IMMOBILIZING METALLIC COPPER ONTO SUBMICRON SILICA SYNTHESIZED FROM RICE HUSK ASH

CỐ ĐỊNH ĐỒNG (Cu) KIM LOẠI LÊN SILICA KÍCH THƯỚC DƯỚI MICRON ĐIỀU CHẾ TỪ TRO TRẤU

Nguyen Van Thuc, Nguyen Vinh Tien
Ho Chi Minh City University of Technology and Education, Vietnam

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ABSTRACT

Rice husk is an abundant low-cost source of silica in Vietnam and copper submicron particles are extensively studied as effective antimicrobial, antifugal and catalytic material with enormous potential applications. Rice husk was washed with acidic solutions and then ashed at 700 ^{o}C. After alkaline leaching silica from the obtained ash, acidic treating with HCl solution in the presence of cetyltrimethylammonium bromide (CTAB) as surfactant yielded silica particles with submicron sizes. Metallic copper was synthesized and impregnated in situ onto silica particles using wet chemical method with $CuSO_4$ as copper precursor and ascorbic acid as reductant. The obtained silica and silica-copper (Cu/SiO_2) composite were characterized by SEM micrographs, EDX, XRD, spectroscopic methods. The obtained results confirmed the formation of submicron silica powders and metallic Cu on the surface of silica. FTIR analysis of the materials showed that some copper ions were covalently bonded with the SiO_2 network and not reduced by ascorbic acid.

Keywords: *Rice husk ash; submicron silica; ascorbic acid; silica-copper; in situ.*

TÓM TẮT

Vỏ trấu là một nguồn sản xuất silica dồi dào và giá thành thấp ở Việt Nam, và vật liệu đồng (Cu) kích thước dưới micron hiện được nghiên cứu rộng rãi như một vật liệu kháng khuẩn, kháng nấm và xúc tác với rất nhiều tiềm năng ứng dụng. Các hạt silica (SiO_2) kích thước nhỏ hơn 1 micron đã được điều chế bằng phương pháp sol-gel sau khi trích tách silica khỏi tro trấu trong môi trường kiềm. Đồng (Cu) kim loại được tổng hợp và cố định in situ lên các hạt silica này trong dung dịch nước với CuSO4 làm tiền chất, acid ascorbic làm chất khử. Các mẫu silica và silica-đồng (Cu/SiO_2) được định tính bằng các phương pháp SEM, EDX, XRD, FTIR. Các kết quả thu được xác nhận sự tạo thành các hạt silica kích thước nhỏ hơn micron, cũng như sự tạo thành Cu kim loại trên bề mặt silica. Phép phân tích bằng FTIR cho thấy rằng một phần ion Cu được liên kết cộng hóa trị với mạng lưới SiO_2 và không bị khử bởi acid ascorbic.

Từ khóa: *Tro trấu; silica; acid ascorbic; silica-đồng; in situ.*

1. INTRODUCTION

Rice husk (RH) is an abundant agricultural by-product and waste with an amount of approximately 600 million tons annually disposed over the world [1]. RH contains 65–75% organic (lignin, cellulose and hemicellulose) and 15–20% inorganic substances (SiO_2) [2]. However, because of its undesirable properties, like slow rate of degradation, low nutrition value and high ash content, until now only a small portion of produced RH is utilized, while a large amount of it is burned to generate heat [3]. During combustion the organic composition is oxidized and rice husk ash (RHA) is yielded. As one of the most silica rich raw materials containing about up to 98% silica, together with its low cost and high abundance, RHA has been exploited to prepare nanostructured silica to be used in biomedical applications [4], as concrete additive [5] or polymer filler. Nanostructured SiO_2 can also be synthesized from RHA through chemical means (acid/alkali leaching and post heat treatment) [6-8] as well as non-isothermal decomposition [9], and combustion after carbonization [10], pressurized hot-water [11], microwave hydrothermal [12], and precipitation [13]. Of the different synthesis methods, the chemical method consisting of simple acid leaching and post annealing is of the most simple and successful techniques to synthesize the ultrafine SiO_2 nanopowder from RHA.

