ORIGINAL RESEARCH PAPER

Green chemistry approach for the synthesis of CuO nanostructure

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ABSTRACT: Molecular sieves MCM-41 were synthesized from rice husk ash (RHA) as alternative sources of silica. The material was synthesized by a room temperature method from a gel with the molar composition SiO_2: 1.6 EA: $0.215HDTMABr$: $325H_2O$ with pH correction. The cetyltrimethylammonium bromide (CTMABr) was used as a structure template. Nanocomposite containing 5.0 and 10.0 wt.% of Cu was synthesized under solid state reaction. The calcinations of samples were done at two different temperatures, 400 and 600 °C. The morphology and the physicochemical properties of the prepared samples were investigated by X-ray diffraction (XRD), UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS), Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). TEM images indicated that nanoparticles size of CuO is ~ 3 nm.

Keywords: *Green Chemistry; Nanocatalyst; Nanocomposite; Semiconductor; TEM*

INTRODUCTION

Rice-husk (RH) is an agricultural by-product material. It constitutes about 20% of the weight of rice. It contains about 50% cellulose, 25-30% lignin, and 15-20% of silica. When rice-husk is burnt rice-husk ash (RHA) is generated.

On burning, cellulose and lignin are removed leaving behind silica ash. The ash of RH contains 87-97 wt% of silica in a hydrated amorphous form which is a good precursor for chemical synthesis involving silicate sources. Pure silica up to 99.98% can be obtained from rice husk ash (RHA). Other than that, RHA can be used as an alternative source for active silica production.

The controlled temperature and environment of burning yields better quality of rice-husk ash as its particle size and specific surface area are dependent on burning condition. For every 1000 kg of paddy milled, about 200 kg (20%) of husk is produced, and when this husk is burnt in the boilers, about 50 kg (25%) of RHA is generated. Completely burnt rice-husk is grey to white in color, while partially burnt rice-husk ash is blackish. The form of silica obtained after combustion of rice husk depends on the temperature and duration of combustion of rice husk [1]. Zeolite with a hexagonal structured mesopore network (MCM-41 and SBA-15) has been extensively studied since the first report dealing with their synthesis [2]. Their high specific surface area, porous volume and adjustable pore size diameter make them ideal support for the preparation of highly dispersed semiconductor nanoparticles [3]. Therefore, MCM-41 as one of the mesopore zeolite is one of the most attractive supports for metal or metal oxide nanoparticles [4]. Cupric oxide (CuO) is a *p*-type semiconductor with an energy band gap of 1.21 eV, which can be excited under sunlight radiation.

CuO has various applications: glucose sensors, field emission emitters, gas sensors, and heterogeneous catalysts. In the present study, the solid state approaches for synthesis of copper oxide

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nanoparticles are considered and are in progress for ultrafine semiconductors in MCM-41 mesoporous material in different concentration of copper. Because of their high surface areas, regular pore channels, and large pore diameters (2-20 nm), ordered MCM-41 mesoporous material has been used as suitable scaffolds for the dispersion of small metal and semiconductor nanoparticles.

EXPERIMENTAL
Preparation of RHA

About 30.0 g of clean rice husk (RH) was stirred with 750 mL of 1.0 mol L^{-1} HNO_3 at room temperature for 24 h. Acid treated RH was washed with a copious amount of distilled water to constant pH, dried in an oven at 100 °C for 24 h and burned in a muffle furnace at 600 °C for 6 h to obtain white RHA [5]. About 3.0 g of RHA was added to 350 mL of 1.0 mol L^{-1} NaOH in a plastic container and stirred for 24 h at room temperature to dissolve the silica. The material (Sodium Silicate) obtained was used as the silica source for the production of MCM-41.

Synthesis of MCM-41 material

The MCM-41 material was synthesized by a room temperature method with some modification in the described procedure in the literature [3]. We used sodium silicate as a source of silicon and hexadecyltrimethylammonium bromide (HDTMABr, BDH, 103,912) as a surfactant template for preparation of the mesoporous materials. The molar composition of the reacting mixture was as follows:

$$SiO_2: 1.6EA: 0.215HDTMABr: 325H_2O$$

EA stands for ethylamine. The MCM-41 prepared was calcined at 550 °C for 5 h to decompose the surfactant and obtain the white powder. This powder sample was used for loading the nanoparticles.

