Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Hydrothermal Growth of ZnO Nanowire Arrays: Fine Tuning by Precursor Supersaturation

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Issues that cause inconsistencies of one batch hydrothermal growth of ZnO nanowires (NWs)

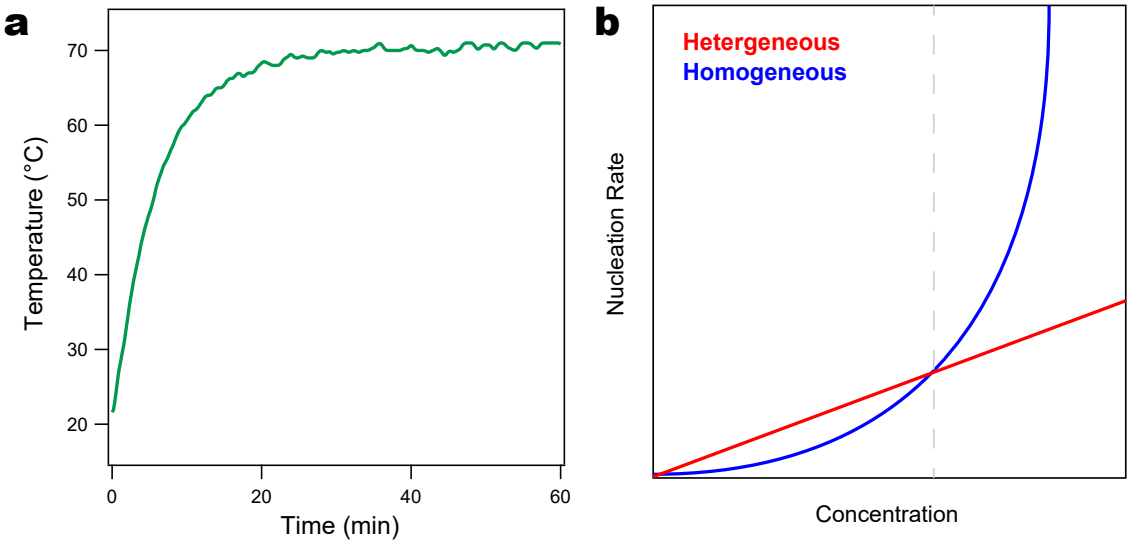

Figure S1: (a) Heating curve for the growth solution of one batch method. It takes up to 20 minutes to reach the equilibrium. (b) Sketch of the competition between homogeneous and heterogeneous nucleation.

The exact reaction starting point of one batch hydrothermal process is difficult to figure out, for the reason that supersaturated solution is highly sensitive to the temperature variations. The growth solution has to be prepared at room temperature, and the whole apparatus will then be transfered to an oil bath to heat up. Since it can take up to 20 minutes for the growth solution to reach the equilibrium temperature (Figure S1a), the reaction will start sometime during the long heat up process yet difficult for us to record the beginning. Moreover, for the commonly used sustained OH^- supplier HMTA, the decomposition rate is also heavily dependent on the temperature, thus the different OH^- concentrations varying from time to time will make the tunable fabrication even more challenging.

On the other hand, high precursor concentration in one batch method will lead to significant homogeneous nucleation creating white precipitates in the solution. As seen in Figure S1b, the competition between heterogeneous nucleation and homogeneous nucleation exist throughout all precursor concentrations. However, heterogeneous nucleation will dominate within relatively di-

lute precursor concentration, while in concentrated solution homogeneous nucleation is more favorable. This is because, according to the collision crystallization theory, heterogeneous nucleation is the first order reaction, which is linear to the precursor concentration. While homogeneous nucleation requires at least two molecules to collide, so that it is a higher order reaction. With that being said, the growth solution should be maintained at a low concentration in order to eliminate the homogeneous nucleation.

