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Metadata Record: [https://dspace.lboro.ac.uk/2134/22398](https://dspace.lboro.ac.uk/2134/22398)

Version: Accepted for publication

Publisher: NSTI

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The use of PEO--PPO--PEO block copolymers in the synthesis of ZnO via the hydrothermal method

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ABSTRACT

Zinc oxide particles were produced by aqueous precipitation in hydrothermal conditions (140°C for 6 hours). The influence of surfactant and base to control morphology was investigated. With a change in surfactant, rod-like bundles of different size were obtained, depending on the core and corona size. By changing the base different complexes were formed which interacted differently with the surfactant present (L64). Platelets, rod-like and elliptical particles were obtained.

Keywords: Zinc Oxide, Hydrothermal, Pluronic, PEO-PPO-PEO

1 INTRODUCTION

Zinc oxide (ZnO) is a widely used semiconductor, which has a band gap of 3.37eV and an exciton binding energy of 59meV. ZnO has a wide range of uses in industry as gas-sensors, varistors and UV light emitters. This is due to its piezoelectric, pyroelectric, semi-conducting and optical properties.1

Two distinct routes can be used to synthesise ZnO: gas phase and solution phase. Gas phase synthesis uses a closed gaseous environment and high temperatures from 500°C to 1500°C, including vapour transport, physical vapour deposition and chemical vapour deposition. Due to the high temperature and the need for a controlled environment these techniques can be expensive. Solution phase synthesis requires the synthesis of the ZnO to be carried out in a solution. Some of the methods used are hydrothermal, solvothermal, precipitation and microemulsion. Unlike the gaseous methods, the simplicity and low cost of solution synthesis make the methods a more attractive route for the fabrication of ZnO.1

Self-assembly, in particular the formation of micelles, represents a facile approach to the control of morphology of oxides. Non-ionic surfactants such as Pluronics (PEO-PPO-PEO), having a range of ordered microdomain morphologies along with their low cost, low toxicity and bio-degradation make them an ideal tool for designed synthesis.2

In this paper the influence of different chain lengths of Pluronic surfactants and different starting precursors on the particle size and morphology of ZnO synthesised were reported.

2 EXPERIMENTAL

2.1 Materials

All chemicals used in this study were analytical grade and used without further purification. Acetone, ethanol and iso-propanol were used as supplied. Distilled water was used throughout the experiments. The surfactants used were three types of Pluronic: L64 (PEO_13PPO_28PEO_13 M_w = 9100), F68 (PEO_10PPO_30PEO_80 M_w = 8400) and P123 (PEO_13PPO_13PEO_13 M_w = 5750). All surfactants were purchased from Sigma-Aldrich.

2.2 Synthesis of zinc precursor solutions

ZnO was prepared by the precipitation. One of the reactions is given as follows:

\[
\text{Zn(CH}_3\text{CO}_2\text{)}_2 + 2\text{NaOH} \rightarrow \text{ZnO} + 2\text{Na(CH}_3\text{CO}_2\text{)}_2 + \text{H}_2\text{O}
\]

For a typical preparation, 7.2x10^{-4}M surfactant (Pluronic L64, F68, P123) was dissolved in 40ml H_2O [Sol A] for 1 hour. This solution was then mixed with another solution of 2x10^{-3}M zinc acetate dihydrate dissolved in 16ml H_2O [Sol B]. After completion of the addition of Sol A to Sol B, the surfactant/salt solution [Sol C] was mixed for 30 minutes. Finally 2x10^{-2}M base (NaOH, TMAH, DEA, NH_4OH) was dissolved in 4ml H_2O was added drop wise using a peristaltic pump to Sol C and left to mix for 30 minutes. All the reactions were carried out at pH = 10. 20ml of the solution was transferred to a Teflon cup and placed in a stainless steel autoclave, which was hydrothermally treated. The remaining solution was washed for characterization.

2.3 Hydrothermal treatment

The hydrothermal treatment of the nanoparticles was carried out in an autoclave at 140°C for 6 hours. All samples were washed three times with distilled water and iso-propanol between centrifugal cycles of 5 minutes at 3000rpm.
2.4 Characterization

The size and morphology of the particles were investigated using Transmission Electron Microscopy (TEM) (JEM 100CX, JEOL Ltd, Tokyo Japan) and Field Emission Gun Scanning Electron Microscopy (FEGSEM). The XRD patterns were recorded on a Bruker D8 X-ray using CuK\(\alpha\) radiation. For TEM, a copper grid coated with carbon film was covered with a drop of the washed zinc oxide solution. For FEGSEM and XRD, the solution was cast onto a clean glass slide and dried for 4 hours at 60°C.

