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A facile preparation of nanosized ZnO and its use in photocatalytic decolorization of methyl orange

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ABSTRACT

Nanoparticles zinc metal was prepared by a simple electrochemical method of a *N,N*-dimethylformamide solution containing 0.1M tetraethylammonium perchlorate in the presence of naphthalene as a mediator in a one-compartment cell fitted with a platinum plate cathode and a zinc plate anode at 60 mA/cm^2 of constant current under a nitrogen atmosphere. The prepared zinc oxide (ZnO_{elec}) was characterized by FE-SEM, TEM, XRD, nitrogen-sorption and DRUV spectrophotometer, which confirmed that the particles of ZnO_{elec} are composed of pure nanosized ZnO with a large surface area and majority of particle size was less than 20 nm. The particles size of the ZnO_{elec} affected its photoactivity, which clearly observed when it was tested on a decolorization of methyl orange under UV illumination. By using ZnO_{elec}, 50% of higher removal percentage of MO was achieved compared to commercial zinc, which only gave 30% after 30 min of contact time. These result shows that ZnO_{elec} has a great potential to be used as a catalyst for the photocatalytic decolorization of industrial dyes wastewater.

| Electrosynthesis | Nanosized Zno | Photocatalytic | Decolorization | Methyl orange |

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1. INTRODUCTION

Synthetic dyes are widely used in industries such as textile, rubber, plastic, paper and etc. Particularly, they are widely used in the textile industries because of their simple dyeing procedure and good stability during washing process [1]. Therefore, large amount of colored dye effluents were disposed which are toxic, non-biodegradable and harmful to aquatic life. The dye color is the first contaminant easy to be recognized even as low as 1 ppm since it is visible to the human eye and affected the quality of water bodies. Consequently, the decolorizing of dye wastewater has become a major environmental problem, which leads to many investigations of physical, chemical and biological methods [2,3] such as coagulation, flocculation, heterogeneous photocatalysis and membrane filtration [4]. However, all these processes have their own limitations, such as sludge generation, formation of aromatic amines and membrane fouling, etc.

Photocatalytic degradation of organic pollutant using semiconductor materials such as TiO_2, ZnO, Fe_2O_3, CdS, GaP and ZnS has been proven useful in the treatment of water pollution [5,6]. They have emerged as an important destructive technology leading to the total mineralization of organic pollutants to water and carbon dioxide gas [6]. TiO_2 became the most popular semiconductor and widely researched for photocatalytic application since it first reported as a photoanode for the photoelectrolysis of water [7]. The demands of TiO_2 worldwide have been raised for the last two decades due to its promising results render exceeding the value of other alternative potential resources as well as reflected comparable efficiency as TiO_2 need to be considered. In addition, TiO_2 has disadvantage when applied to industry such as after the photodegradation processes, filtration is required [8]. Therefore, primary scientific and technological objectives have been focused on exploring new photocatalysts with photo- and thermal operational stability, high selectivity, and relatively low cost of preparation method [9].

Among the semiconductors, ZnO turn out to be a potential photocatalyst investigated in recent years. Analogous to TiO_2, ZnO could serve as an ideal photocatalyst candidate that is cost-effective and environment-friendly. The comparable intrinsic band gap energy of ZnO (3.37 eV) [10] to that of TiO_2 (3.2 eV) [11] also makes it (ZnO) a suitable candidate in absorbing UV-light as an excitation source. Likewise, various reports have shown that ZnO are good photocatalyst material. For instances, in some cases, ZnO exhibits a better photocatalytic efficiency than TiO_2 [12,13]. There are

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various methods in the synthesis of ZnO such as microwave irradiation [14], sol-gel process [15], chemical precipitation [16], hydrothermal [17,18] and sonochemical methods [19]. However, simple, cheap and mild conditions for the preparation of pure ZnO are extremely required. Moreover, the particles size of ZnO is also important factor for the specific application. In fact, chemical, microstructural and physical properties of ZnO powders are dependent on the synthesis procedure.

