



# Controlled growth of zinc oxide microrods by hydrothermal process on porous ceramic supports for catalytic application



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## ABSTRACT

The growth of zinc oxide (ZnO) microrods on porous ceramic substrates by mild hydrothermal process was studied. One-dimensional ZnO microrods were grown on ZnO nanoparticle seeded substrates by using equimolar concentration of zinc nitrate and hexamethylenetetramine at temperatures lower than 100 °C. We found that the growth of ZnO microrods on alumina and diatomite substrates were affected due to hydrolysis of substrate surfaces. Stunted ZnO microrod growth on  $\gamma$ -alumina and diatomite substrates were attributed to arise due to the degradation of hexamine molecules in the growth solution. Adjusting the pH prior to the growth of ZnO microrods on both alumina and diatomite lead to the growth of ZnO microrods similar to what is observed on flat glass substrates. Cordierite does not hydrolyze easily and hence ZnO microrods with aspect ratio as high as 24, were obtained without any pH control of the growth solution. Copper nanoparticles deposited on ZnO microrods were utilized as a catalyst for methanol steam reforming and about 14% hydrogen yield was obtained with almost 90% methanol conversion at reforming temperature of 350 °C.

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## 1. Introduction

Porous ceramics are important for many industries where high surface area, chemical physical and thermally resistant materials are a requirement [1,2]. Applications of porous ceramics extends from filtration to use in mechanical seals and as catalyst supports.

Zinc oxide (ZnO) nanostructures have recently attracted considerable attention due to diverse potential applications [3]. ZnO crystals have anisotropic structure with polar and non-polar surfaces that lead to the possibility of growing nanorod or nanowire structures [4]. One-dimensional structures like nanorods or nanowires of ZnO have been used in a wide range of applications from gas sensors, solar cells, optoelectronics to piezoelectric devices. It is generally agreed that varying the morphology suits different applications of ZnO nanomaterials [4]. For gas sensor applications, high surface area of the sensing parts in devices can improve sensitivity and allow the possibility to miniaturize devices [5]. While highly dense ZnO microrods on a substrates are preferred for gas sensor and solar cell applications [6], ZnO based nanogenerators require gap between nanorods for bending during the energy harvesting processes [7–9]. ZnO as a component in catalysts for hydrogen

production through methanol reforming process is also being pursued by several groups including ours [10–14]. Copper–zinc oxide–alumina (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>) has been used as a catalyst for methanol synthesis and it was demonstrated that the use of catalyst support enhanced catalytic stability due to its ability to withstand higher temperatures [14,15].

Several techniques have been utilized to synthesize ZnO nanorod arrays such as chemical vapor deposition, sol–gel and hydrothermal processes, etc. Chemical vapor deposition is an expensive technique while sol–gel and hydrothermal processes are relatively straight-forward as they do not require any complicated systems during synthesis. Hydrothermal process is a simple and low temperature technique for the growth of zinc oxide single crystals [16]. Vayssieres et al. first proposed the low temperature epitaxial growth of ZnO microrods on various substrates from equimolar concentrations of zinc nitrate ((Zn(NO<sub>3</sub>)<sub>2</sub>) and hexamethylenetetramine (hexamine, C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>) precursors [17]. Since this early work, ZnO microrods were successfully grown on flat substrates such as glass [4], transparent conducting oxide film [18], stainless steel [14], paper and flexible polymeric fibers [19,20], amongst others. Though many groups have worked on ZnO microrod growth on solid substrates, there still is a gap in the understanding of hydrothermal growth of ZnO microrods on porous ceramic substrates.

In this study, we compare the growth of ZnO microrods on popular ceramic substrates specifically, alumina, calcined

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diatomite and cordierite with an aim to understand and control the growth of ZnO microrods by hydrothermal process on porous substrates. The ZnO microrods on ceramic supports were utilized as a catalyst support for methanol steam reformation (MSR). Different catalysts have been used for methanol steam reforming amongst which copper (Cu) on ZnO supports show very high catalytic activity and hydrogen selectivity [21]. In this work, copper nanoparticles were deposited on ZnO microrods (Cu–ZnO MR) by conventional impregnation technique. Prepared Cu–ZnO MR catalysts were then utilized for examining the catalytic activities on MSR using a packed tubular reactor operating at temperatures up to 350 °C.