Copper, an inexpensive metal, has been used since ancient times in many applications due to its good mechanical, electrical and thermal properties. Recently, many Cu-based nanomaterials have been considered a promising catalyst for the hydrogenolysis of C-O bonds [14], the epoxidation of propylene [15] etc. Due to its high selectivity, activity and low cost. However, the synthesis and the use of Cu nanomaterials is challenging due to their readiness of oxidation [16].

In this study we synthesized submicron silica powder from rice husk as an low-cost and renewable source and then incorporate metallic Cu onto it by using wet chemical reactions. The obtained material can be used in the future as potential catalyst for many organic reactions.

2. MATERIALS AND METHODS

2.1 Materials

Rice husk was purchased locally in Vietnam. NaOH, HCl (36.5%), cetyltrimethylammonium bromide (CTAB) and ascorbic acid were purchased from XILONG SCIENTIFIC CO.LTD. (Guangzhou, China).

2.2 Methods

2.2.1. Pretreatment of rice husk

The procedures of obtaining silica rom rice husk was adapted from known methods [6]. In a typical experiment, dried rice husk was ground and treated with 10% (w/w) HCl and then 30% (w/w) H_2SO_4 solutions to remove small amounts of minerals. The residue was then burned at 700^oC in a furnace to remove all organic matter and a grey rice husk ash (RHA) was obtained. RHA was washed with 10% HCl solution and then 30% H_2SO_4 solution at 100^oC for 2 hours to leach out soluble inorganic substances. After that, RHA was vacuum-filtered from the slurry and washed several times with distilled water until the filtrate showed pH=7.

2.2.2. Preparation of submicron silica from RHA

In a flask equipped with a reflux condenser, the pretreated RHA and 100 mL of 5M NaOH were added, magnetically stirred and boiled for 5 hours in order to leach silica into sodium silicate according to reaction:

$$SiO_2 + 2\,NaOH \rightarrow Na_2SiO_3 + H_2O \qquad (1)$$

The Na_2SiO_3 solution was vacuum-filtered and washed with hot distilled water.

A 1:1 (v/v) n-butanol/water solution containing 2.0 wt. % CTAB as surfactant was prepared in advance. The Na_2SiO_3 solution derived from RHA was added to 100mL of the surfactant solution and stirred for 15 minutes at 60 ^oC. While the solution was stirred, a 2.5 M HCl solution was added drop-wise from a buret until the solution reached a pH of about 7.

The obtained gel solution was aged while stirring for 5 h 60^oC and then centrifuged at 5000 rpm for 10 minutes. The obtained silica was washed with distilled water and then with absolute ethanol several times. The wet silica powder was dried and then calcinated in a furnace for 4 h at 550^oC.

2.2.3. Depositing metallic copper onto silica powder

Metallic copper was deposited onto silica powder by chemical reduction method. 1,0 g of SiO_2 was added to 10 mL of 0.5 M $CuSO_4$ solution and stirred for 2 hours. The solid was then filtered and washed with 100 mL of distilled water, then added to a solution of 1 M ascorbic acid. The dispersion was stirred for 2 h at 80°C. The pink solid product was vacuum-filtered, washed with distilled water several times and then dried in vacuum.

3. RESULTS AND DISCUSSIONS

3.1. SEM micrographs analysis

Scanning electron microscopy (SEM) image (Fig. 1, upper) showed submicron sizes and irregular shapes of the obtained Cu/SiO_2 particles. It is well-known that SiO_2 synthesized from sodium silicate by sol-gel method produced less monodispersed particles than from tetraethyl orthosilicate by standard Stöber method [17]. The advantage of sodium silicate from RHA is its low cost, its renewable and waste source.