Packing density of ZnO NWs for different samples

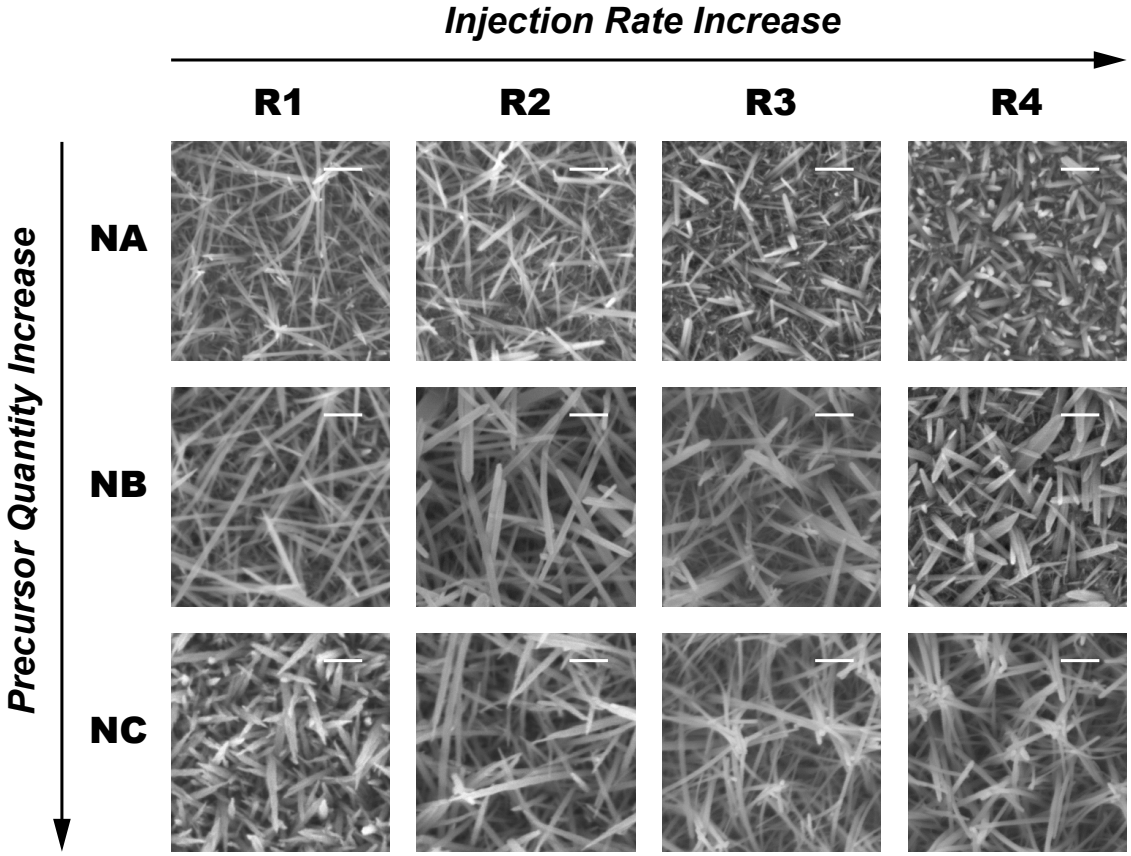

Figure S2: Top-view SEM images of ZnO NWs prepared with different parameters. Pumping parameters have a strong impact on the packing density of each sample Scale bar = 200 nm.

From the top-view SEM images, the nanowire packing density η for each sample can be seen. We can have an intuitively comprehension of the trending that at low precursor concentration (NA and NB), faster dripping rate will lead to a higher nanowire density. That is due to, as mentioned in the article, caused by different supersaturation degree in the growth solution.

Experimental method for measuring absorbance of nanoscale materials using UV-Vis Spectroscopy