## 2. Experimental

ZnO microrods were grown using a modified method suggested by Guo et al. [4] that compose of ZnO seeding on a substrate followed by a hydrothermal growth process for the microrod growth [4]. Seeding the substrates lead to the formation of ZnO microrods in a preferential direction [22]. Prior to seeding and growth processes, all ceramic and reference glass substrates were prepared and cleaned to remove any surface contaminants.

The glass slides were immersed in detergent solution, sonicated for 20 min and then thoroughly washed with deionized water. The glass slides were then dried in an atmospheric oven at 95 °C overnight. Three types of ceramic substrates namely alumina, calcined diatomite and cordierite which were selected to study the growth of ZnO microrods on porous substrates, and were prepared from commercially available materials (Table 1) that were uniaxially pressed using a hydraulic press to form 1–2 mm thick pellets of 20 mm diameter. All pellets were then calcined at 1000 °C for 2 h in the ambient for strengthening, prior to further use. All pellets were then cleaned by sonication in deionized water for 5 min and dried in a furnace at 200 °C for 1 h in air. Substrate densities were examined by following ASTM C20 (2010) protocol [23]. Specific surface areas (S.S.A.) of substrates were determined using gas adsorption technique (Autosorb-1C; Quantachrome Ins.) where 0.5 g of each sample was outgassed at 300 °C for 5 h prior to the 5-point BET measurements. X-ray diffraction analysis (XRD; PANalytical, X'Pert PRO) was carried out to study the crystal structure of the modified ceramic substrates.

### 2.1. Zinc oxide seeding process

All chemicals used for ZnO nanoparticle synthesis were of analytical grade. Zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) and sodium hydroxide obtained from Merck were used as a zinc and hydroxyl precursors to synthesize ZnO nanoparticles. 4 mM zinc acetate solution was gradually mixed with 4 mM sodium hydroxide in ethanol (Merck) and then the  $\text{Zn}^{2+}$  sol was allowed to hydrolyze under controlled aging in air at 60 °C for 3 h. Hydrolyzed  $\text{Zn}^{2+}$  sol initially formed  $\text{Zn}(\text{OH})_2$  gel that turns into ZnO colloids upon aging. Seeding the substrates were then conducted by dipping ceramic substrates into ZnO colloids for 15 min and then dried in an oven for 15 min; this process was repeated thrice. The seeded substrates were then annealed at 350 °C for 5 h in air and stored in a dehumidified chamber for further use.

### 2.2. Hydrothermal growth of zinc oxide microrods

Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) purchased from Merck was used as a zinc precursor during the ZnO microrod growth. The seeded substrates were inserted in an equimolar solution of zinc nitrate and hexamine heated to 95 °C for up to 10 h. In a sealed chemical bath, equimolar (5–10 mM) solution of zinc nitrate and hexamine was replenished every 5 h to ascertain the ready availability of zinc ions in the growth solution [24]. The substrates after ZnO growth were finally annealed at 350 °C for 1 h in the ambient prior to further use. Each specimen was investigated using field emission scanning electron microscope (FESEM,

JEOL-6301) working at 20 kV to record the morphology of microrods. Shape and sizes of ZnO microrods were determined from the micrographs by using standard image analysis software (ImageJ software).