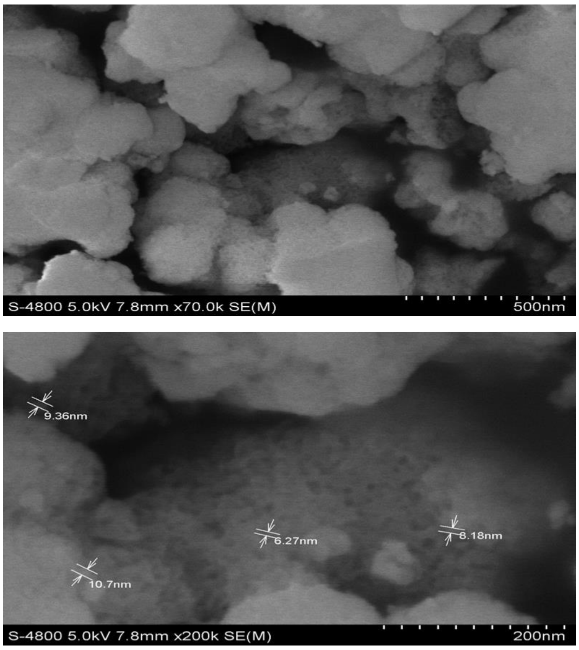

***Figure 1**. SEM images of silica submicron particles*

SEM image with higher magnification (Fig. 1, lower) showed that the surface of the SiO_2 particles is covered with nanoscale holes, which may serve as places for adsorption of copper ions and growth of copper nanoparticles.

3.2. EDX and XRD analysis

Energy-dispersive X-ray spectroscopy (EDX) spectrum showed that after treating silica powder with $CuSO_4$ and ascorbic acid solutions, its surface is covered with copper element. However, it was unclear that the peak of copper contributed to Cu or Cu_2O, because copper nanoparticles are easily oxidized by oxygen [18]. X-ray diffraction (XRD) diagram of the obtained material showed 3 distinct peaks at 43.3, 50.4 and 74.1degree of diffraction angles, which agree with copper metal at (111), (200) and (220) planes, respectively [19]. No other distinct peaks of Cu_2O [20] implied that the immobilized metallic Cu was stable to oxidation by air.