Preparation of CuO

The copper-containing catalysts (5.0 and 10.0 wt.% copper loading) were prepared by solid state reaction of 1 g of MCM-41 with amount 0.038 and 0.076 g of $Cu(CH_3COO)_2$. After mixing, the solid phase samples were calcined in airflow at 400 and 600 °C for 5 h. The prepared samples are termed as xCuO/MCM-41-t (x is 5.0 and 10.0 wt.% and t is 400 and 600 °C).

Characterization

Powder X-ray diffraction patterns of the samples were recorded using an X-ray diffractometer (Bruker D8 Advance) with Co Kα radiation (λ = 1.789 A°) under the conditions of 40 kV and 30 mA, at a step size of 2θ = 0.02°. The UV-Vis diffused reflectance spectra (UV-Vis DRS) obtained from UV-Vis Scinco 4100 spectrometer with an integrating sphere reflectance accessory. $BaSO_4$ was used as reference. The infrared spectra on KBr pellet were measured on a Bruek spectrophotometer. The transmission electron micrographys (TEM) were recorded with a Philips CM10 microscope, working at a 100 kV accelerating voltage. Samples for TEM were prepared by dispersing the powdered sample in acetone by sonication and then drip drying on a copper grid coated with carbon film. The surface morphology of the samples was obtained using a Jeol-JSM-5610 LV scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

The FT-IR spectra of the RHA obtained in the wave number range 400-4000 cm^{-1} are presented in Fig. 1. The broad band around 3432-3469 cm^{-1} is due to the stretching vibration of O-H bond in Si-OH and the HO-H vibration of the water molecule adsorbed on the silica surface [6]. The band at 1634-1645 cm^{-1}can be assigned to the bending vibration of H_2O trapped within the silica matrix. The band at 1074-1090 cm^{-1} was attributed to asymmetric Si-O-Si stretching vibration of the structural siloxane bond. The band at 466 cm^{-1} is due to Si-O-Si bending vibrations [6]. The band at 806 cm^{-1} can be assigned to the symmetric Si-OH stretching vibrations [7].

The powder XRD patterns of the RHA is presented in Fig. 2. A very broad peak in the range of 22.6-23.4 ° (2Tetha) was observed as a result of the amorphous nature of the silica [8].

The low angle X-ray powder diffraction patterns of te prepared matrix are presented in Fig. 3. The XRD patern of MCM-41 shows typical characteristic three-pek pattern with a very strong one at a low 2θ and two peaks at higher 2Tetha values [2, 9].

No peak is observed between 2Tetha = 10- 80° for mtrix (not shown) [2, 9]. Fig. 4 shows the XRD results obained in wide-angle region for xCuO-MCM-41-t sample calcined at t = 600 °C (x is 5.0 wt.%). There is
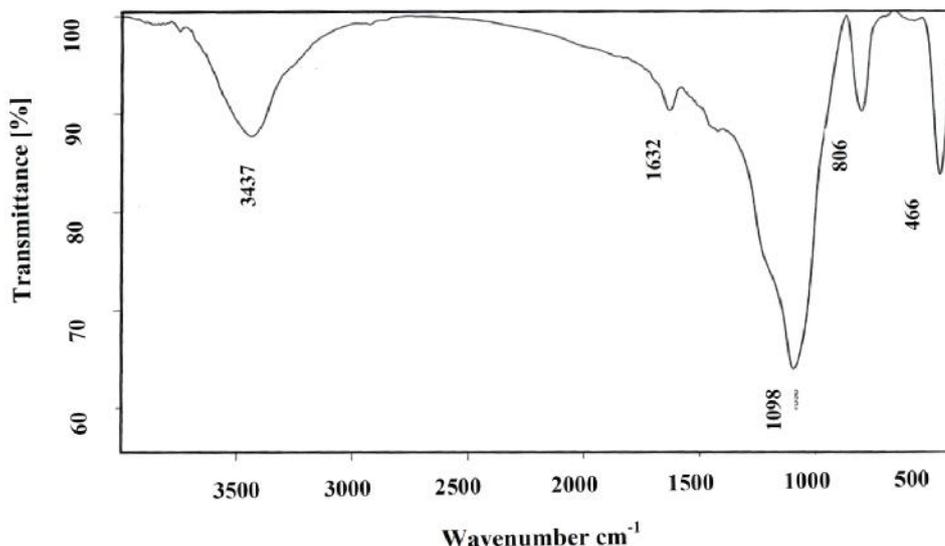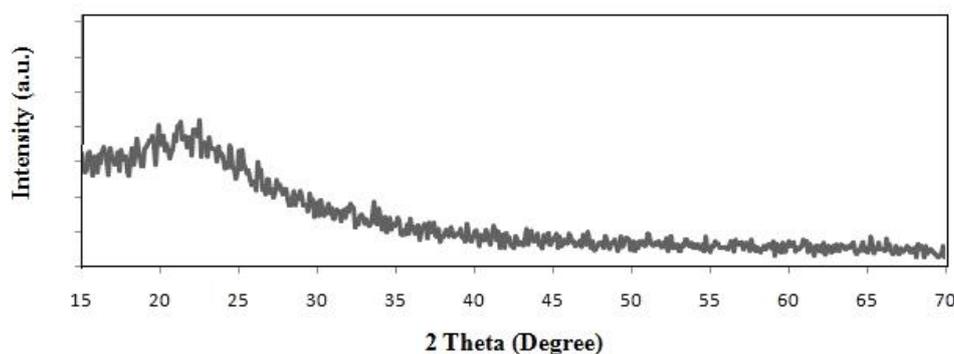
Fig. 1: FT-IR spectra of RHA.

