the particle sizes were found to be the smallest and the size, shape distributions were the most uniform among these three samples. The main focus of BET theory was to determine the mean pore size, mean surface area, as well as the mean pore volume. The results of BET and a comparison with an unsupported CuO reported by Ren et al. [19] are tabulated in Table 2. It could be noted that supported copper oxide synthesized in this experiment has significantly smaller pore size and larger surface area, which is favorable.

CONCLUSIONS

An in-situ glycine nitrate process was successfully developed as a synthesis process of copper oxide nanoparticles supported on halloysite nanotubes. The characterization tests, including raman spectroscopy, FTIR and EDX results had further confirmed the presence of both copper oxide and halloysite nanotubes in the samples. Based on BET results, copper oxide nanoparticles supported on halloysite nanotubes using in-situ glycine nitrate process showed larger surface area as compared to other supported copper oxides synthesized by other researchers. The use of chitosan formed a better dispersion of the copper ions in the gel, allowing a uniform distribution of the copper ion, resulting a sample with more uniform size and shape distribution. For the best sample of this project, the optimum conditions were analyzed to be 600°C and 5 hours.

| Table 1 EDX Results of Sample of CuO-HNT Calcined at 600°C for 5 h |
|-----------------|-----------------|-----------------|
| Element         | Weight%         |
| O K             | 49.14           |
| Al K            | 12.27           |
| Si K            | 13.15           |
| Cu K            | 25.44           |
| Totals          | 100.00          |

| Table 2 BET analysis and comparison with unsupported CuO reported by Ren et al. (2009) |
|-----------------|-----------------|-----------------|
| Supports        | Mean Pore Size (nm) | Mean Surface Area (m²/g) | Mean Pore Volume (cm³/g) |
| CuO-HNT         | 11.08           | 38.96           | 0.11            |
| Unsupported CuO | 60.69           | 15.69           | -               |

ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the Ministry of Science, Education, and Innovation (MOSTI) of Malaysia for providing research funding under the e-Science scheme grant number 03-02-10-SF0259. Monash University Malaysia is also highly admired for providing the facilities to complete this project.

REFERENCES