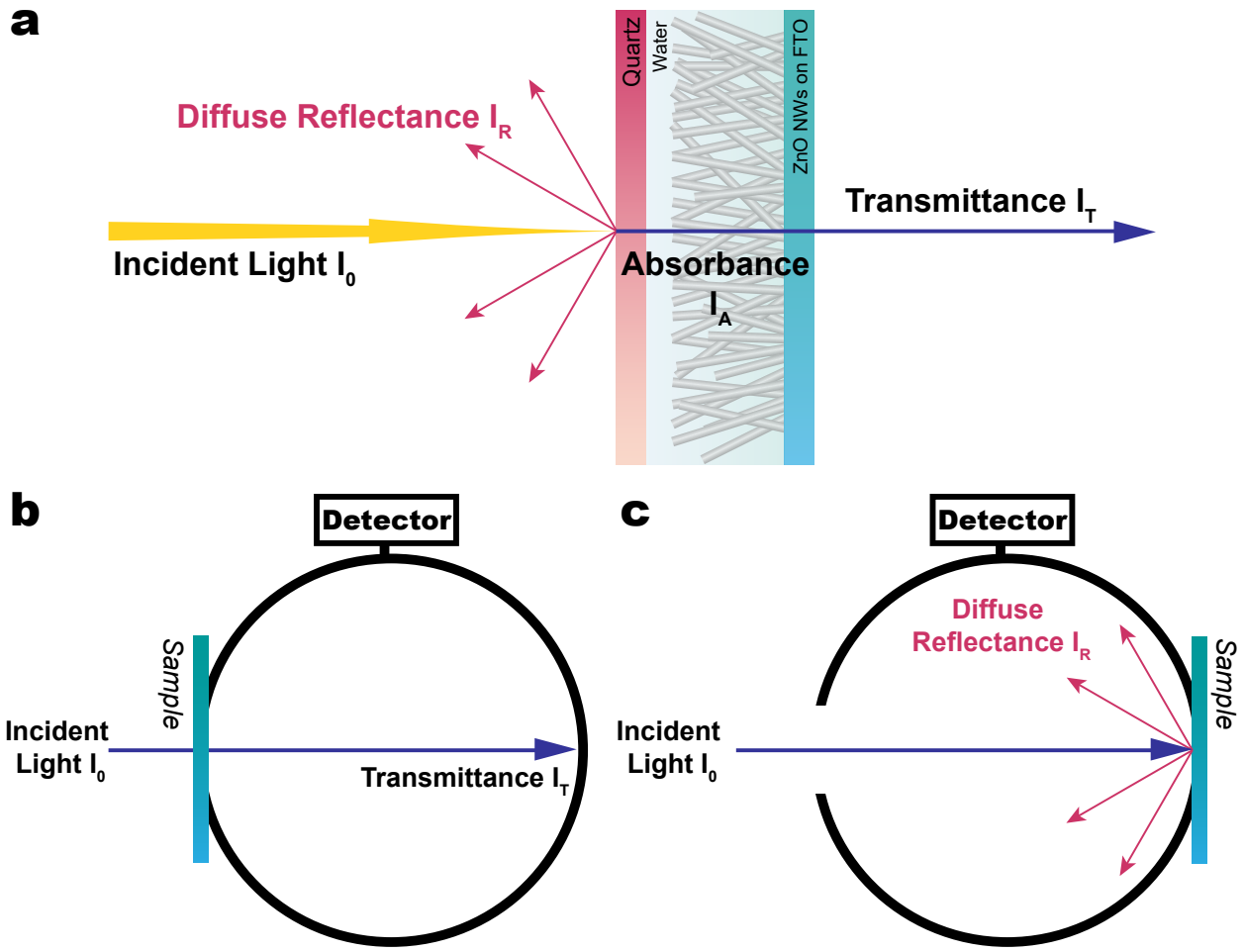

Figure S3: Experimental setup and the illustrated beam path for UV-Vis spectroscopy with integrating sphere. (a) Typical beam path during a traditional transmittance measurement. During the characterization of nanostructured materials, errors in transmittance raised from scattering could be significantly impacting measurement to obtain trustful results. (b) UV-Vis measurement in the front transmittance port of an integrating sphere, that the transmittance could be measured. (c) UV-Vis measurement in the back diffuse reflectance port of an integrating sphere, that the diffuse reflectance could be measured.

Accurate packing density η can only be calculated based on trustable absorbance measurement. To best imitate the conditions of light absorbed by the photoelectrode within a PEC cell, ZnO NWs samples are covered with a water layer and a piece of quartz during the UV-Vis measurement (Figure S3a). Conventionally, absorbance A for each sample can be obtained by measuring the

value of its transmittance T:

$$A = \log_{10} \frac{1}{T} \tag{S1}$$

where $T = I_T/I_0$. Here, I_0 is the incident light intensity, and I_T is the transmittance intensity.

However, nanostructured materials like ZnO NWs would have strong scattering effect on the surface, so that the diffuse reflectance light intensity I_R becomes too significant to be ignored when calculating A, otherwise the absorbance will be overestimated. As can be seen in Figure S3a, the actual incident intensity $I_0' = I_0 - I_R$, so the T rewrites as:

$$T = \frac{I_T}{I_0 - I_R} \tag{S2}$$

and absorbance A rewrites as:

$$A = \log_{10} \frac{I_0 - I_R}{I_T} \tag{S3}$$

or:

$$A = \log_{10} \frac{1 - R}{T} \tag{S4}$$

where $R = I_R/I_0$ is the reflectance of the sample measured.