Recently, we have reported a new preparation method for a very fine particle of Zn metal with high reactivity by using a simple electrochemical technique [20,21]. The Zn could undergo oxidative addition with various organic halides to produce the corresponding organozinc compounds in high yields, which then were applied efficiently in the synthesis of anti-inflammatory agent precursors [21,22]. As an extent of the study, herein we attempted to use the corresponding zinc oxide as a photocatalyst. The structural and optical properties of the prepared ZnO were compared with commercial ZnO (ZnO_{com}) and then its photoactivity was tested on the decolorization of methyl orange.

2. EXPERIMENTAL

The zinc metal (Zn_{elec}) was readily prepared by electrolysis of a *N,N*-dimethylformamide solution containing 0.1M tetraethylammonium perchlorate in the presence of naphthalene as a mediator in a one-compartment cell fitted with a platinum plate cathode (2 x 2 cm^2) and a zinc plate anode (2 x 2 cm^2). Electrolysis was carried out at 60 mA/cm^2 of constant current under a nitrogen atmosphere. After electrolysis the zinc metal was filtered and washed with ether several times to remove organic compounds. Finally the Zn was calcined at 823 K for 4 hours and ready for characterization.

The structural characterization was carried out by field emission scanning electron microscopy with energy dispersion X-ray spectrometer (FESEM-EDX) (JSM-6300F) and transmission electron microscopy (TEM) (JEOL JSM-6701F). The crystallinity and crystal phases of the synthesized nanostructures were determined by the X-ray diffraction (JDX-3500 JEOL X-Ray Diffractometer) with Cu Kα radiation. The surface area of the synthesized ZnO was determined by using a Quantachrome apparatus. Samples were treated and outgassed at 110^{o}C for 3 hours before subjected to nitrogen (N_2) adsorption. Optical properties of the ZnO_{elec} were analyzed by the diffuse reflectance UV (DRUV Perkin Elmer) spectrophotometer.

3. RESULTS & DISCUSSION

Fig. 1 represents the diffractograms of ZnO_{com} (a) and ZnO_{elec} (b) powder. It could be observed that all of the peaks in Fig. 1(b) are well matched with that of Fig. 1(a) which confirms that the synthesized powder is single crystalline and possesses wurtzite hexagonal structures of ZnO (International Center for Diffraction Data, JCPDS 36-1541). A series of ZnO characteristic peaks was observed at 32.0^o (100), 34.5^o (002), 47.5^o (102), 57.5^o (110), 63.0^o (103) and 68.0^o (112) whereas a peak observed at 36.5^o (002) was corresponding to Zn characteristic [23]. However, there is no other peak related to impurities was observed in the spectrum within the detection limit of the X-ray diffraction, which validates that the ZnO_{elec} is pure ZnO. In addition, we noted that the peaks in Fig. 1(b) are relatively wider than that in Fig. 1(a), which shows that the ZnO_{elec} particles are apparently composed of ZnO nanoparticles [24].

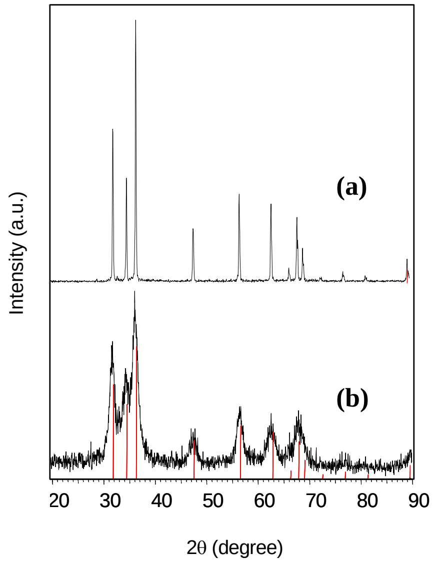

Fig. 1. Characteristic parts of X-ray powder diffraction patterns: (a) commercial ZnO (Zn_{com}) (b) ZnO_{elec}

The general scanning electron morphologies of the ZnO_{com} (a) and ZnO_{elec} (b) are shown in Fig. 2. It could be observed that Fig. 2(b) consists of very fine evenness particles compared to Fig. 2(a). This observation was supported by TEM image in Fig. 2(c), exhibiting the particles size of Zn_{elec} was less than 20 nm in average. Furthermore, SEM image of Zn_{elec} was looks like rice shape with irregularly agglomerate with each other compare to pure ZnO with a diamond shape look [25]. From Fig. 2(a), (b) and (c), it can be seen and proved that nano-sized ZnO photocatalyst was successfully be synthesized.