Fig. 2: The XRD pattern of the RHA.

characteristic diffraction peaks of CuO and Cu^{2+}-ion exchange MCM-41 mesopore in all samples. But, strong diffraction peak of CuO and Cu^{2+} ions is observed for 5CuO-MCM-41-600 sample with respect to other copper samples. In fact, intensity in 5CuO-MCM-41 samples is higher than 10CuO-MCM-41 samples (not show). Probably, in high content of copper, Cu is present in nanocomposite in the forms of CuO and Cu nanoparticles. The average crystallite sizes of matrix and CuO calculates by Scherrer,s equation. All the CuO-MCM-41 samples have almost the same crystallite sizes (ca. 5 nm for CuO and 90 nm for MCM-41 matrix), implying that the deposition of CuO clusters on the MCM-41 surface has no obvious influence on the crystallite size. TEM was

further used to study the morphology and microstructures of the CuO-MCM-41 samples.

Fig. 5 shows a typical TEM image (5CuO-MCM-41-600). As can be seen in Fig. 5, CuO nanoparticles of ~ 3 nm were formed and stuck to the surface of MCM-41 nanoparticles. No free CuO nanoparticle was found.

The UV-Vis diffuse reflectance spectra of MCM-41 matrix and 5CuO-MCM-41-600 sample is shown in Fig. 6. Synthesized MCM-41 shows an intense peak located at ~320 and 380 nm. These bands are attributed to a charge transfer transition of framework tetrahedral atoms.

The Cu^{2+} ions have a $3d^9$ electronic structure. In the presence of a crystal field generated by ligands
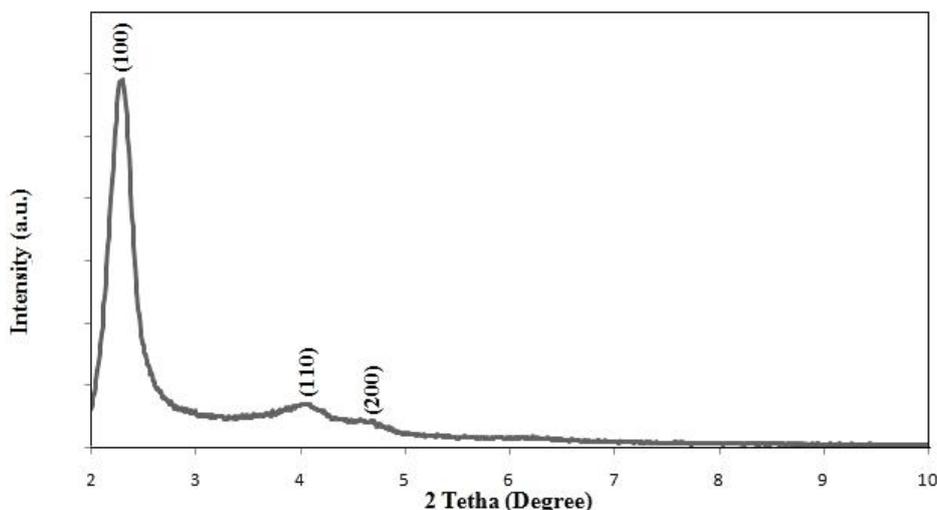
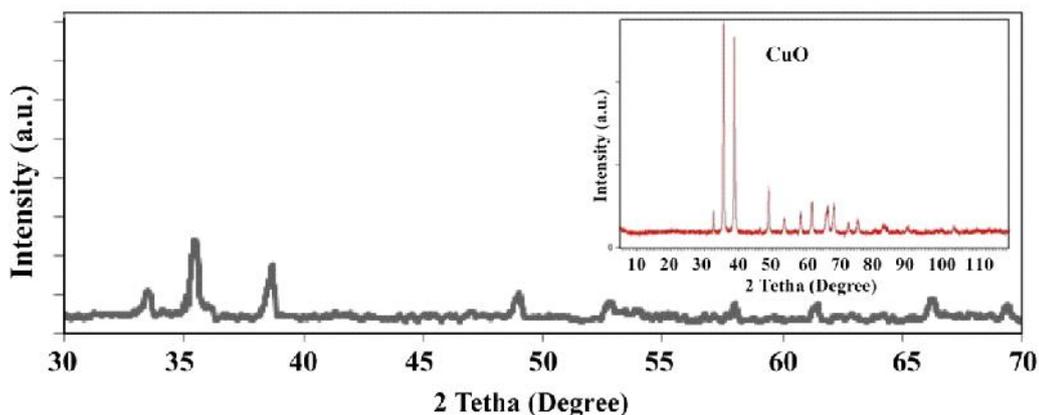Fig. 3: The XRD pattern of MCM-41

