Effect of pH on the growth of zinc oxide nanorods using Citrus aurantifolia extracts

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ABSTRACT
The effect of pH during sol–gel synthesis of ZnO nanorods using Citrus aurantifolia juice extracts has been investigated. Zinc nitrate solutions and C. aurantifolia fruit extracts mixtures were heated at 90 °C at pH of 5, 7 and 9. Solid reaction products were annealed in air at 300 °C yielding nanorods with diameters of about 100 nm for all samples. XRD analysis showed pure hexagonal wurtzite ZnO structure. Room temperature visible photoluminescence spectroscopy revealed emissions which were attributed to the common defects states associated with ZnO. Nanorods growth in acidic solution was found to be inhibited compared to nanorods from neutral and alkaline solutions. This was due to preferential erosion of ZnO (0001) face in acidic solution and the enhanced growth in neutral and alkaline solutions which favored the formation of Zn(OH)2 which is an intermediate molecule in the reaction to form ZnO.

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1. Introduction

In recent years, there has been increasing interests in using biomaterials in sol–gel techniques especially in the synthesis of gold and silver nanoparticles [1,2]. The attraction of using biomaterials lies in the low cost of easily available and renewable reaction materials. Furthermore, waste effluents from the process are expected to be more eco-friendly compared to conventional chemicals. There have been a number of reports on the sol–gel synthesis of ZnO nanoparticles using biomaterials such as aloe vera leaf extracts [3], the milky latex of Calotropis procera [4], gum tragacanth [5] and gelatine [6]. Recently we demonstrated the use of Citrus aurantifolia juice extracts under acidic conditions of pH 3.7 and 4.0 [7]. In this article, we report the effect of pH on ZnO nanorods synthesized using C. aurantifolia at pH 5, 7 and 9 which covered the acidic, neutral and alkaline environments.

2. Materials and methods

Citrus aurantifolia fruits purchased at the local market were peeled and the pulp obtained was blended with DI water. The blended slurry was initially filtered with muslin cloth to remove large solid particles. Then the filtrate was further filtered with a 200 nm pore syringe filter. The filtered juice was kept at 4 °C until used. To prepare the zinc oxide nanoparticles, three stock solutions of 4.4 g zinc nitrate in 100 mL C. aurantifolia juice were prepared. The initial pH of the solutions was about 3.5. To each solution 0.1 M NaOH was added until

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the pH values reached 5, 7 and 9, respectively. The solutions were heated at 90 °C under continuous stirring for 2 h and then left for 24 h at room temperature. White precipitates recovered from the solutions were thoroughly rinsed in DI water and then annealed in air at 300 °C for 6 h. The samples obtained were characterized using field emission scanning electron microscopy (FESEM), x-ray diffraction (XRD) and photoluminescence spectroscopy (PL).

3. Results and discussion

Fig. 1 shows the FESEM images of zinc oxide nanorods obtained at the different pH values. For all samples, nanorods were obtained but with varying aspect ratios. At pH value of 5 (Fig. 1(a)), the nanorods were smaller and shorter when compared to those obtained at pH 7 (Fig. 1(b) and 9 (Fig. 1(c)). Control experiments conducted without using C. aurantifolia yielded ZnO in particulate form (refer to Fig. S1 in the Electronics Supplementary Materials). The enhanced growth in alkaline solution has been reported where the abundance of OH⁻ contributed to the formation of the intermediate molecule, Zn(OH)₂ which facilitated the formation of ZnO [8]. However, our results showed that there seemed to be little difference between ZnO nanorods synthesized using neutral (Fig. 1(b)) and alkaline (Fig. 1(c)) solutions. The shorter and smaller diameter nanorods obtained using acidic solution can be attributed to the preferential erosion of the (0001) compared to other ZnO crystal faces [9]. From the FESEM images the aspect ratio of ZnO nanorods synthesized in neutral and alkaline solution were about 10 and those synthesized in acidic solution were about 5.

The XRD patterns of ZnO nanorods obtained at various pH values are shown in Fig. 2. All the diffraction peaks can be indexed to the hexagonal wurtzite ZnO crystal structure. The main diffraction peaks located at 2θ values of about 31.6°, 34.4°, 36.2°, 47° and 56.9° are assigned to the (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0) reflection planes of ZnO, respectively. The slightly dominant peak due to the (1 0 1) reflection plane for samples synthesized at pH 7 and 9 may be due to the direction of the nanorods which were generally inclined at an angle with respect to the direction of
the incident x-ray beam as evident from the FESEM images in Fig. 1. As for the sample synthesized at pH 5, the peak due to the (1 0 1) reflection plane was less dominant due to smaller aspect ratio resulting in a more random orientation of the nanorods with respect to the direction of x-ray probe beam. This is an indication that the nanorods were single crystal and growth was along the c-axis.

Fig. 3 shows the PL spectra in the visible region measured at room temperature using a probe beam at 325 nm. The broad spectra were fitted to Gaussian peaks and the resulting peak positions were summarized in Table S1 in the Electronics Supplementary Materials. The blue peaks at about 490 nm can be attributed to the transition from oxygen vacancy [10]. The peaks at around 518.57 nm corresponded to the recombination of a photo-generated hole with a singly charged ionized state of oxygen vacancy [11] and the peaks at about 536 nm were attributed to transition from deep donor level by the oxygen vacancies to valence band [12].

Dominant peaks at about 559 nm can be attributed to transition of zinc interstitial (\(\text{Zn}_i\)) to zinc vacancies (\(\text{V}_{\text{Zn}}\)) [13]. The peak at 589 nm observed in the sample synthesized at pH 5 can be due to oxygen interstitial (\(\text{O}_i\)) in the ZnO nanorods as a result of the acidic environment [14]. For the samples synthesized in neutral and alkaline solutions, peaks at about 596 nm were observed which may be due to the presence of hydroxyl groups on the sample surface [15].

### 4. Conclusions

ZnO nanorod have been synthesized in C. aurantifolia extract solutions at different pH values using the sol–gel method. XRD analysis showed all the samples were pure ZnO with wurtzite structure with evidence of single crystal nanorods with growth along the c-axis. Room temperature PL in the visible region consisted of a few overlapping peaks arising from recombination on common points and surface defects. Growth inhibition was observed in the samples synthesized at pH 5 which can be due to preferential erosion of ZnO (0 0 0 1) face. Enhanced growth in alkaline solution at pH 9 was due to the more abundance OH\(^-\) ion compared to acidic solution, which promoted the intermediate molecule Zn(OH)\(_2\). Equally efficient growth at pH 7 indicated that erosion process dominated the inhibition of nanorod growth over enhancement due to the presence of OH\(^-\) ion.

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### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [http://dx.doi.org/10.1016/j.matlet.2014.09.033](http://dx.doi.org/10.1016/j.matlet.2014.09.033).

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