ZnO Nanoflakes Self-assembled from Water Splitting Process by Hydroelectric Cell

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Text S1- Simulation dynamics based on Reitveld refinement on ZnO sample.

Bragg-Brentano geometry is taken into consideration for the obtained X-ray diffraction pattern. Marquardt least square fitting method has been used to minimize the difference between simulated and experimental data points. Various fitting parameters are used to assess the quality of fitting simulated data on the experimental plot. Reliability index parameters in form of R_p, R_{wp}, R_{exp} has been estimated. R_p is the residual error, R_{wp} is the weighted residual error, R_{exp} is the expected residual error (equation 1, 2, 3).

$$R_p = \frac{\sum_{i,n} |Y_i - Y_{ci}|}{\sum_{i,n} Y_i} \quad \text{.....(1)}$$

$$R_{wp} = \frac{\sum_{i,n} w_i (Y_i - Y_{ci})^2}{\sum_{i,n} w_i Y_i^{\,2}} \quad \text{.....(2)}$$

$$R_{exp} = \left[\frac{(N-P)}{\sum_{i,n} w_i Y_i^{\,2}} \right]^{\frac{1}{2}} \quad \text{.....(3)}$$

Here, Y_i, Y_{ci} is the respective experimental and calculated intensity value, w_i is the variance, N is the number of points, P is the number of refined parameters, (N-P) is the degree of freedom.

The fitting quality is assessed from the estimated goodness of fit parameter (equation 4). Best fit are the ones where $\chi^2 < 2$.

$$\chi^2 = \left[\frac{R_{wp}}{R_{exp}}\right]^2 \text{.....(4)}$$

Preferred orientation along [002] crystalline plane than [100] plane has been assessed using March Dollase equation for texturing effect (equation 5).

$$W_{hkl} = \frac{1}{N}\left(\sum_{i,n} r^2 cos^2\alpha + \frac{1}{r} sin^2\alpha\right)^{\frac{-3}{2}} \text{.....(5)}$$

Here, W_{hkl} is the preferred orientation factor, r is the refined orientation parameter, α is the angle between preferred orientation vector and the perpendicular to the hkl plane.

XRD peak broadening effect in ZnO were estimated using Williamson Hall method which considers the contribution from crystallite size induced and lattice strain induced broadening.

$$\beta = \beta_D + \beta_\epsilon \text{ ……..(6)}$$

Here,β is the overall line broadening, β_D is broadening due to crystallite size, β_ϵ is the broadening due to lattice strain. It is based on the assumption of isotropic strain in all directions in a crystal lattice Lattice strain is estimated from the plot of βcos (Θ) vs 4ϵsin(Θ) using equation 2. Here, ϵ is the lattice strain. The straight line obtained with high positive slope 0.00319 is indicative of expansive lattice strain (**Figure S1**).

$$\beta\cos(\theta) = \frac{K\lambda}{D} + 4\epsilon\sin(\theta) \ldots\ldots\ldots(7)$$

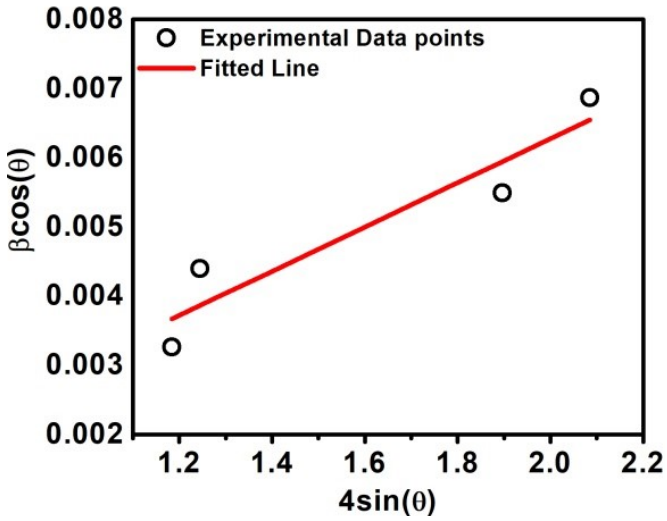

Figure S1: Williamson-Hall Plot for calculation of lattice strain (R^2_{est}= 0.84).

