INVESTIGATING THE HYDROPHILICITY OF ZINC OXIDE NANOPARTICLES USING XYLENE AND WATER FOR IBUPROFEN ADSORPTION

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ABSTRACT

In this work, zinc oxide nanoparticle (ZoN) hydrophilicity was investigated using the sample dispersion method. ZoNs were created by a templating method, using gelatin as a natural template and block copolymer F127 as a synthetic template, and calcined at 550°C for 6 h. The resulting textural and structural characteristics of ZoNs were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier-transform infrared (FTIR) spectroscopy. The hydrophilic characteristics of the nanoparticles were examined using a mixture of water and xylene through the sample dispersion method. In this experiment, groups of ZoNs were dried for 24 h either at room temperature, at 100°C or at 150°C and were labelled as t-ZoN, 100-ZoN and 150-ZoN, respectively. Three samples of ZoNs were then poured into the xylene and water mixture. The motion time of ZoNs in each phase was visually monitored for later comparison. In the last step of the experiment, each ZoN sample was used as an ibuprofen (IBP) adsorbent. Results clearly show that the amount of adsorbed water in the t-ZoN samples was significantly lower than that of the 100-ZoN and 150-ZoN samples, which matched the IBP adsorption results. This information may aid in improving IBP adsorption in other drug delivery studies.

Keywords: zinc oxide nanoparticle, hydrophilicity test, ibuprofen, adsorption.

INTRODUCTION

Zinc oxide nanoparticles (ZoNs) have attracted the attention of scientists due to their unique characteristics, including their large surface area, stability, ordered structure, non-toxicity, high photosensitivity and high pore volume. Zinc oxide is widely applied as a catalyst carrying material [1], potential adsorbent [2], photocatalyst [3], anti-bacterial and anti-tumour agent [4], semiconductor plate [5], sensing system [6] and drug delivery material [7] as well as in solar cells, laser diodes, ultraviolet lasers, thin films and piezoelectric transducers [8]. Zinc oxide can be obtained through several synthesis methods, namely synthesis by the sol-gel process [9], nanocasting [10], precipitation [11], mechanical milling [5], organometallic synthesis, spray pyrolysis, hydrothermal reactions and mechano-chemical synthesis[12].

Nanocasting is a widely used synthesis method. ZoNs are synthesised through the nanocasting method by using irregular mesoporous carbon as a hard template [10]. The first step in the hard templating method is to dissolve a zinc precursor into a solution. After the mixture is stirred for several minutes, a piece of an irregular hard template is added to the solution and stirred until the solution evaporates entirely. The resulting powder was heated by nitrogen gas to convert zinc precursor
into zinc oxide in the hard template channel. Charging and heating are undergone twice to reach higher loads. Next, the hard template is released through calcination using a furnace. Hard templates can also be released using a solution of NaOH or HF to remove any residue. However, hard template ZoN synthesis is not often carried out because ZnO framework is susceptible to dissolving in a solution of NaOH or HF. Although it is widely used, this method is expensive, and the release process is corrosive and not environmentally friendly.

One method of synthesising environmentally friendly ZoNs is the sol-gel method. This approach is simple and able to control particle size and morphology [13], allowing it to produce regular structures quickly. Previous research has reported using an alkaline template for zinc precursor growth. After a reaction, the sol-gel method forms white zinc oxide. However, zinc oxide resulting from an alkaline template has an irregular shape and size. Nothing ordering structure appears after the synthesis. To solve this problem, the alkaline template is replaced by a long chain template that offers high stability during synthesis. A popular soft template that has been reported is block copolymer 127. The green issue requires the minimisation of a synthetic soft template using natural templates, such as gum, starch, gelatines or sucrose. Gelatins with high molecular mass and hydrophilic-hydrophobic functional groups have successfully produced rare materials, such as wormhole-like carbon [14] and carbon foam [15].

In this paper, we report the synthesis of ZoNs using the soft templating method. Single-crystal ZnO is relatively hydrophilic [16]; this property was tested via the dispersal method using a mixture of xylene and water because both solutions can be easily accessed. In addition, water is polar while xylene is nonpolar, so the mixture reveals whether ZnO is hydrophilic or vice versa. It is also important to study its ability to adsorb ibuprofen (IBP).