### 2.3. A catalyst support application of ZnO microrods on cordierite substrates

#### 2.3.1. Preparation copper/zinc oxide microrod catalysts (Cu–ZnO MR)

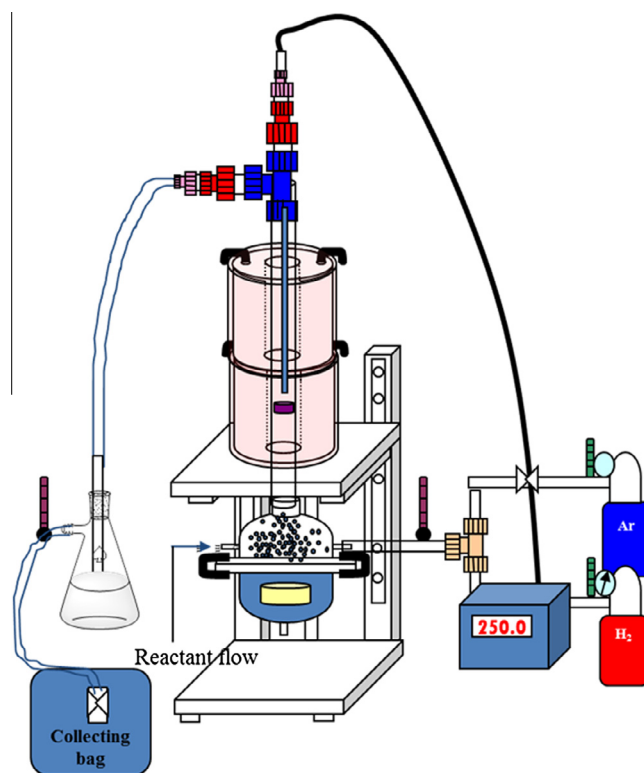
Copper nanoparticles used in this work have been prepared as a colloidal dispersion by heterogeneous precipitation. The synthesis was carried out in an aqueous solution under constant stirring using 0.46 mM copper nitrate as a copper precursor and hydrazine as a reducing agent [25,26]. Polyvinylpyrrolidone (PVP) 5 wt% in deionized water was added for stabilization of the colloids. Copper nanoparticles were deposited on ZnO microrods grown on the substrates by impregnation technique. The ZnO microrod supports were immersed in the copper colloidal suspensions at 95 °C for 2 h. Excess copper nanoparticles which did not attach to the microrods were then removed by rinsing the samples with deionized water. The immersed samples were finally calcined at 300 °C for 1 h in air. Each specimen was investigated using field emission scanning electron microscope (FESEM, JEOL-6301) working at 20 kV to record the morphology of copper nanoparticles on ZnO microrods. Copper and zinc contents were determined using inductively coupled plasma-optical emission spectrometer (ICP-OES: Horiba, Activa). First, the catalyst samples were weighed and heated at 95 °C and then soaked in strong sulfuric acid for 3 h to allow metals and metal oxides to be released from the substrates. Zinc oxide, copper and copper (I) oxide are readily dissolved in sulfuric acid while copper (II) oxide forms copper sulfate before dissolving in water. Adjusted final volume of released metal ions in the solution were used to determine the contents of copper and zinc using ICP-OES.

#### 2.3.2. Steam reforming of methanol

The steam reforming of methanol were carried out at atmospheric pressure in a packed electrically heated tubular reactor of 20 mm diameter in a 20 cm long heated zone schematically represented in Fig. 1. Methanol steam reforming was performed at varying temperatures ranging from 200 °C to 350 °C in the presence of 0.5 g of as-prepared catalysts that were ground and packed in the reactor. Prior to methanol steam reforming process, catalyst were activated by flowing 60 mL/min of 5%  $\text{H}_2$  in argon at 300 °C for 1 h. Water to methanol ratio of 0.8 mol was used for all the reforming experiments. An ultrasonic transducer was used to generate aerosols of the reactant which was then carried into the reaction zone by flowing 20 mL/min of argon gas through the aerosol generator chamber. Gas products were collected and analyzed by a gas chromatograph (GC, Buck Scientific) connected to a thermal conductivity detector (TCD). Packed columns of Hyesep D (polyvinylbenzene, PVB) and molecular sieve 13x were used to separate the gas mixtures.

**Table 1**  
Properties of the ceramic substrates used in this work.

Substrates	Source	Specific surface area ( $\text{m}^2/\text{g}$ )	Substrate density ( $\text{g}/\text{cm}^3$ )
Alumina ( $\gamma\text{-Al}_2\text{O}_3$ )	Merck	11.21	0.76
Calcined diatomite	China	9.11	1.58
Cordierite	Zhongtian, Jiangxi, China	14.41	1.70



**Fig. 1.** Schematically experimental set up for methanol steam reforming system.

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