A Novel Route to Zeolite-Templated ZnO Quantum Wires

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Abstract. ZnO nanoparticles were synthesised within the pores of the zeolite ferrierite (FER) by a novel molten salt impregnation method and compared to a traditional wet impregnation method. The structure and optical properties were characterised by powder XRD, photoluminescence and UV-visible diffuse reflectance spectroscopy. The XRD results reveal a distinct difference in the effect of the impregnation method on the zeolite framework. The optical data show blue-shifts in the absorption and emission profiles of encapsulated ZnO with respect to the bulk material.

1. Introduction

Wide band gap semiconducting materials are of great interest to photonic materials research because of their potential applications as blue/UV emitters, solar cells, etc. Over the past decade there has been intensive research into the growth and synthesis of nanostructured, semiconducting materials, such as quantum dots, wires and nanorods, with the promise of altered and improved optical properties as a result of quantum confinement effects. [1]

ZnO; a wide direct band-gap II-VI semiconductor with a bulk band gap of 3.37 eV at 298 K and a relatively high exciton binding energy of 60 meV[2] that allows significant exciton emission at room temperature, has been studied in this work. Previous attempts at nanoscale production of ZnO particles have utilized methods such as colloidal precipitation[3] and metal organic chemical vapour deposition (MOCVD) [4], which can lead to aggregation of ZnO particles. From 2006 Su et al.[5] investigated a method of nanoscale ZnO production that aimed to resolve this problem by wet impregnation of nanoscale and mesoporous silica and zeolite templates, which has been followed by several other groups. [6, 7]

The advantages of using aluminosilicate zeolites as templates for optoelectronic materials are the relative rigidity of the frameworks, their chemical and thermal stability, pore size, shape and distribution regularity and the vast choice of available framework geometries. The typical pore dimensions of zeolites range from ~0.2 nm to ~0.8 nm and they are generally stable to temperatures of approx. 800 °C. Su et al studied the use of both ZSM-5 and faujasite (FAU) to encapsulate ZnO. ZSM-5 consists of long channels with diameters of 0.55 nm that run the length of the zeolite particles and FAU contains well defined, 0-dimensional cages with diameters of 1.3 nm, i.e.; quantum wire and quantum dot templates respectively. The zeolite investigated in this work is ferrierite (FER); an aluminosilicate zeolite with a 2D pore system of intersecting perpendicular channels with diameters of 0.54 nm and 0.48 nm that run the length of the particle.
This work investigates a novel method of zeolite impregnation and the effect of impregnation method on the optical properties of ZnO templated by FER with the aim of altering the band structure of ZnO as a result of quantum confinement.

2. Experimental

The FER used in this work was supplied by Zeolyst International in the NH$_4^+$ form with Si:Al ratio of 20. The ammonium zeolite was converted to the protonated form (HFER) by calcining at 400 °C in air overnight. This was then dried prior to being subjected to the two impregnation treatments.

Incorporation of ZnO via the molten salt method was achieved by grinding the dried FER together with Zn(NO$_3$)$_2$.6H$_2$O (melting point = 36 °C) in a 1:10 molar ratio and heating to 110 °C under nitrogen for several hours. The cooled sample was then washed with a small amount of distilled water (~20 cm$^3$) and filtered under vacuum to remove any surface Zn(NO$_3$)$_2$.6H$_2$O not absorbed by the zeolite. Oxidised samples are hereafter denoted FER/ZnO-M.

Wet impregnation was carried out by adding a known amount of FER to an aqueous solution of Zn(NO$_3$)$_2$ and stirring for several hours with gentle heating until the solvent evaporated. In using this method a precise Zn loading of the zeolite was achieved. Zn loadings of 5 – 50 wt% were used. Oxidised samples are hereafter denoted FER/ZnO-Wx%, where x is the Zn wt% loading.

The dried FER/Zn(NO$_3$)$_2$ samples were then heated to 800 °C in air at a ramp rate of 1 °C min$^{-1}$, held at 800 °C for 5 hours and cooled at 1 °C min$^{-1}$ to produce ZnO nanoparticles encapsulated within the pores of the host zeolite.

3. Characterisation

Powder X-ray diffraction (XRD) patterns were recorded at room temperature using a Philips X’Pert Pro Diffractometer with Ge-monochromated Cu-K$_\alpha$ radiation with a wavelength of 1.54056 Å. Data were collected over the range 3 – 60 ° in 2θ with a step size of 0.02 ° and were analysed using Rietveld refinement with Topas Academic. UV-visible diffuse-reflectance spectra were recorded using a Jasco V-630 equipped with a 60 mm integrating sphere. Data were collected over a range of 200-1000 nm at a scan rate of 400 nm min$^{-1}$. Photoluminescence (PL) data were recorded at room temperature using a Nd:YAG laser at 255 nm as the excitation source with an optical fibre to transmit the luminescence signal to a spectrometer (S2000, Ocean Optics Inc (OOI)) and the acquired spectrum was interpreted via OOI software.

