Shape and Size Effect of ZnO nanocrystals on Photocatalytic Activity

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Supporting Information

1. Analytical Techniques

1.1 Powder X-Ray Diffraction (XRD)

X-ray diffraction data was collected using a Philips PW1729 diffractometer, operating in Bragg-Brentano focusing geometry and using $Cu_{K\alpha}$ radiation (λ = 1.5418 Å) from a generator operating at 40 kV and 30 mA. Samples were prepared by placing a drop of nanoparticle suspension on a glass slide and allowing the solvent, hexane, to evaporate. This process was repeated many times until a smooth layer of material was deposited on the slide surface. The Scherrer equation was used to estimate average particle size from the mean value derived from the (100), (002) and (101) taking the instrumental line broadening into account.

1.2 Low Angle XRD

Low angle X-ray diffraction was used to obtain the diffraction pattern at low angles in the range 1-10 °2θ. Low angle data in this range can give information about structural periodicity with d-spacings of up to 90 Å. The low angle X-ray diffraction data was collected using a PANalytic X'Pert Pro diffractometer, also operating in Bragg-Brentano focusing geometry. The samples were prepared in the same way as for high-angle XRD.

1.3 Transmission Electron Microscopy (TEM)

TEM images were obtained using a JEOL 2010 microscope with a high resolution pole piece. The samples were prepared by placing a drop of nanoparticle suspension onto a carbon-coated copper grid, and allowing the solvent, hexane, to evaporate.

1.4 Sample Preparation and Catalytic Testing

The precursor zinc acetate dihydrate (1.40 g, 6.38 mmol) was first heated in an oven at 120 °C overnight to remove water. In a standard synthesis this precursor was then mixed with oleic acid in a designated molar ratio, in 15 ml (12.00 g, 33.93 mmol) of trioctylamine solvent. The mixture was heated under nitrogen to 290 °C. The 3-necked flask was attached to a reflux condenser, and the mixture was magnetically stirred throughout. The solution turned yellow initially, then the presence of the nanoparticles was indicated by the solution turning cloudy (within 1 hour of heating). Heating was continued for a further ten minutes, and then the mixture was allowed to cool to room temperature. The white precipitate was collected by centrifugation at 3000 rpm for 20 minutes, after which the supernatant was decanted and discarded. The solid was washed repeatedly with acetone and water to remove excess stabiliser and solvent from the particles. The hydrophobic stabiliser remnant on nanoparticle surface was removed by first employing a ligand exchange reaction, using the tetramethylammonium salt of the bipolar surfactant 11-aminoundecanoic acid. 20 mg of surfactant was dispersed in 2 mL of dichloromethane, and this dispersion was added to a hexane dispersion of ZnO nanoparticles synthesised as above (20 mg in 0.2 mL), and then repeatedly centrifuged and washed with dichloromethane to separate the nanoparticles from the supernatant, and to remove the hydrophilic surfactant with water. This method is similar to that employed by Sun *et al.* with iron oxide nanoparticles.[13] TGA shows less than 1.5% weight loss up to 500°C. The samples could be readily dispersed in water after less than a minute of ultra-sonication hence ready for photocatalysis, and no changes were found in the XRD patterns of samples before and after such treatment. Nearly quantitative ZnO nanoparticles were produced in syntheses from the starting materials using varying quantities of oleic acid stabiliser (as specified while keeping the amounts of zinc acetate dehydrate and trioctylamine solvent constant).