The sample was put into a mixture of water and xylene, and its movement in each phase was observed by timing it with a stopwatch and photographing it with a camera. The mixture was then stirred with a magnetic stirrer for 1 min and let to stand for approximately 10 min until it stabilised. Next, each sample was observed while moving by being timed with a stopwatch and photographed with a camera. The effect of the temperature of ZnO during the IBP adsorption process was examined through variations in room temperature.

IBP, or 2-[-4-(2-Methylpropyl)phenyl] propionic acid, is known to have non-steroidal, anti-inflammatory, analgesic and antipyretic effects [17]. IBP molecules are 1.36×0.74×0.52 nm² in size and are classified as large molecules, so they require other materials to be utilised. [18]. However, based on previous research, it is known that IBP in concentrations of 0.018 to 2.110 μg L⁻¹ can be found in America, Germany and several aquatic environments around the world [19]. This phenomenon indicates the negative effects IBP has on the planet’s ecosystem as a whole. In humans, it can also affect the digestive system’s performance and damage the brain system [20].

Several methods for reducing concentrations of IBP have been found, such as oxidation, filtration, radiation and adsorption [21]. The most popular method is adsorption as a result of its low cost, simple design, ease of application, insensitivity to toxic substances and ability to remove pollutants even from aqueous solutions [2]. IBP adsorption is influenced by several factors, including the initial concentration of the IBP, the type of activated carbon or adsorbent and composite used, temperature, pH, the concentration of pollutants and contact time.

Adsorbents commonly used in the adsorption process include wood, activated carbon, zeolites, silica and carbon [22]. However, these adsorbents have small surface areas, which reduce their adsorption capacities. Recently, researchers have succeeded in synthesising adsorbents with large surface areas, such as mesoporous silica, mesoporous carbon, nanosilica, nanometal and nanozeolites [2]. The most popular IBP adsorbent is activated carbon due to its low cost, simple design, ease of application, insensitivity to toxic substances and ability to remove pollutants even from aqueous solutions [2]. IBP adsorption using ZoNs remains rare and will be examined in this study.

**EXPERIMENTAL**

**Materials**

The materials used in this study were poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (EO106PO70EO106; Pluronic F127), provided by BASF Corp; phloroglucinol(C6O3H6; 99%); gelatin purchased from Acros Organics; zinc sulphate (99%) purchased from Fischer and ethanol purchased from Pharmco.

**Synthesis of ZoNs**

The first step in this experiment was to synthesise ZoNs using a soft templating method. Ethanol was dripped into a Pluronic F127 solution using a burette (1
drop per 20 seconds) at room temperature. After all the ethanol had been added, the resulting solution was mixed for 4 h at 150 rpm under closed conditions. Next, gelatin was added to the mixture at room temperature, and the mixture was stabilised for 1 h. The ethanol, Pluronic F127 and gelatine were added at a respective ratio of 98.1:1.8:1. Next, ZnSO$_4$ was added to the mixture at room temperature, and the mixture was stabilised for 20 h. ZnSO$_4$ was added at a ratio of 1:6.3. The mixture was then inserted into a hydrothermal reactor at a temperature of 100ºC for 24 h. Then, it was cooled, white solids were filtered out and the resulting substance was washed with distilled water with a pH of 7. The resulting solid was then dried at 100ºC for 24 h and calcined at 550ºC for 24 h. The samples were then stored in sealed, clear, plastic bottles and labelled as ZoNs. In the last step before hydrophilicity and IBP adsorption testing, three ZoN samples were evaporated separately at different temperatures - room temperature, 100ºC and 150ºC, for 24 h, and the resulting samples were labelled as t-ZoN, 100-ZoN and 150-ZoN, respectively, before their hydrophilic characteristics were tested. ‘T’ refers to temperature.