UV-Vis spectroscopy equipped with integrating sphere (Figure S3b,c) can easily measure both transmittance and reflectance for each sample. By placing the sample in the front transmittance port (Figure S3b) the transmittance could be measured, while the reflectance could be measured by placing it in the back diffuse reflectance port (Figure S3c). So that a more accurate absorbance A can thus be calculated using Eq.(S4).

Multiple linear regression to find out credible constant coefficient values m and n

By fitting our L, D and i into the empirical relationship $i = kL^mD^n$, we can get values of the coefficients m and n. By taking natural logarithm to the equation:

$$\ln i = m \ln L + n \ln D + \ln k$$

and then these coefficients can be figured out via multiple linear regression, with independent variables $\ln L$ and $\ln D$ to dependent variable $\ln i$. The regression results are summarized in Table S1.

Table S1: Major results of multiple linear regression for $\ln L$ and $\ln D$ to dependent variable $\ln i$.

Regression Statistics			**Coefficients**	**Standard Err.**	**t-Stat.**	***p*-value**
Multiple R	0.95	$\ln k$	-39.5	0.99	-40.0	1.9×10^{-11}
R Square	0.91	$\ln L$	0.48	0.14	3.48	7.0×10^{-3}
F	46.3	$\ln D$	1.80	0.28	6.31	1.4×10^{-4}

We can see from the table that $R^2 = 0.9$, indicating that the data has a very good fit into the above equation. Besides, the F value far exceeds the critical value of the F-distribution ($F_{critical} = 4.25$, with 5% probability, 2 degrees freedom of regression and 9 degrees freedom of residual), which indicates that the multiple regression is valid considering the strong correlation between $\ln L$ and $\ln D$ with $\ln i$.

In Table S1, we can find out that $m = 0.48 \pm 0.14$, and $n = 1.80 \pm 0.28$. t-statistics can help us determine whether the coefficients are credible. Besides, the t-stat value for each coefficient all fall within the range $(-\infty, -2.23) \cup (2.23, +\infty)$ to be considered credible, according to a two-tail T-distribution with 95% confidence. Also, both p-value for m and n is way less than 0.05, indicating the confidence in the values.

To conclude, the empirical model ($i = kL^mD^n$) is suitable for our data, and the constant coefficients figured from the regression analysis is highly credible.