3 RESULTS AND DISCUSSION

3.1 The effect of surfactants

The effect of the change of non-ionic surfactants on the particle shape and size of zinc oxide particles after hydrothermal heat treatment are shown in Figure 1. It can be seen that without surfactant the ZnO formed into thin platelets. With the addition of surfactant rod-like structures were formed in all cases. In the case of the L64 and F68 surfactants, bundles of rods were formed with sizes of 1\(\mu\)m and 2\(\mu\)m respectively. For the addition of P123, singular rods were formed, ranging in length from between 1 – 2\(\mu\)m. Figure 2 shows the XRD results for pre and post –

hydrothermal treatment of the solution with P123 as the surfactant. The definitive peaks within the 30 – 40 degree range indicated the formation of ZnO after hydrothermal treatment.\(^3,4\)

It was reported that the growth velocity of the ZnO particles and the micelle dimension of the surfactant controlled the size and arm lengths.\(^3\) It is possible to control the growth velocity by the use of a peristaltic pump and a constant heat treatment.

The formation of the ZnO begins with the addition of NaOH, which reacts with Zn(CH\(_3\)CO\(_2\))\(_2\) to form

![Figure 2: TEM micrographs of hydrothermally grown ZnO particles synthesised with NaOH and a different surfactant [A] No surfactant [B] L64 [C] F68 [D] P123](image)

![Figure 2: XRD patterns for pre hydrothermal (bottom) and post hydrothermal treatment (top).](image)
Zn(OH)$_2$. It is known that triblock copolymers such as Pluronics, can spontaneously assemble into aggregates, such as micelles, vesicles or lyotropic mesophases in a given circumstance.\cite{4} In this case it is considered that the surfactants form micelles.\cite{3} In the aqueous solution, the surfactant forms a hydrophobic core consisting of PPO and a hydrophilic corona (or tails) with the PEO blocks. It is thought that surface of the PPO could be adsorbed onto the surface of the Zn(OH)$_2$, while the PEO blocks are in constant contact with H$_2$O. This could mean that during the hydrothermal treatment, the ZnO nuclei formed from the Zn(OH)$_2$ were restricted to the hydrophobic PPO core. During the heat treatment, the ZnO should grow in its preferential (0001) direction, resulting in the formation of rods. The difference in bundle size may be explained by the difference in aggregation size of the two surfactants. F68 (PEO$_{80}$PPO$_{30}$PEO$_{80}$) and L64 (PEO$_{13}$PPO$_{30}$PEO$_{13}$) share the same core size, but different corona size. This increase in corona size, would lead to an increase in micelle size, leading to the bigger rod size, as shown in Fig. 1c

However when P123 (PEO$_{13}$PPO$_{80}$PEO$_{13}$) was used similar rod like structure, but with less aggregated bundles were observed (Figure 3) which is possible due to the change in core size. With a much bigger core size, the adsorbed Zn(OH)$_2$ were not confined to a small area unlike in L64 and F68. This means that instead of a core packed with aggregated ZnO crystallities, they were spread around the core. This may well lead to undisturbed growth to form more defined crystals.

Figure 3: FEGSEM micrograph of hydrothermally grown ZnO with NaOH and P123

Figure 4: TEM micrographs of hydrothermally grown ZnO particles synthesised with Pluronic L64 and a different base [A] NaOH [B] TMAH [C] DEA [D] NH$_4$OH
3.2 The effect of base

Figure 4 shows the typical TEM micrographs of ZnO particles synthesised with different bases and L64 surfactant. As shown previously, the addition of NaOH results in the formation of bundles of rod-like structures. With the addition of TMAH (Fig. 4b) and NH₄OH (Fig 4d) a platelet structure is formed. In both cases the platelets were between 500nm – 1µm in length. The shape of the platelets were not uniform. By using DEA (Fig 4c) as the base, hollow elliptical shaped particles were obtained. A more detailed FEGSEM image is shown in Figure 5. The sizes of the particles are between 750nm – 1µm in length and a width of approximately 200-300nm.

These results suggest that different bases have an effect on the morphology of ZnO formed which is probably due to the change in complexes formed when the Zn(CH₃CO₂)₂ was reacted with the base. By using TMAH and NH₄OH, the results show a similar morphology (platelets) to that of no surfactant (Fig. 1a). This would suggest that there is no interaction between them and the surfactant.

The most interesting result is when DEA was used as a base in which hollow elliptical particles were formed. It is suggested that a Zn-DEA complex was produced in solution instead of Zn(OH)₂. With the increase in pressure and temperature, Zn-DEA complex began to hydrolyze into ZnO crystallites. The formation of the hollow particles was maybe due to the ZnO crystallites beginning to grow on the outside surface of the micelle instead of inside the core like before. During hydrothermal treatment, the process of Ostwald Ripening increased the size of the ZnO crystallites and a much larger hollow particle was formed.4

4 CONCLUSIONS

In summary, we demonstrated the preparation of a variety of different morphologies of ZnO, by a simple change of surfactant and base. It was found that the by using a Pluronic surfactant, rod like structures were formed. By changing the size of the surfactant, in particular the core size, it was possible to change the size and aggregation of the rods. By changing the choice of base used in the reaction with Zn(CH₃CO₂)₂ the new complexes formed would also behave differently with the surfactants (L64). Though TMAH and NH4OH did not interact with the surfactant, the addition of DEA caused hollow elliptical particles to be formed. Ongoing investigations are focusing on the effect of ionic surfactants, heat treatment changes and on the doping of the zinc. It is expected that these variables will lead to more interesting structures, with a potential to be used in such applications as photovoltaic devices, gas sensors and catalysts.

REFERENCES