ZoNs Characterisation

The textures and structures of the obtained ZoNs were characterised by X-ray diffraction (XRD) to determine the type of particles that were synthesised, scanning electron microscopy (SEM) to observe their particle morphology and Fourier-transform infrared (FTIR) spectroscopy to determine the functional groups within them. XRD was performed using a D/Max-Ra X-ray diffractometer (Ouyatu, Japan; Cu Kα radiation = 1.54 Å) in an angular range of 10 - 80° (2θ) with a step of 0.02° (2θ). SEM was used to explore the morphology of the ZnO-SiO$_2$ particles using a Hitachi field emission scanning electron microscope (Hitachi S4800, Tokyo, Japan) at a voltage of 10 kV. The FTIR spectroscopy was carried out to explore the changes in the functional groups within ZnO nanoparticles using a Nicolet iS50FTIR spectrometer (Madison, WI, USA). The samples were finely pulverised and then diluted in dried KBr to form a homogeneous mixture based on the sample: KBr ratio of 1:200, so as to explore the changes in the functional groups of ZoNs.

Hydrophilicity Testing

The hydrophilic properties of ZoNs were tested by the dispersion method in a mixture of xylene and water. Equal parts of xylene and water were added to a beaker. The sample was added to the mixture, and its movements in each phase were timed with a stopwatch and photographed with a camera. The mixture was then stirred with a magnetic stirrer for 15 min and let to stand for approximately 2 min until it stabilised. Next, each sample’s movements were timed with a stopwatch and photographed with a camera.

IBP Adsorption

The effect of ZnO’s temperature during the IBP adsorption process was examined at various temperatures: room temperature, 100ºC and 150ºC. A 100 ppm IBP solution was stirred into 100 mg of ZoNs at room temperature. After a homogeneous solution was created, the filtrate was removed from the mixture at 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70 and 75. The absorbency of the filtrate was measured using UV-Vis at a wavelength of 291.5 nm. The absorption capacity of IBP was calculated and analysed using concentration data and the absorbance measurements of the samples in several different temperature conditions. The amount of IBP adsorbed on ZoNs (q) was calculated using the Eq. (1).

\[ q = \frac{C_o - C_e}{w} \times \nu \]  

where \( C_o \) is the initial concentration of IBP, \( C_e \) is the equilibrium concentrations of IBP, \( \nu \) is the volume of solution used during measurement and \( w \) is the amount of ZoNs material used as adsorbent.

RESULTS AND DISCUSSION

SEM Analysis

Fig. 1 shows the morphology and microstructure of ZoNs at 5000× magnification. The SEM results show that the crystal structure of the nanoparticles is arranged fairly regularly. The nanoparticles’ morphology, shown in Fig. 1, reveals a cubic-like structure with some over lapping ball-cubic structures. The average size of ZoNs was found to be 2.01 ± 0.52 μm. Several broken cubes (see the black circles in Fig. 1) may indicate the effect of calcination on the sample. Higher magnification SEM analyses revealed nanostructures with the porosity of the nanocrystallites on the surfaces of the microzinc oxide. As evidenced in these micrographs, microspheres were formed by loosely bonded nanocrystallites at average sizes of 10.5 ± 0.4 μm. The SEM results have been confirmed via FTIR spectroscopy and XRD patterns.
**FTIR Spectroscopy Analysis**

Fig. 2 shows the IR spectra of ZoNs at wavenumbers of 4000 - 400 cm\(^{-1}\). The spectra at 3431.51 cm\(^{-1}\) indicate the presence of –OH groups. Spectra at 1622.2 cm\(^{-1}\) reveal the presence of Zn-O-Zn groups. Spectra at 1122.62 cm\(^{-1}\) indicate the presence of Zn–O groups. Spectra at 600.85 cm\(^{-1}\) and 648.11 cm\(^{-1}\). A Zn-O-Zn group was noted in spectra at 1059.93 cm\(^{-1}\). Thus, the synthesised ZoNs contain –OH, C=C, Zn–O and Zn-O-Zn functional groups.