The specific surface area is an important microstructural parameter of ZnO particles which depends on the geometrical shape and porosity of the particles. Table 1 shows the BET specific surface area of commercial ZnO_{com} and ZnO_{elec}. The specific surface area of the ZnO_{elec} was found to be 28.27 m^2/g, which is about 6 times larger than that of the ZnO_{com} powder. This result further confirms that ZnO_{elec} consist of very fine particles compared to ZnO_{com}, which are in accordance with the results of SEM and TEM that ZnO_{elec} has smaller particle size with average particle size less than 20 nm in diameter.

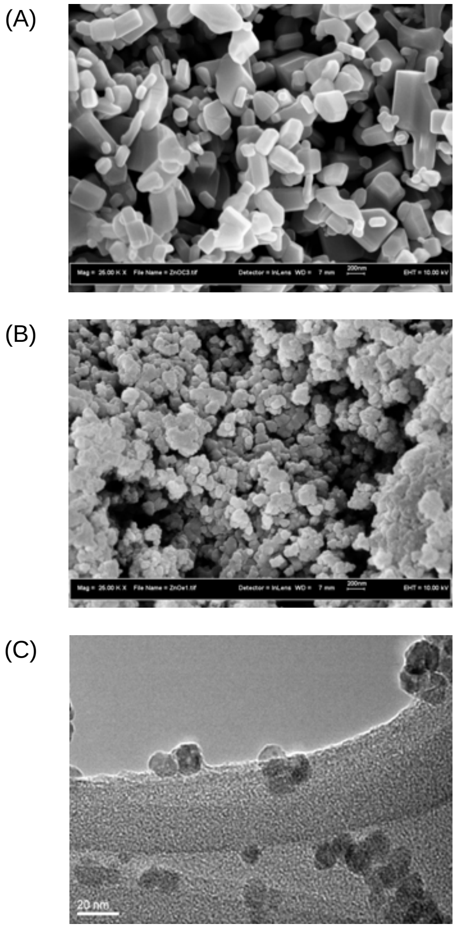

Fig. 2. FE-SEM images of commercial ZnO (a) and ZnO_{elec} (b), and TEM images of ZnO_{elec} (c)

Fig. 3 shows DRUV absorption spectrum of ZnO_{elec} powder. A broad band was observed at 366 nm, which is a characteristic band for the wurtzite hexagonal pure ZnO [26]. No other peak was detected in the spectrum which proves that the synthesized products are ZnO only [27]. As shown in Fig. 3, the ZnO_{elec} photocatalyst had a broad absorption band at ultraviolet region and the absorbance of the photocatalyst slightly increase as the wavelength decrease (380 nm and below), which indicate that the ZnO_{elec} photocatalyst has a potential capacity of photocatalytic activity irradiated with UV-light. It is well known that the optical absorption behaviour of photocatalyst significantly affects the photocatalytic activity of the photocatalyst [28-30]. In general, the red-shift in the absorption band edge and the increase in absorption intensity attributed to the increased formation rate of electron-hole pairs on the photocatalyst surface, resulting in the photocatalytic exhibiting higher photocatalytic activity [31].