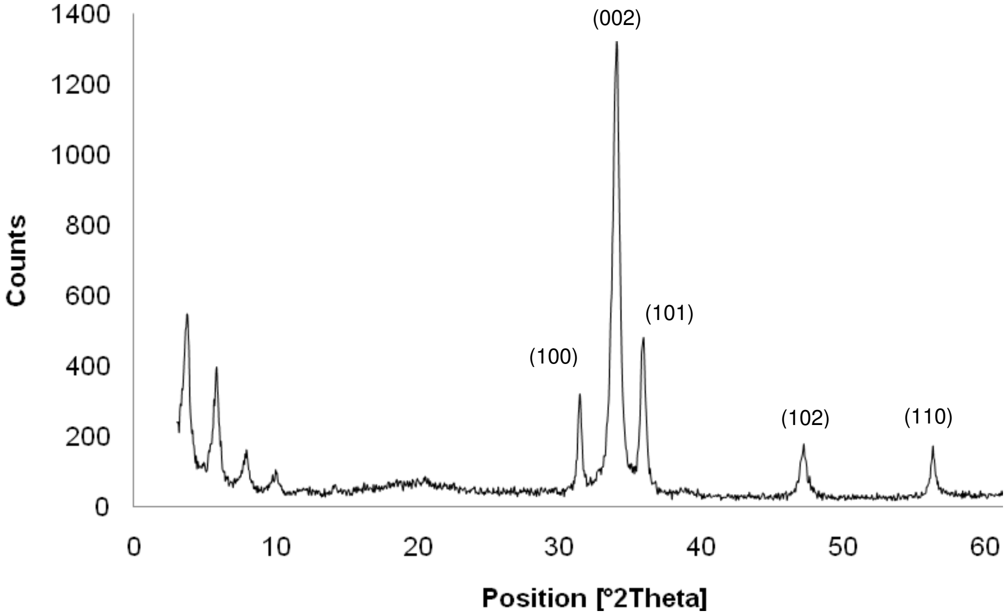
It is noted that this new chemical synthetic route to ZnO nanostructures with controlled morphology is clearly different from the alternative routes with control of shape and size of ZnO in literature (for example, Angewandte Chemie, International Edition (2003), 42, (43), 5321-5324 and Materials Letters 61 (2007) 4832–4835). Our method is based on a simple variation in oleic acid concentration.

The dye methylene blue was used as a model contaminant. For each testing run 10 mg of catalyst was dispersed in 100 ml of 15 mg l^{-1} aqueous methylene blue solution. The mixture was ultra-sonicated for 10 minutes and then magnetically stirred in the dark for 30 minutes before the reaction, to encourage even dispersion of the nanoparticles and to allow absorption/desorption equilibrium to establish itself. The photocatalytic reaction was conducted at room temperature, with constant magnetic stirring to ensure full suspension of the particles throughout. The reaction took place in a Luzchem photoreactor, fitted with eight UVA tubes centred at 350 nm. The typical intensity inside the chamber was 0.3 mW cm^{-2}. Each reaction was conducted for 1 hour, with 3 ml aliquots of reaction mixture extracted at 10 minute intervals. These aliquots were centrifuged for 10 minutes at 3000 rpm prior to UV-vis measurements, to remove any suspended solid. A Perkin-Elmer LAMBDA 19 UV/vis/NIR spectrometer was used to follow the decomposition of methylene blue. Absorption measurements were taken at 664.1 nm, as initial scans showed this to be the maximum absorbance wavelength for relevant concentrations of the dye. Concentrations were then determined by comparison to a calibration curve.

Two k values derived from the pseudo-first order plots for each sample (linear fitting coefficient of over 0.99 was obtained) with good reproducibility were averaged. The test was deliberately carried out using excess of methylene blue with the initial rate collected at short testing durations and low substrate conversions in order to avoid possible changes in catalytic activity due to complex secondary reactions and on stream deactivation. However, we have not yet carried out the recyclability test nor monitoring/buffering the pH of solution, which could somehow affect observed catalytic activity.

2. *Nanoparticle Synthesis and Characterization*

The X-ray diffraction pattern of a sample synthesized under standard conditions (in trioctylamine, at 290 °C, with an oleic acid to zinc acetate precursor ratio of 1:1) is shown in typical S Fig. 1.



