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# Facile Synthesis of a Zinc Oxide Nanoparticle by electrochemical method

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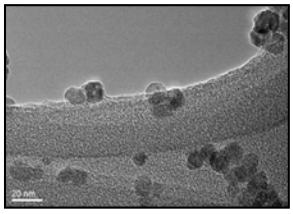
**GRAPHICAL ABSTRACT**



**ABSTRACT**

An electrogenerated zinc oxide (EGZnO/Naph) nanoparticle was successfully synthesized by electrolysis of a *N,N*-dimethylformamide (DMF) solution containing naphthalene and a supporting electrolyte in a one-compartment cell fitted with a platinum cathode and a zinc anode. X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies showed that the EGZnO/Naph consists of pure single crystalline wurtzite of hexagonal structure with average diameters of 10-15 nm. The BET surface area of the EGZnO/Naph was 65 $m^2/g$, which is 15 times larger than that of commercial ZnO powder. The zinc oxide was also confirmed by Fourier transform infrared (FTIR) results which showed vibrational bands at 500 and 434 $cm^{-1}$. Furthermore, the absorption peak of the EGZnO/Naph obtained at 366 nm (3.35 eV), is very close to the band gap of the ZnO 1s–1s electron transition (3.37 eV). Based on these results, this study reports a new pathway to synthesize nanosize of ZnO particle using a simple electrochemical process.

*Keywords: Nanostructures, Chemical synthesis, Electron microscopy, Infrared spectroscopy, X-ray diffraction*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## 1. INTRODUCTION

Nanostructured zinc oxide (ZnO) has become one of the most attractive materials in recent years because of its electrical, catalytic and optical/electronic properties [1-4]. Size, shape, and surface morphology of nanoparticle play pivotal roles in controlling the physical, chemical, optical and electronic properties of this nanoscopic material [5]. Many methods have been studied to synthesize ZnO nanostructures, since their physical and chemical properties are strongly influenced by the method of synthesis. Some of the successful methods, including microwave irradiation [6], hydrothermal [7], sonochemical [8] and sol-gel [9,10] processes, have been reported in the literature. However, in most of these works, the synthesized ZnO particles have an average diameters of 100-600 nm, whereas only a few published reports presented average diameters of 20-50 nm of ZnO [9,10]. In addition, simple and mild conditions for the preparation of high-quality ZnO nanostructures are required. Undoubtedly, one of the most promising methods for such synthesis is electrolysis. This method is a simple, inexpensive and safe option, since the electrons are considered clean reagents in contrast to the harmful oxidative or reducing agents used otherwise [11].

Tokuda et al. have reported a new and simple preparation method for highly reactive electrogenerated zinc (EGZn/Naph) using a platinum cathode and a zinc anode in the presence of naphthalene as a mediator. This EGZn/Naph was an aggregation of very fine particles that passed through usual filter paper and did not precipitate, even after being kept overnight. It was efficiently used in the cross-coupling of halide compounds for the synthesis of anti-inflammatory agent precursors [12]. Due to the physical observation and high reactivity of this EGZn/Naph, we expect that it is made up of nanoparticles with a larger surface area than that of EGZn [13-17] and commercial zinc powder. However, the nature and structure of EGZn/Naph is not clear at the present stage, since it undergoes immediate oxidation when exposed to air to form EGZnO/Naph. In a parallel study, we studied the chemical and physical properties of EGZnO/Naph. In this paper we report the characterization of this nanoscopic material by XRD, FESEM, TEM, FTIR, $N_2$ physisorption, and UV spectroscopy. The activity of EGZnO/Naph has been enhanced and made useful for any practical application compared to commercial ZnO due to its increased surface area and to changes in surface properties, such as surface defects [17-18]. Here, we present the preparation of much smaller high purity ZnO nanoparticles using our simple, low energy consumption and green electrochemical method.

## 2. EXPERIMENTAL

Electrogenerated highly reactive EGZn/Naph (6 mmol) was prepared via the electrolysis of a *N-N* dimethylformamide solution (10 mL) containing 0.1 M

tetraethylammonium perchlorate ($Et_4NClO_4$, 230 mg) and a naphthalene mediator (12 mmol) in a one-compartment cell fitted with a platinum plate cathode (2x2 $cm^2$) and a zinc plate anode (2x2 $cm^2$). At the end of the electrolysis, the black solution was filtered and calcined at 550 $^oC$ to give the white powder of the EGZnO/Naph, which was then characterized.

The crystalline structure of the EGZnO/Naph was investigated via X-ray diffractometry (XRD) using a Bruker Advance D8 Siemens 5000 diffractometer with Cu Kα radiation (λ = 0.15418 Å, 40 kV, 40 mA) over the diffraction angle (2θ) at range of 2-90$^o$. While, the surface areas were calculated according to the method of Brunauer, Emmett and Teller (BET). The morphologies and nanostructures were observed with a Transmission Electron Microscope (TEM, JEOL JEM-2100) equipped with an Energy Dispersion X-ray Spectrometer (EDX).