Table 1. BET specific surface area of ZnO

Sample	Specific Surface Area (m^2/g)
ZnO_{com}	4.40
ZnO_{elec}	28.27

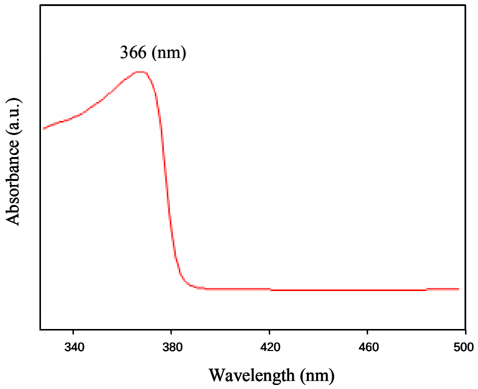

Fig. 3. Typical DRUV spectrum of EGZnO/Naph

The photoactivity of ZnO_{elec} was then tested on decolorization of methyl orange (MO) and compared with the Zn_{com} (Fig. 4). ZnO_{elec} gave 50% of higher MO removal percentage than ZnO_{com} (30%) after 30 min of UV illumination. These results gave the intuitional impression about the effect of particles size on the MO removal efficiency for both of the catalyst. Decrease in ZnO crystal size leads to an increase of amount of dispersion particles per volume in the solution. As a result, the photon absorbance was enhanced and gave higher removal percentage of MO [32].

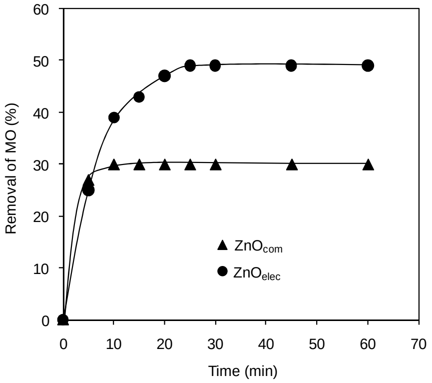

Fig. 4. Photocatalytic decolorization of methyl orange by ZnO (pH 5, MO: 5 mg L^{-1}, ZnO: 1.0 g L^{-1}, 300 K)

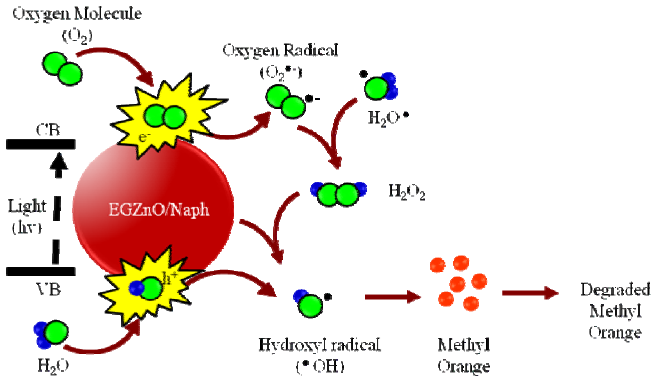

Fig. 5. Proposed reaction mechanism of photocatalytic degradation of MO

On the basis of the above explanations for the photocatalytic decolorization of MO over the nano ZnO_{elec}, the proposed reaction mechanism of photocatalytic activity was illustrated in Fig. 5. In this work, MO was initiated by photo-excitation of the ZnO_{elec}, followed by the formation of an electron-hole pair on the surface of the catalyst. High oxidative potential of the hole (h_{VB}^{+}) in the catalyst permits the direct oxidation of organic matter (dye) to reactive intermediates. In parallel with decomposition of water or the reaction of the hole with ^{-}OH, a very reactive hydroxyl radical was formed, which is an extremely strong, non-selective oxidant that leads to the degradation of organic chemicals [33-34]. Electron in the conduction band (e_{CB}^{-}) on the catalyst surface can reduce molecular oxygen to superoxide anion. In addition, this radical, in the presence of organic scavengers, may form organic peroxides or hydrogen peroxide (H_2O_2). The excess of H_2O_2 reacts with hydroxyl radicals and holes to form $HO_2\bullet$. In opposition, electrons in the conduction band are also responsible for the production of hydroxyl radicals, which have been indicated as the primary cause of organic matter mineralization [33,35].

4. CONCLUSION

A new simple electrochemical method for the synthesis of nanosized ZnO was developed. The properties of the ZnO_{elec} were studied by FE-SEM, TEM, XRD, BET surface area and DRUV spectrophotometer. The results confirmed that the ZnO_{elec} is pure and consist of even nanosized particles with wurtzite hexagonal structures. The size of the majority of these nanoparticles in these powders is less than 20 nm. The activity test of ZnO_{elec} on decolorization of MO showed that with further developments, it is believed that it could be used in wastewater treatment.

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