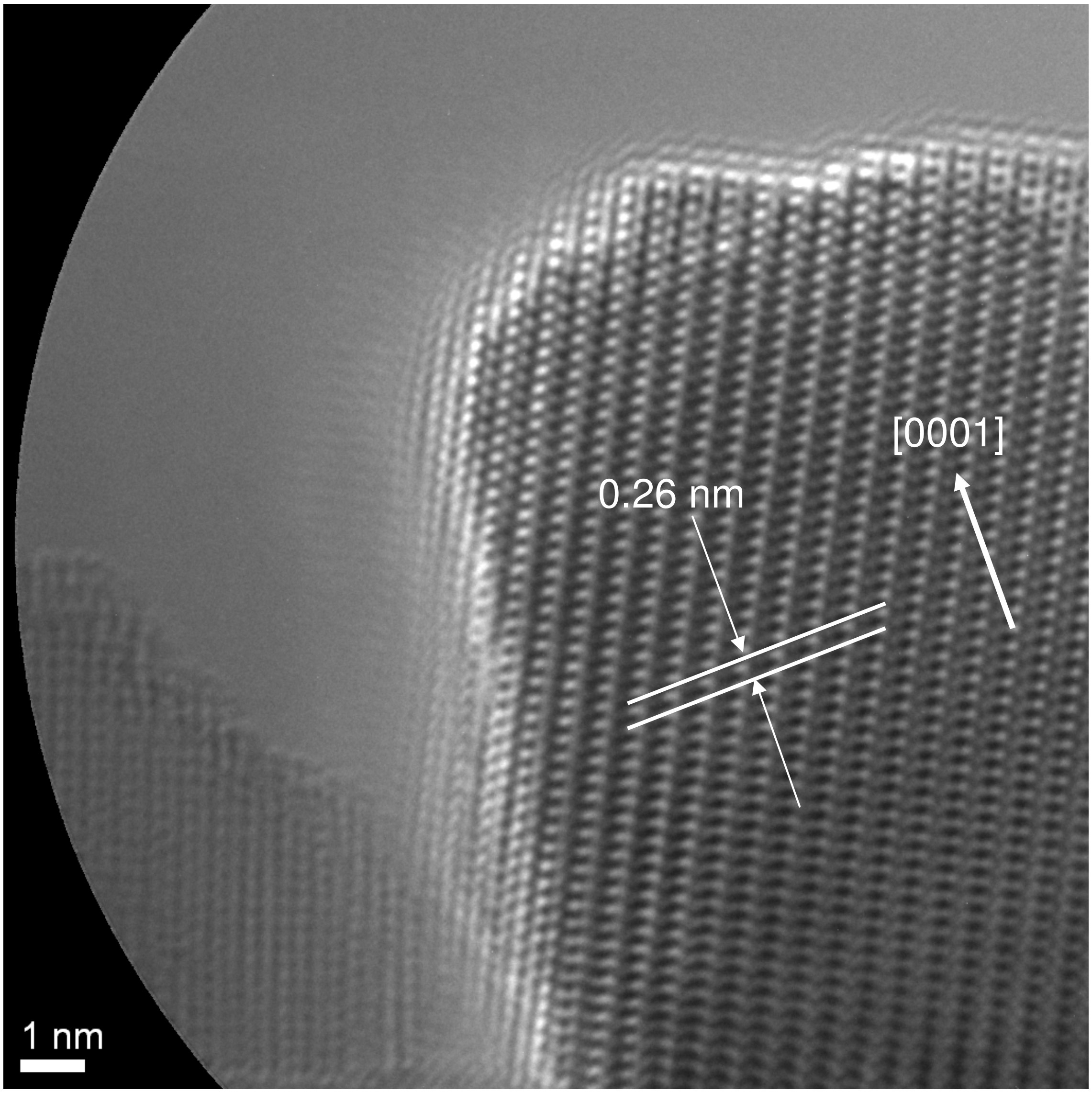
S Figure 1. XRD pattern of a sample made by the standard synthesis

All the diffraction peaks above 30 °2θ can be indexed to hexagonal phase wurtzite ZnO (JCPDS card No. 36-1351). The lattice parameters were calculated using the formula:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+k^2+l^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right)$$