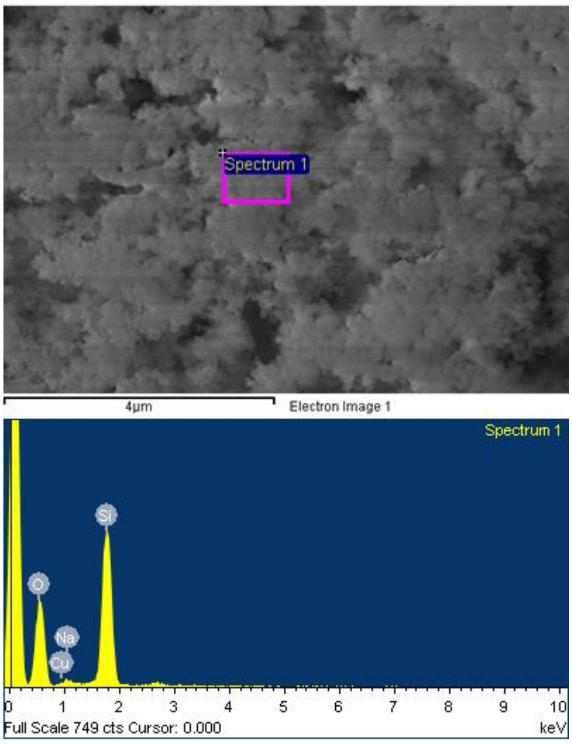

***Figure 2.** SEM image (upper) of the Cu/SiO_2material and EDX spectrum (lower) at the rectangle.*

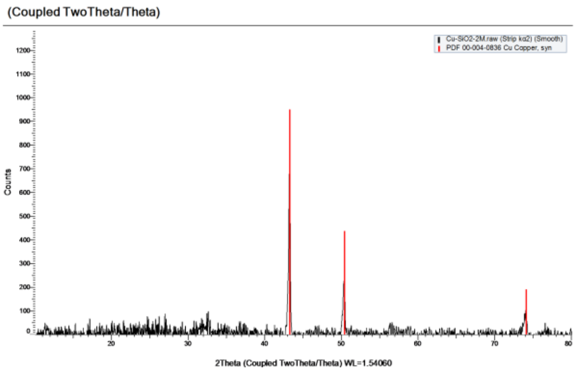

***Figure 3.** X-ray diffraction diagram (XRD) of the Cu/SiO_2 sample (black) and standard Cu (red)*

3.3. FTIR spectra analysis

FTIR spectra of the synthesized SiO_2 and Cu/SiO_2materials are shown in Figure 4. The interpretations of appeared peaks are summarized in Table 1.

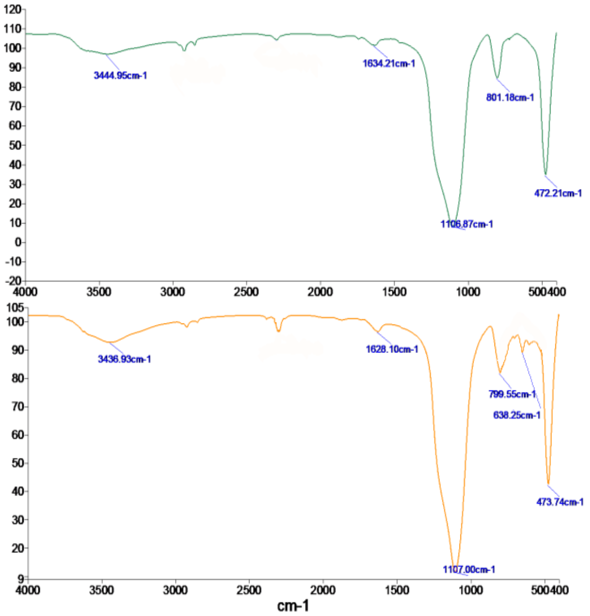

Figure 4. *FTIR spectra of SiO_2 (upper) and Cu/SiO_2 (lower) samples*

These spectra were almost the same with an exception of the appearance of a peak at 638.25 cm^{-1} for Cu/SiO_2sample. This can be explained by the formation of some covalent bonds between ion Cu^+ or Cu^{2+} with O atom in the free silanol groups on the surface of SiO_2 network.

Table 1. *Interpretation of peaks in FTIR spectra of the synthesized SiO_2 and Cu/SiO_2samples.*

Peak position, cm^{-1}		Type of vibration [21]
SiO_2	SiO_2-Cu	
3444.95	3436.93	Free SiO-H stretching
1634.21	1628.1	H-O-H (water) bending
1106.87	1107.00	Si-O-Si bending
801.18	799.55	Si-O-H bending
472.21	473.74	Si-O-Si bending
-	638.25	Cu-O stretching

4. CONCLUSION

This work demonstrates the feasibility of synthesizing submicron silica material from a waste and renewable source. Onto the surface of this material metallic copper was prepared and immobilized *in situ* by adsorbing cupric ions and then reducing them with ascorbic acid.

SEM micrographs confirmed the submicron sizes and irregular shapes of the obtained powders. EDX and XRD spectra confirmed the formation of metallic Cu, as well as the absence of Cu_2O on the surface of silica particles. FTIR spectra revealed some copper ions covalently bonded with silica network and not reduced by ascorbic acid. The synthesized materials were low-cost, robust to oxidation by air and thus suitable for catalytic applications, as well as antibacterial and antifouling materials in the future.

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Corresponding author:
Nguyen Vinh Tien, PhD
Ho Chi Minh City University of Technology and Education
Email: tiennv@hcmute.edu.vn