Table 1 shows that ZnO contains several functional groups. The –OH functional group revealed by the appearance of spectra with sharp intensity at 3431.51 cm\(^{-1}\) indicates the presence of alcohol (R–OH) and carboxyl (RCOOH) groups as impurities at Zn surface. This is confirmed by the appearance of a spectrum at 1122.62 cm\(^{-1}\), which indicates the presence of Zn-O-Zn strain vibration (from an alcohol or an ether functional group), proving that a hydroxyl group is present. The emergence of absorption spectra at 771.56 cm\(^{-1}\) further strengthens suspicions of the presence of a hydroxyl group. Meanwhile, the spectra at 2928.07 cm\(^{-1}\) and 2858.63 cm\(^{-1}\) indicate the presence of Zn ion at alkyl groups (–CH\(_2\) and –CH\(_3\)) as complementary ZnO chains. These complementary chains also appear in the spectra at 963.48 cm\(^{-1}\), 516.94 cm\(^{-1}\) and 433.04 cm\(^{-1}\). The main ZnO chain is shown at the peak with the sharpest and strongest intensity, namely in the spectra at 3431.51 cm\(^{-1}\). Based on the peak data provided by the FTIR spectrum, it can be concluded that ZnO has an oxide-based chemical structure.

According to the spectrum, the absorbance peak at 771.56 cm\(^{-1}\) reveals Zn–OH stretch. The absorbance peak of the hydroxyl group in zinc hydroxyl bending vibration shows ZnO’s characteristic structure. ZnO spectra at 1345 cm\(^{-1}\) and 1347 cm\(^{-1}\) illustrate the connecting effect of the hydroxyl group in the product. The wavenumbers 3317 cm\(^{-1}\) and 3319 cm\(^{-1}\) correspond to the flexural vibration peak of Zn–OH in the two moving products at 958 cm\(^{-1}\) (the peak vibration of Zn–OH stretch vibration). The absorbance peaks of the hydroxyl group in ZnO structure were 952 cm\(^{-1}\) and 954 cm\(^{-1}\), respectively. This change shows the connecting effect between the hydroxyl group and the Zn–OH reaction during the preparation process. The absorption peaks of the hydroxyl group in ZnO structure were at 952 cm\(^{-1}\) and 954 cm\(^{-1}\), respectively. This change indicates that the hydrothermal vibrations reflect the connecting effect between the hydroxyl group and the Si–OH reaction.
during the process of preparing ZnO structure.

In addition, the –OH material in ZnO shifted to the 952 cm\(^{-1}\) and 954 cm\(^{-1}\) spectra. This change indicated that hydrothermal vibrations cause the peak of the water to be adsorbed on ZnO surface during ZnO preparation process. The shear vibration peak of –OH occurs at 1580 cm\(^{-1}\) and 1579 cm\(^{-1}\) and produces a hydrogen Si–OH coupling bond. In addition, –OH in Zn–OH was calcined, and –OH bond in the adsorbed water disappeared from the peak of the curved vibrations of the water adsorbed on the surface of ZnO after the calcination process. High-temperature calcination is known to cause water evaporation and dehydration condensation reactions in Zn–OH to produce Zn–O–Zn chemical bonds. The number of identified –OH groups indicates that ZnO has high hydrophilicity.

**XRD Analysis**

Fig. 3 shows the XRD pattern obtained after examining ZoNs. All the peaks shown in this figure are indexed as the wurtzite ZnO phase (part of space group P6\(_{3}\)mc) with lattice parameters of \(a = 0.3298\) nm and \(c = 0.5206\) nm (ICDD: 36-1451). The XRD pattern of ZoNs with no visible impurity peaks suggests that a thermal decomposition duration of 7 h is sufficient to completely decompose zinc sulphate in this experimental condition; however, this is not a sufficient amount of time for primitive cubic formation to be completed.

The XRD pattern of ZoNs shows a strong, broad peak near 20 of 23°, revealing the main phase and an amorphous phase. This phase corresponds to the main phase of SiO\(_2\), which is an amorphous phase that also corresponds to the structure of ZnO. In the XRD pattern, the peaks reveal an amorphous phase. The peaks at 31.8°, 34.5°, 36.3° and 47.5° correspond to ZnO diffraction peaks in the amorphous phase. The peaks corresponding to ZnO diffraction also indicate the presence of Zn\(^{2+}\) peaks, which reveals that Zn\(^{2+}\) causes a change in ZnO after a thermal reaction. The process of changing into ZnO through a thermal reaction still involves impurities, so calcination must be undergone to produce pure ZnO.