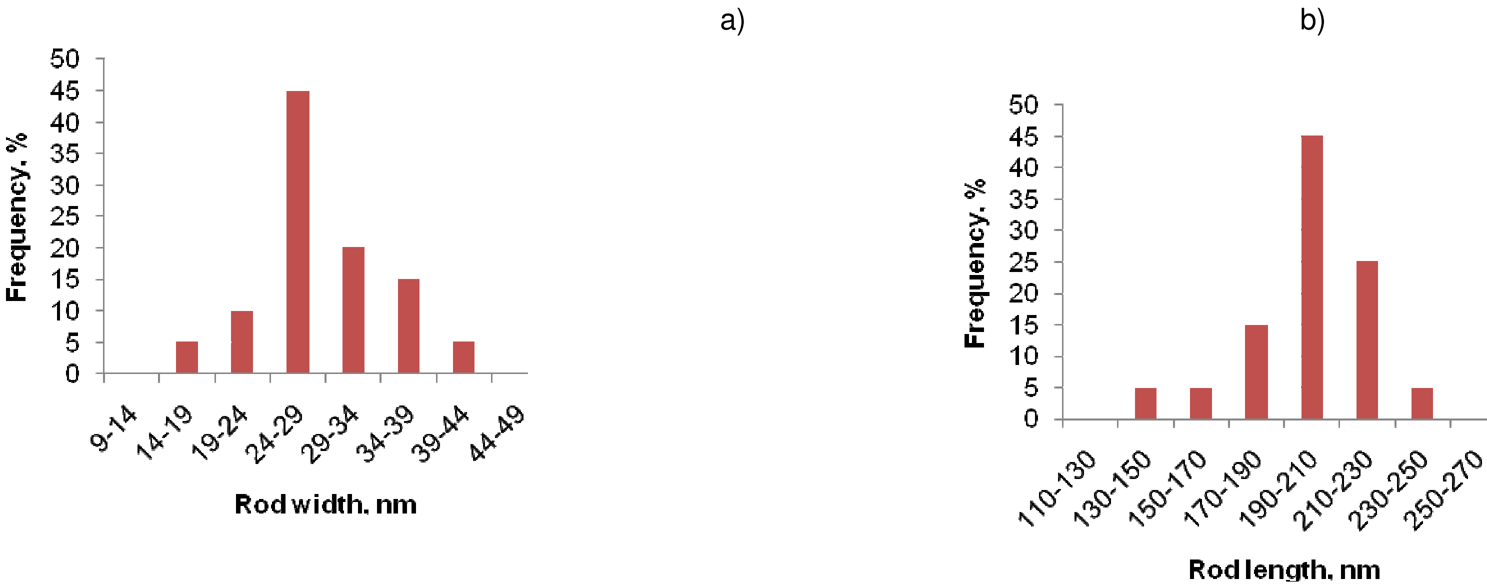
where *d* is the spacing between planes, *h*, *k*, and *l* are the indices that define the orientation and inter-planar spacings, and *a* and *c* are the lattice parameters that describe the dimensions of the unit cell.

The (100) reflection was used to find *a*, and the (002) reflection to find *c*. They were found to be $a = 3.2449$ Å (literature value $a = 3.2514$ Å) and $c = 5.2122$ Å (literature value $c = 5.2138$ Å). This indicates the formation of highly crystalline zinc oxide, which is further confirmed by the high resolution TEM image in S Fig. 2.