Table S1: Rietveld refined lattice parameters and estimated Reliability Factors (R_{wp}, R_p, R_{exp}, χ^2) for simulated XRD pattern of ZnO sample.

TABLE-S1

a=3.25288Å	**b=3.25288 Å**	**c=5.212 Å**	**α=β=90°; γ=120°**	**Unit cell Volume-55.15 Å^3**
ρ=5.838g/cm^3	**R_{wp}= 7.33%**	**R_p=5.33%**	**R_{exp}=4.82%**	**χ^2 =1. 51**

Table S2: Preferred orientation effect with consideration of March Dollase Coefficient and associated weight factor for (002) and (100) lattice planes.

TABLE-S2

Diffraction Plane	March Dollase Coefficient	Weight Factor

(002)	**0.4308**	**0.75**
(100)	**0.6**	**0.85**

Text S2: Calculation of Urbach Energy in ZnO nanostructure.

High effective surface area and defect concentration in nano-crystallites results in enhanced band tailing near valence and conduction bands.

Urbach energy is associated with band tailing effect observed near valence and conduction band. Exponential dependence of absorption coefficient (α) on photon energy (hν) exists near band edge region (equation 8)[i].

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{E_u}\right) \text{.....(8)}$$

Here, urbach energy (E_u) denotes the width of defect band tail associated with the localised states formed in forbidden gap region.

Urbach energy has been calculated by taking the reciprocal of linear fit slope in the lower photon energy region. Vacancy defects and interstitial defects form trap levels widening urbach band bending tail[ii].

FTIR of ZnO nanoflakes:

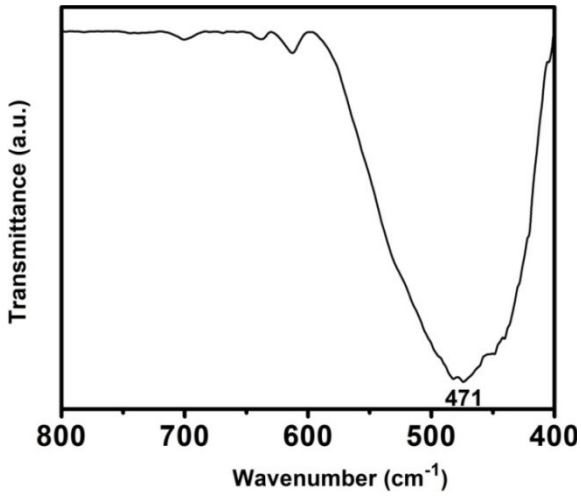

Figure S2: FTIR spectra of ZnO nanoflakes.

Text S3: The cumulative surface area and average pore size of ZnO nanoflakes have been determined by BET and BJH nitrogen adsorption−desorption isotherms shown in Figure S4. ZnO nanoparticles BJH isothermal curve exhibited a type II isotherm with hysteresis according to the IUPAC conventions[iii]. The BET surface area has been found 144.2876 m^2 /g, calculated by t-plot data. The pore volume and average pore size distribution has been obtained 0.2328 cm^3/g and 7.1 nm by BJH isotherm plot.