The FTIR spectra were recorded using a Perkin-Elmer Spectrum One FTIR spectrometer with a resolution of 4 $cm^{-1}$ in the mid IR region (400–4000 $cm^{-1}$). The measurements were made in the solid phase using KBr pellets. DRUV-visible absorption spectra were recorded using UV-Vis Diffuse Reflectance (Perkin-Elmer Lambda 900 spectrometer). The scanning wavelength range was 300-500 nm.

## 3. RESULTS & DISCUSSION

### 3.1 X-ray diffraction & BET surface area

Fig. 1 shows the XRD pattern of ZnO nanoparticles. Fig. 1(b) shows the XRD pattern of a typical sample prepared via the electrolysis of a DMF solution, containing naphthalene as a mediator in a cell, fitted with a platinum cathode and zinc anode at 0$^o$C. The diffractograms of the sample were quite similar to those of commercial ZnO (Fig. 1(c)), which are well-matched with the typical single crystalline wurtzite hexagonal phase bulk ZnO (JCPDS file No. 36-1451, Fig. 1(a)) [19]. No characteristic peaks of other impurities were detected in the pattern. The sharp diffraction peaks indicate a good crystallinity of the EGZnO/Naph [20]. The lattice constants are calculated to be a=0.32427 nm (utilizing the observed (100) diffraction) and c=0.51948 nm (utilizing the observed (101) diffraction), which are slightly smaller than 0.32498 nm and 0.52066 nm for the bulk ZnO powder. This indicates that by using our simple electrolysis method, we have succeeded in the producing of high purity of ZnO nanoparticles.

The surface areas of commercial ZnO and the EGZnO/Naph were measured to be 4.40 and 65.56 $m^2/g$, respectively. Parallel to the TEM results, the BET results show that the surface area of the EGZnO/Naph is 15 times higher than that of commercial ZnO.

### 3.2 FTIR

The quality and composition of the EGZnO/Naph were characterized using FTIR spectroscopy at room temperature in the range of 400-4000 $cm^{-1}$ as shown in Fig. 2. The obtained spectrum shows two absorption bands at 500 and 434 $cm^{-1}$, which are the typical characteristic bands of the wurtzite hexagonal phase pure ZnO [21-22]. The band at ~3460 $cm^{-1}$ is related to the existence of a hydroxyl group, may be due to its high reactivity. Furthermore, the bands at 1634 and 1100 $cm^{-1}$ belong to CONH and C-N, respectively.

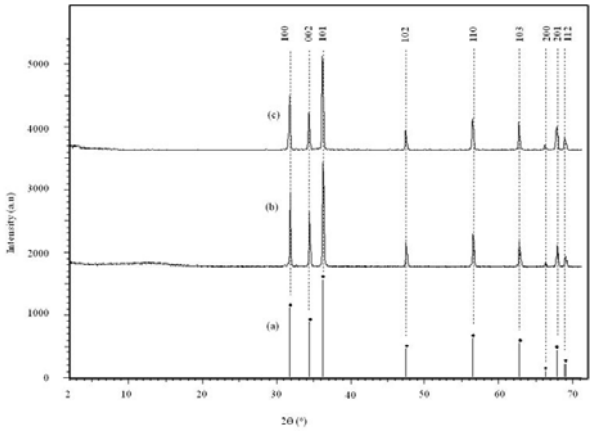



Fig. 1 XRD patterns of the ZnO samples: (a) ZnO peaks (b) EGZnO/Naph (c) Commercial ZnO

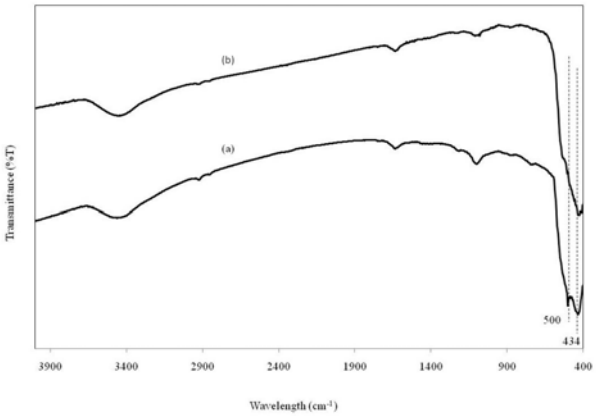



Fig. 2 FTIR image of the ZnO samples: (a) EGZnO/Naph (b) Commercial ZnO

### 3.3 TEM observation

Fig. 3(b) shows TEM images with high magnification, from which it can be clearly seen that the EGZnO/Naph consisted of particles 10–15 nm in size, which is over 10 times smaller than that of commercial ZnO (100 – 500 nm), be evidence in Fig. 3(a) . Fig. 3(c) is an enlargement of Fig. 3(b), and illustrates the high-resolution transmission electron microscopic (HRTEM) image of the EGZnO/Naph. More detailed insight from the HRTEM image shows that the interplanar spacing of the EGZnO/Naph is approximately 0.2595 nm, which may correspond to the distance between two (002) planes of

hexagonal ZnO, indicating that the EGZnO/Naph nanosphere is single crystalline in nature [23]. The formation route of this EGZnO/Naph is similar to the mechanism which was reported by Tokuda et al [12].