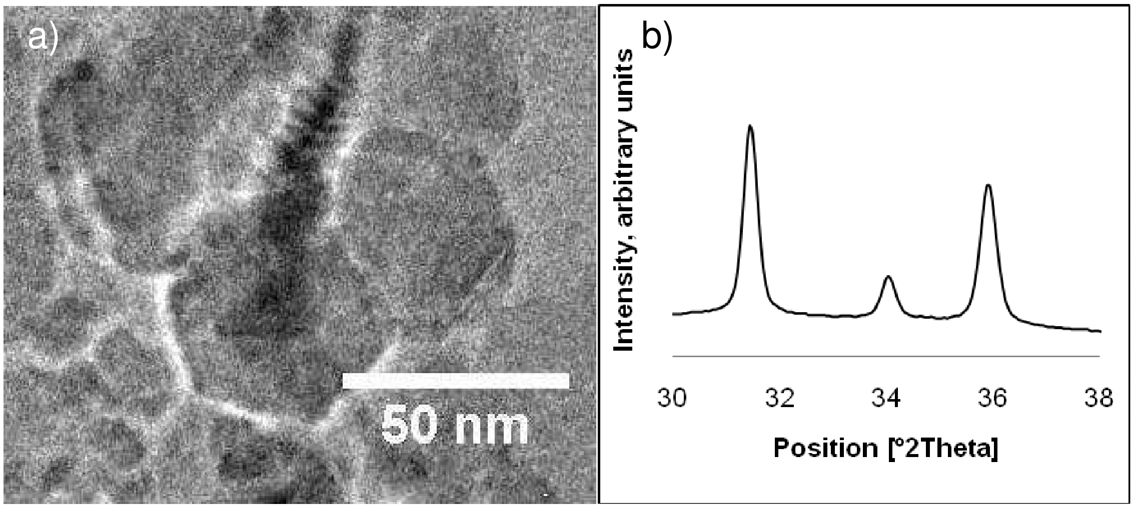


S Figure 2. HRTEM image of rod shape ZnO nanoparticle synthesized under standard conditions (oleic acid to zinc ion ratios =1). This shows well ordered crystalline planes with a spacing of 0.26 nm, corresponding to the (0002) planes of zinc oxide.

Histograms showing the typical length and width distributions of nanorods (based on measurements of 20 particles from a TEM image) are shown in S Fig.3.

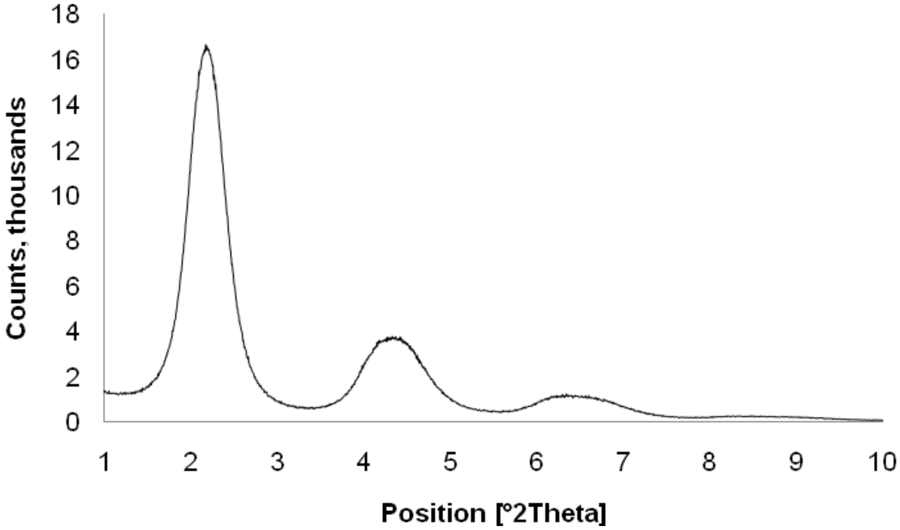


S Figure 3 (a) histogram showing the width distribution of nanorod; (b) histogram showing the length distribution of nanorods (oleic acid to zinc ion ratios= 1)



S Figure 4 (a) TEM image of plate-like nanoparticles synthesized (oleic acid to zinc ion ratios= 30); (b) XRD pattern of the same sample, showing (100), (002) and (101) reflections.

Low angle XRD measurements were taken between 1 and 10 °2θ, and an additional peak was found in this region as shown in S Fig.5.