Fig. 4: XRD pattern of 5CuO-MCM-41-600. The insert shows XRD patterns of CuO nanoparticles.

or oxygen ions, d-d transitions appear in the visible or near-IR range. The band at 380 nm is due to $O_2 \cdots Cu^{2+}$ ligand to metal charge transfer transition where the copper ions occupy isolated sites over the support.

In Fig. 7, intensity of peaks decreases in Cu-containing MCM-41 samples at 320 and 380 nm. This decrease is attributed to presences of copper in mesoporous matter and O_2----Cu^{2+} ligand to metal charge transfer transition. The 5CuO-MCM-41-600 sample shows three broad bands at about 450-500, 500-600 and 600-720 nm (Fig. 7).

These bands are due to atomic copper cluster, Plasmon resonance band and octahedral Cu^{2+} ions in MCM-41 matrix, respectively. At 5CuO-MCM-41-400 sample that temperature is low, peaks due to atomic copper cluster and Plasmon resonance disappeared. This fact confirms that when amount of copper species in matrix is low, probably they are present in MCM-41 material in form of CuO.
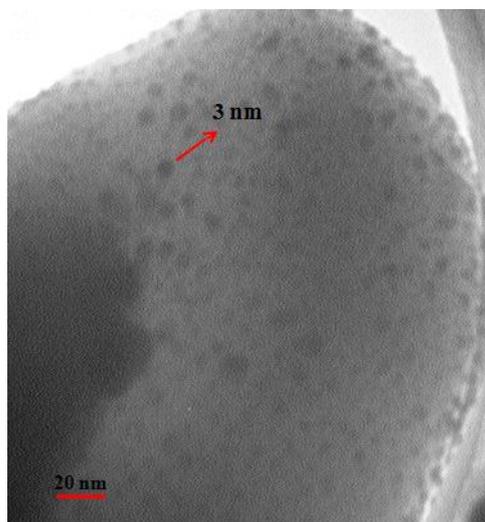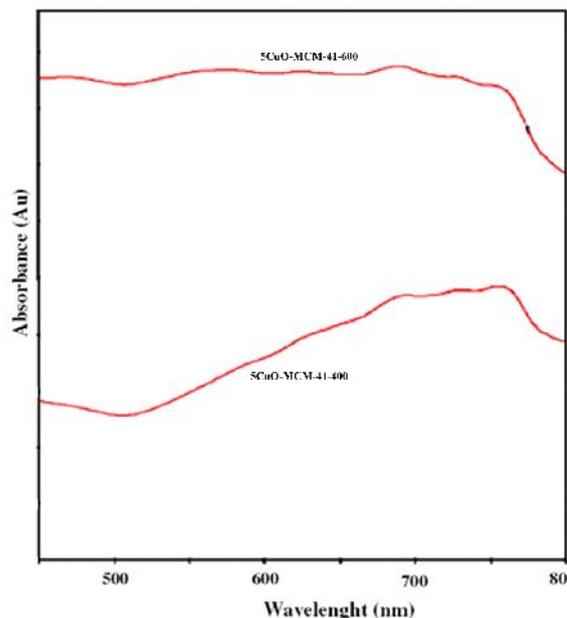
Fig. 5: TEM image of 5CuO-MCM-41-600 nanocomposite.