Fig. 4 illustrates an EDX analysis of the EGZnO/Naph, in which it can be seen that the nanosphere is in high purity and contains only Zn and O without the presence of a contaminant. The atomic ratios of Zn and O are calculated to be approximately 1:1. To the best of our knowledge, this is the first report of the synthesis of a high purity ZnO nanosphere with an average particle size of less than 20 nm using an electrochemical method.

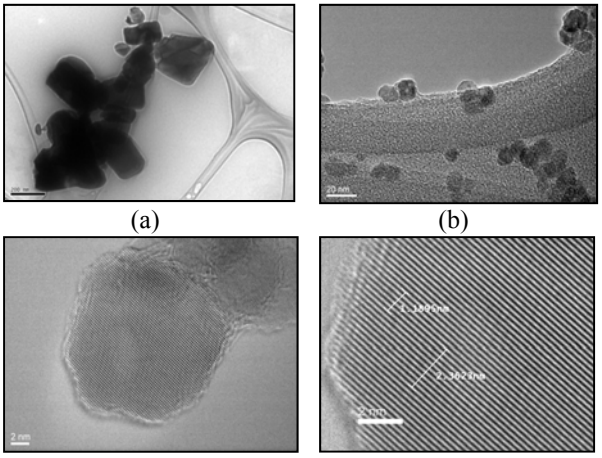
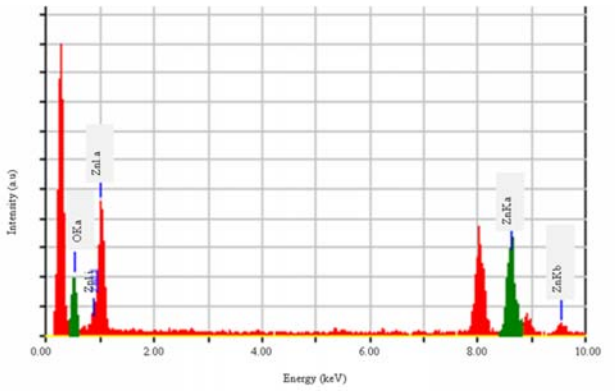



Fig. 3 TEM micrographs of the ZnO: (a) Commercial ZnO (b) EGZnO/Naph (c, d) HRTEM image of EGZnO/Naph.




Thin Film Standardless Standardless Quantitative Analysis
Fitting Coefficient: 0.6999

| Element | (keV) | Mass% | Counts | Error% | Atom% | K |
|---|---|---|---|---|---|---|
| O K | 0.525 | 20.15 | 471.77 | 0.06 | 50.76 | 0.8256 |
| Zn K (Ref.) | 8.630 | 79.85 | 1543.74 | 0.05 | 49.24 | 1.0000 |
| Total | | 100.00 | | | 100.00 | |

Fig. 4 Energy Dispersive X-ray (EDX) spectra of the EGZnO/Naph

### 3.4 DRUV-visible

Fig. 5 depicts the typical DRUV–vis spectrum of the EGZnO/Naph measured at room temperature. A broad band can be seen at 366 nm (3.35 eV), which is very close to the band gap of the ZnO 1s–1s electron transition (3.37 eV) [24]. Thus, this result indicates that the prepared EGZnO/Naph nanoparticles absorb visible-light as well as ultraviolet-light [22]. Therefore, EGZnO/Naph nanoparticles are predicted to be good alternatives for visible-light photocatalysis materials in practical applications, though this is still under study.

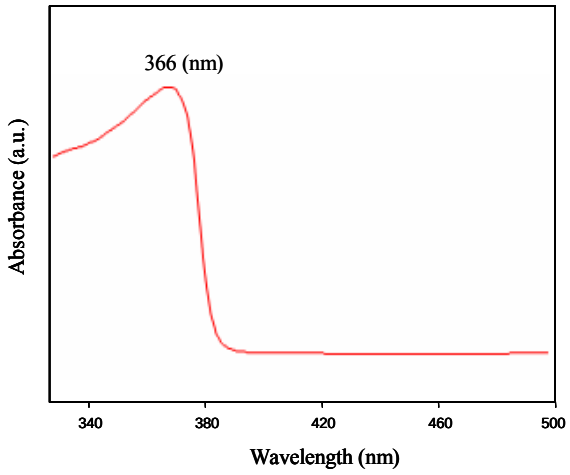



Fig. 5 DRUV–visible spectrum of EGZnO/Naph at room temperature

## 4. CONCLUSION

A nanosized EGZnO/Naph has been successfully synthesized via the simple electrolysis of a DMF solution in the presence of naphthalene. It is confirmed that the EGZnO/Naph is a pure metal oxide with a typical single crystalline wurtzite hexagonal structure. Its average diameter is 10-15 nm with 0.2595 nm of lattice spacing, and it has a surface area that is 15 times larger than that of commercial ZnO. We have also found that the absorption peak of the EGZnO/Naph is very close to the band gap of the ZnO 1s–1s electron transition. Therefore, this simple electrolysis appears to be an excellent method for preparing high purity ZnO nanoparticles with much smaller particle sizes.

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