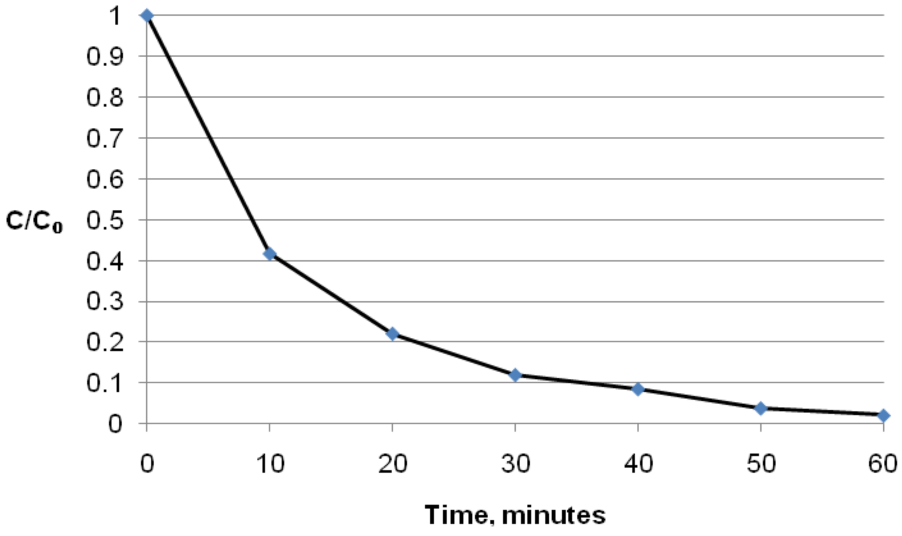


S Figure 5. Low angle XRD pattern for sample made via the standard synthesis

The peaks shown in S Fig. 5 correspond to *d*-spacings of 40.3, 20.3, and 13.7 Å. The *d*-spacing ratio of approximately 1:(1/2):(1/3) indicates clearly regular supramolecular lateral or lamellar packing,[17] with an inter-planar distance of 40.3 Å (comparable to dimension of bilayer of oleic acid which is longer than trioctylamine molecule). The peaks can be indexed as (00*l*) reflections. These peaks appeared only when zinc acetate, oleic acid and trioctylamine were all present even at room temperature after their mixing. This is similar to the our previous system involving oleic acid, an amine, and a metal cation (Na^+ in that case) to give a self-assembled organogel structure with hydrophilic channels.[17]

2.2 *Catalytic Testing*

Initially catalytic testing was performed as detailed in Experimental in the main text of the manuscript. A commercial photocatalyst, TiO_2 P25 Degussa was first used to establish the methodology. S Fig.6 shows the degradation of methylene blue as a function of time.

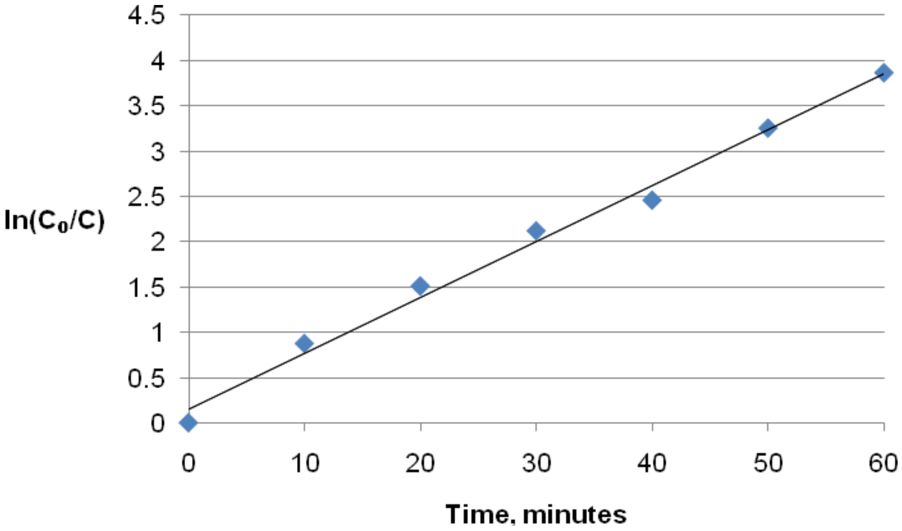


S Figure 6. Graph to show the degradation of methylene blue against time, using TiO_2 P25 Degussa.

It was found that the reaction followed the equation:

$$ln\left(\frac{C_0}{C}\right) = kt$$

where C_o is the initial concentration, C is concentration, k is the apparent rate constant and t is the time.
That is to say, the reaction shows pseudo-first order reaction kinetics, and the apparent rate constant was calculated to be $k = 0.0617\ min^{-1}$. The hydrophilic ZnO samples were studied accordingly.



S Figure 7. Graph to show the pseudo-first order nature of reaction

As suggested by the reviewer of this paper, it would be ideal to deduce the specific photocatalytic activity of a particular crystallographic plane (100, 101, 001) if one could estimate quantitatively its surface area. Such quantitative analysis could be compared with photocatalytic activities of ZnO surfaces made using UHV techniques. Since these methods of ZnO fabrications have shown a pronounced effect on size and shape dependent catalytic activity (Huihu Wang et al., Journal of Hazardous Materials 141 (2007) 645–652; Li Wang et al., Inorg. Chem. 2008, 47, 1443-1452 and X. Ren et al. Materials Research Bulletin 42 (2007) 807–813). Future work will be focused in the area.