Fig. 7: The UV-Vis diffuses reflectance spectra of xCuO-MCM-41-t samples in range of 450-800 nm.
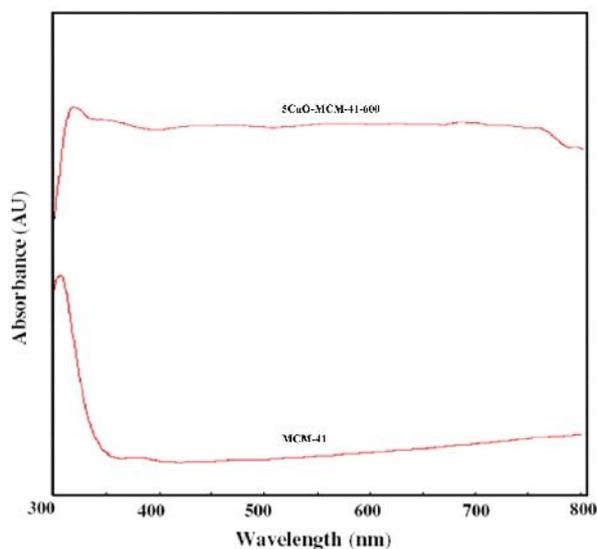
that the modified samples retain the mesoporosity. Also, XRD results support the presence of crystalline CuO at low copper loadings (5 wt.%). There is no appreciable change in pore diameter and unit cell parameter in CuO-MCM-41. As can be seen in TEM image, CuO nanoparticles of ~ 3 nm were formed and stuck to the surface of MCM-41 nanoparticles.

ACKNOWLEDGEMENTS

Fig. 6: The UV-Vis diffuses reflectance spectra of MCM-41 matrix and 5CuO-MCM- 41-600 nanocomposite.

CONCLUSION

The molecular sieve obtained from RHA as an alternative source of silica has similar properties to those synthesized materials with conventional silica, without requiring chemical treatment of RHA. The RHA, of a negligible cost, can be a promising replacement for the high cost silica. The FTIR and XRD data demonstrated that the highly pure MCM-41 was successfully synthesized from RHA. XRD studies reveal

REFERENCES

1. Tan W-Ch., Yap S-Y., Matsumoto A., Othman R.,Yeoh F-Y., (2011), Synthesis and characterization of zeolites NaA and NaY from rice husk ash. *Adsorption*. 17: 863-868.

2 Beck J. S., Vartuli J. C., Roth W. J., Leonowicz M. E., Kresge C. ., Schmitt K. D., Chu C. T. W., Olson D. H., Sheppard E.W., 2012), A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc.* 114: 10834-10843.

3. Pourahmad A.,(2013), Nanocomposite prepared from ZnS nanoparticles and molecular sieves nanoparticles by ion exchange method: Characterization and its photocatalytic activity. *Spectrochim Acta: A*. 103: 193-198.

4. Pourahmad A., (2012), Ag_2S nanoparticle encapsulated in mesoporous material nanoparticles and its application for photocatalytic degradation of dye in aqueous solution. *Superlattice Microst.* 52: 276-287.

5. Srivastava V. C., Mall I. D., Mishra I. M., (2006), Characterization of mesoporous rice huskash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. *J. Hazard. Mater: B.* 134: 257-267.

6. Ahmed A. E., Adam F., (2007), Indium incorporated silica from rice husk and its catalytic activity. *Micropor. Mesopor. Mater.* 103: 284-295.

7. Endud S., Wong K. L., (2007), Mesoporous silica MCM-48molecular sieve modified $SnCl_2$ in alkaline medium for selective oxidation of alcohol. *Micropor. Mesopor. Mater.* 101: 256-263.

8. Thuadaij N., Nuntiya A., (2008), Preparation of nanosilica powder from rice husk ash by precipitation method. *Chiang Mai. J. Sci.* 35: 206-211.

9. Pourahmad A., (2015), Fabrication of nanocatalyst in aqueous solution with photocatalytic activity of methylene blue. *Synth. React. Inorg. Met.-Org. Chem.* 45: 1080-1086.