4. Results and Discussion

4.1. Powder XRD

Figure 1 shows powder XRD of ZnO (Sigma Aldrich, ≥ 99.0%), HFER, FER/ZnO-M and FER/ZnO-W10%.
It is evident from Figure 1 that during both the molten salt and solution impregnation and subsequent oxidation processes the zeolite retains its structure. A good Rietveld refinement profile fit (R < 20) is achieved with only 1.57 % ZnO content in FER/ZnO-M, suggesting the absence of large, extra-zeolite ZnO crystallites. The profile of FER/ZnO-W10% shows 3 % ZnO, which is more prevalent than in FER/ZnO-M, at 2θ = 31.8, 34.5 and 36 ° (*). This is attributed to surface ZnO as the wet impregnation process relies on diffusion in order to distribute Zn(NO₃)₂ throughout the pore system, whereas the molten salt process relies on capillary forces.

What is less noticeable from Figure 1 is that the unit cell parameters for each FER sample are slightly different. By performing Rietveld refinement and including both FER and ZnO phases in the model it is found that although the zeolite structure is retained, the unit cell for FER is slightly larger along all 3 axes for FER/ZnO-M than for FER/ZnO-W5% to -W50% by 0.004 Å along a to 0.02 Å along c. When compared with FER/ZnO-W0%, which has smaller a and c cell parameters (see Figure 2), one can see that the presence of Zn(NO₃)₂ within the pores has the effect of supporting the structure during the high temperature oxidation, which causes contraction of the framework. The b parameter is larger when x < 10 % than when x > 10 %, but is larger still in FER/ZnO-M. This phenomenon has also been consistently recorded in work with other zeolites, such as ZSM-5 and faujasite, and other guest species, such as GaN and Zn₃N₂ and will be published elsewhere at a later date.

4.2. Optical Properties
The PL emission and UV-visible diffuse-reflectance absorption spectra are presented in Figure 3.

Figure 2: Zeolite FER viewed along [001]. [⁹]

Figure 3: PL and diffuse-reflectance spectra. Arrows mark E_PL and E_Abs.
As is clear, the emission wavelength of ZnO (Sigma Aldrich, ≥ 99%) is blue shifted upon zeolite inclusion and is dependant on the impregnation process. There is a shift in PL energy from 3.084 eV for bulk ZnO to 3.125 eV for FER/ZnO-W15% and to 3.158 eV for FER/ZnO-M.

By applying the Brus equation\(^{[10]}\), the measured shift in the band gap can be compared to the expected sizes of the zeolite-templated nanoparticles (i.e. comparable to the pore sizes):

\[
\Delta E \approx \frac{\hbar^2}{8\mu R^2} - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon_\infty R}
\]

where \(\mu\) is the exciton effective mass (0.217 m\(_e\) for ZnO\(^{[11]}\)), \(R\) is the particle diameter and \(\varepsilon_\infty\) is the high-frequency dielectric constant (3.7). By applying this equation to the data presented in this work we obtain estimated ZnO particle sizes of 2.2 nm for FER/ZnO-W15% and 2.05 nm for FER/ZnO-M. At first glance these figures suggest the formation of particles larger than the pore size within which ZnO is intended to be confined, but this is not the case as the Brus equation assumes spherical particles. The intention of this work is to create confined particles; resulting in the formation of nanorods with the long axis several times greater than the two short axes; therefore the Brus equation doesn’t fully apply, but can be used as a fair estimation of confinement effects.

The absorption data show a slight deviation from the emission spectra, in accordance with a Stokes shift of 181 meV for bulk ZnO, 131 meV for FER/ZnO-W15% and 125 meV for FER/ZnO-M. The band gaps according to absorption data were calculated using a 1st derivative approach.

5. Conclusions
To conclude, this work presents a novel method of producing nanoscale optical materials using nanoporous zeolites as templates and a solvent-free route to impregnation of zeolites with semiconductor precursor materials. Powder XRD studies suggest the inclusion of dense guest phases within the pores that support the pore structure of the host zeolite during the subsequent relatively harsh reaction conditions. Room temperature optical measurements confirm that the band gaps of semiconducting materials are blue-shifted upon zeolite templated quantum confinement and the magnitude of Stokes shift is similar to those observed in bulk ZnO. Although the Brus equation cannot be fully relied on, it has been used to show that a degree of quantum confinement has been achieved with approx. particle sizes (averaged over all 3 axes) of 2.05 nm for FER/ZnO-M and 2.2 nm for FER/ZnO-W15%. HRTEM measurements are planned to confirm these findings.

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