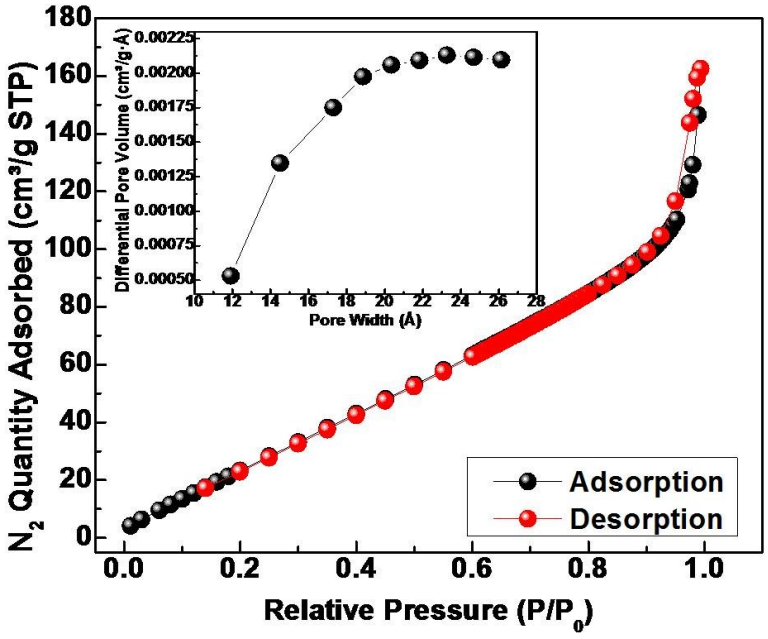

Figure S3: N_2 adsorption-desorption isotherm BJH plot of ZnO nanoflakes and average pore size distribution (inset plot).

Survey scan of ZnO Nanoflakes:

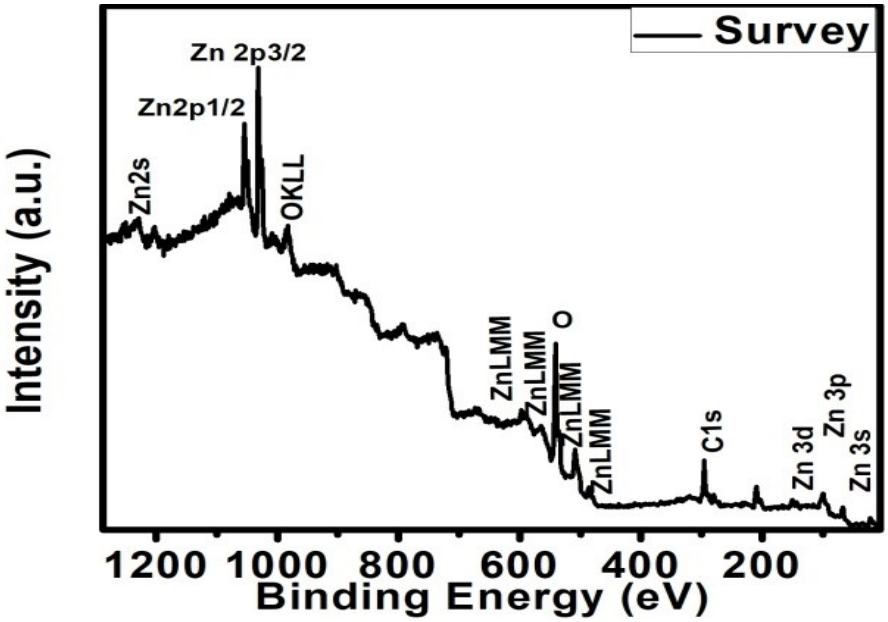

Figure S4: XPS survey spectra of synthesized ZnO sample.

References:

[i]Boubaker K 2011 A physical explanation to the controversial Urbach tailing universality Eur. Phys. J. Plus 126 10

[ii]Electrical conductivity and optical properties of ZnO nanostructured thin film MujdatCaglara,*, SalihaIlicana, YaseminCaglara, FahrettinYakuphanoglub Applied Surface Science 255 (**2009**) 4491–4496

[iii] Liebau, F. Ordered Microporous and Mesoporous Materials with Inorganic Hosts: Definitions of Terms, Formula Notation, and Systematic Classification. Microporous Mesoporous Mater, 58, (**2003**), 15−72.