Band gap of ZnO nanowire by Tauc Plot

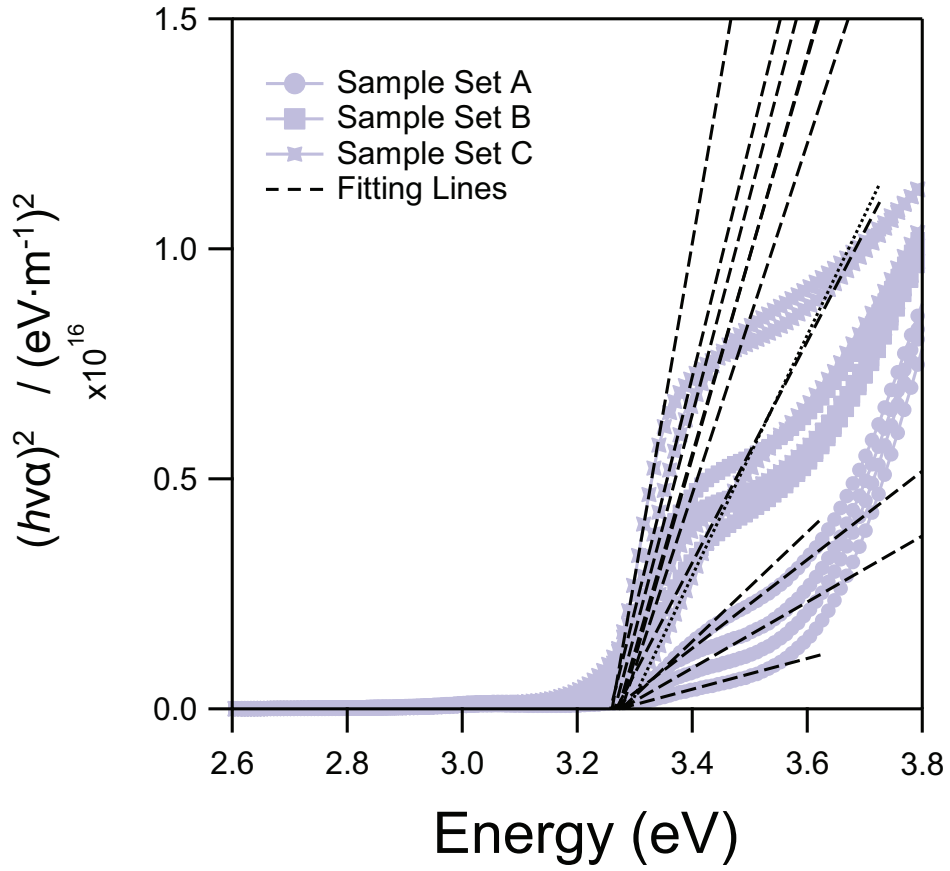

Figure S4: Direct band gaps determined from Tauc Plots of all the samples. Despite differences in morphologies, all 12 samples have the same band gap at 3.70 ± 0.01 eV.

Tauc plot is a method that is widely used for band gap determination, which follows the relation:

$$(h\nu\alpha)^{1/n} = A\left(h\nu - E_g\right) \tag{S5}$$

where h is the Planck's constant, ν the frequency, α the absorption coefficient,A the proportional constant, and E_g the band gap. For direct allowed transition, the exponent n equals $1/2$. By analyzing the optical absorption spectrum of our samples we find despite their different geometries, their direct band gaps are at 3.27 ± 0.01 eV.

Repeatability and Stability of ZnO nanoarrays' PEC performance

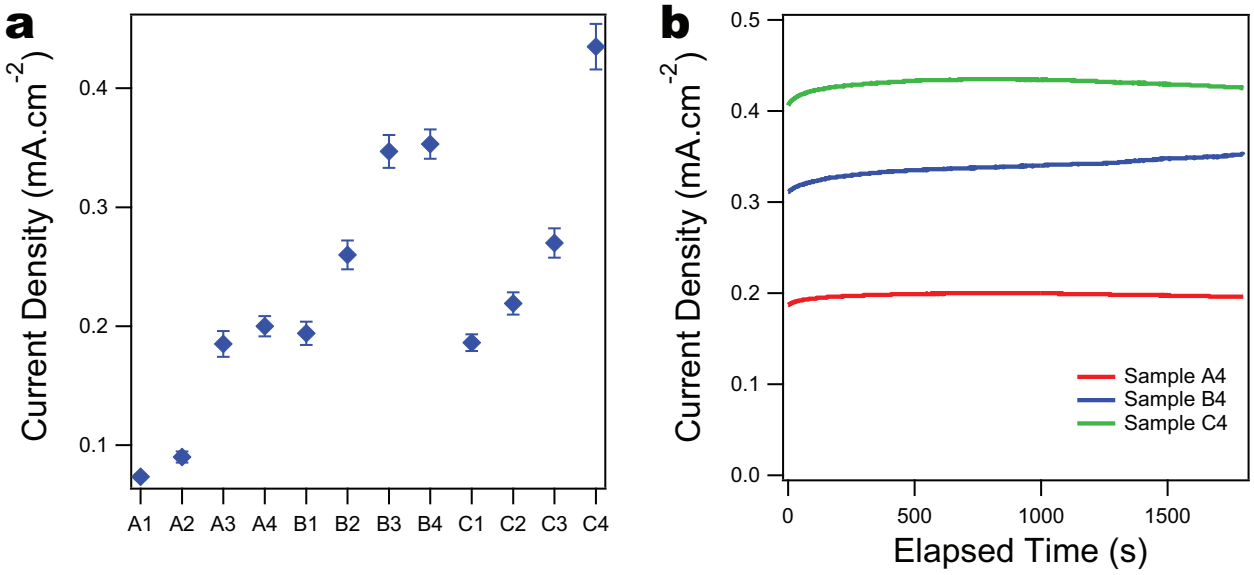

Figure S5: (a) The repeatability of all 12 samples mentioned in the manuscript. Each marker represent the photocurrent at 1.23 V_{RHE} under AM 1.5 illumination. Error bars indicate the deviations for different samples. (b) The stability for Sample A4, B4 and C4 for 1800s. The photocurrents are measured at 1.23 V_{RHE} under AM 1.5 illumination.

ZnO nanoarrays fabricated by syringe pump assisted hydrothermal growth method have great repeatability in PEC performance. In the meantime, the photocurrent is stable over a long period of time to make our conclusion of relationship between geometry and photocurernts valid.