**Hydrophilicity Testing**

Figs. 4 - 6 show the hydrophilicity test results of the three sample ZoN groups. The time required for the samples to be dispersed in the same xylene phase was 2 s, and the three samples were each dispersed over the

![Fig. 3. XRD pattern obtained from examining ZoNs.](image-url)
interface at different times: the t-ZoN sample at $t = 3$ seconds, the 100-ZoN sample at $t = 4$ seconds and the 150-ZoN sample at $t = 5$ seconds. After the third movement of the stable sample, each sample was stirred with a magnetic stirrer for 15 min. Water, xylene and ZnO powder were mixed. Next, the mixture was left to sit until the water and xylene were separated and stable, and the movements of each sample were re-examined until they were stable. After the stirring, the 150-ZoN sample revealed the best hydrophilic properties, as it only required 5 s to return to its stable state. The t-ZoN sample required 63 s, and the 100-ZoN sample required 11 s. This is because ZnO sample was in a completely dry and pure state, which improved its hydrophilic properties. In addition, when ZoNs are heated at 150ºC, a morphological change is undergone in the forms of the spherical particles and the sheet-based aggregates, which may allow the formation of porous ZnO structures [24]. These porous structures increase the surface areas of the particles, augmenting their hydrophilicity.

Fig. 4. (a) The initial dispersion of t-ZoN (at $t = 2$ s); (b) t-ZoN dispersing over the interface (at $t = 3$ s); (c) t-ZoN dispersing in xylene, the interface and water after being stirred (at $t = 63$ s).

Fig. 5. (a) The initial dispersion of 100-ZoN (at $t = 2$ s); (b) 100-ZoN dispersing over the interface (at $t = 4$ s); (c) 100-ZoN dispersing in xylene, the interface and water after being stirred (at $t = 11$ s).

Fig. 6. (a) The initial dispersion of 150-ZoN (at $t = 2$ s); (b) 150-ZoN dispersing over the interface (at $t = 5$ s); (c) 150-ZoN dispersing in xylene, the interface and water after being stirred (at $t = 5$ s).
IBP Adsorption

Fig. 7 shows the adsorption capacities of t-ZoN, 100-ZoN and 150-ZoN as well as their maximum capacities. The t-ZoN sample has a maximum adsorption capacity of 215 mg/g, the 100-ZoN sample has a maximum adsorption capacity of 205 mg/g and the 150-ZoN sample has a maximum adsorption capacity of 225 mg/g.

The adsorption capacity measurements show 150-ZoN has the highest adsorption capacity. This is because when the sample was heated at 150ºC, it became completely dry and pure, allowing it to adsorb the maximum amount of IBP. Because the t-ZoN and 100-ZoN samples were still not completely dry, they contained a degree of impurity, which reduced their adsorption capacities. In addition, when ZoNs are heated at 150ºC, the particles’ pores open more widely, increasing the nanoparticles’ adsorption capacity. This result is supported by data from the hydrophilicity test of ZoNs, which indicated that the best hydrophilicity properties occurred in the 150-ZoN sample. The hydrophilicity test using the dispersal method and a mixture of xylene and water indicated that ZoNs heated at 150ºC offered the best hydrophilic properties and the greatest capability to adsorb IBP. This is because at this temperature, ZnO is completely pure and its pores are open wide, increasing its adsorption ability. This is also indicated by the results of the adsorption test, which showed that 150-ZoN has the highest maximum adsorption capacity at 225 mg/g. Not only pore factor, but hydrophilicity also play role during adsorption IBP. Based on hydrophilicity result we can see that at 150ºC the OH- group of Zn-OH increase because the inner water in the ZnO framework will start to cover the surface so that the interaction between IBP-Zn and IBP-OH as hydrophilicity effect increases during the adsorption process. The hydrophilicity factor is one of the factors that causes chemical adsorption to occur. In addition, another impact at high temperatures is likely that the ZnO pores will open up and increase the absorption capacity.

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