Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information

Continuous Growth and Improved PL Property of ZnO Nanoarrays with Assistance of Polyethylenimine

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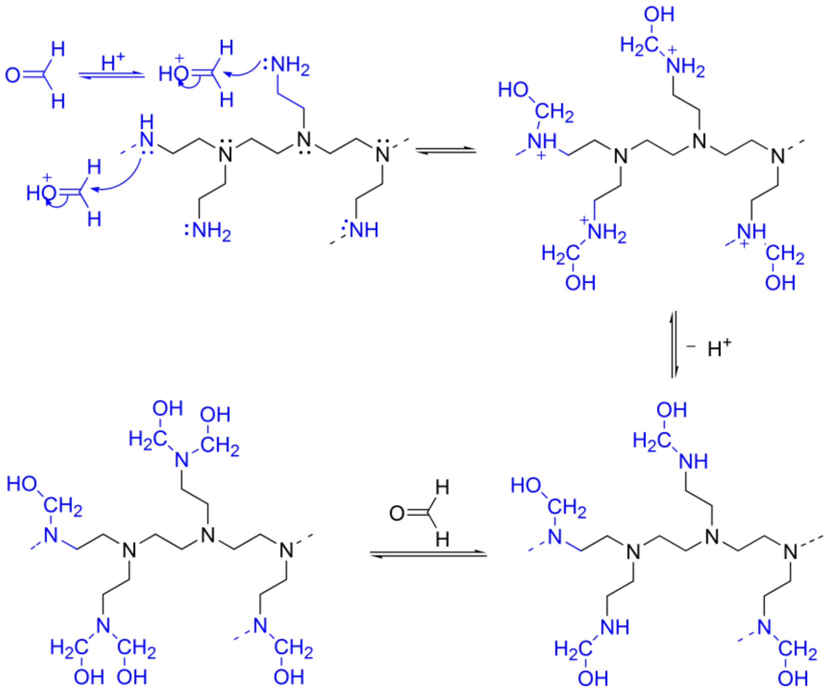
Contents

There are four possible reactions between PEI and HCHO, as listed in the followings:

(1) Hydroxymethylation of amine groups.

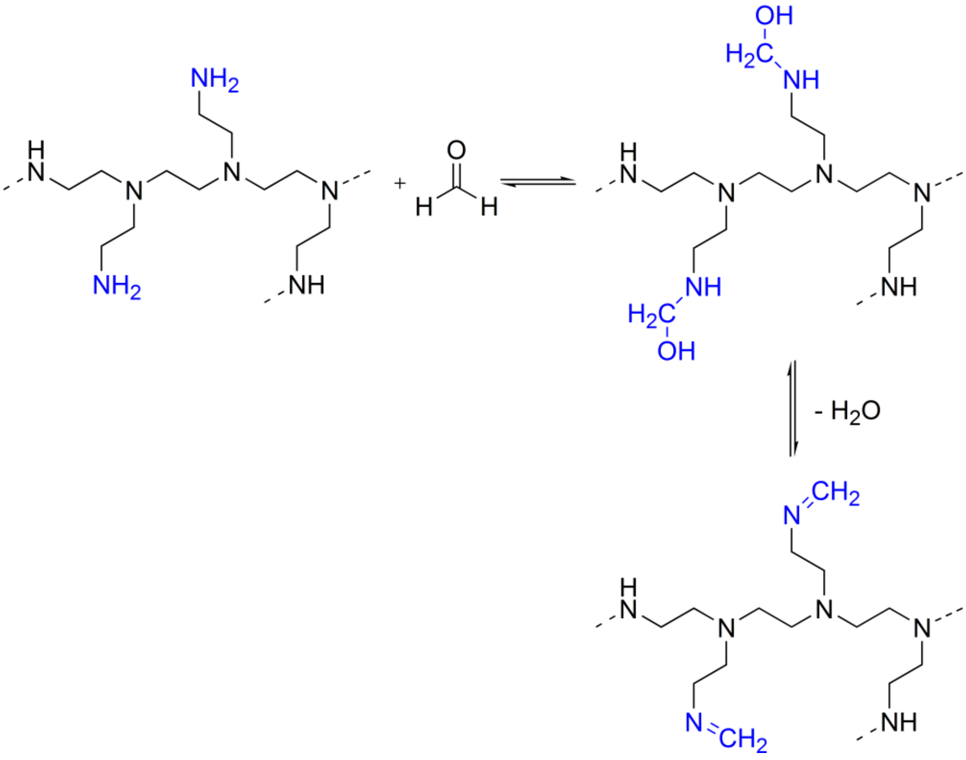
Scheme 1 shows the hydroxymethylation of amine groups. This occurs easily in solution containing amines and aldehyde at low temperature. The active H ions of amines (-NH_2) in the PEI molecule attack carbonyl (C=O) groups of formaldehyde, forming the secondary amine (-NH-) and form hydroxymethyl (-CH_2-OH), respectively. Both the newly formed and the existing –NH- groups of PEI will further react with HCHO, turning into the tertiary amine (). If formaldehyde in the solution is enough, all amines, including -NH_2 and –NH- groups, will turn into the tertiary amine. Following these reactions, the pH of the solution will slightly decrease because the tertiary amine shows lower alkalinity in the solution compared with the –NH_2 and –NH- groups. Also, the chelating ability of PEI will be decreased. Therefore, the Zn^{2+} chelated with PEI might be released and providing the growth units. However, it is noted that the hydroxymethylation of amine groups by HCHO usually proceeds at the relatively low temperature, and at such a temperature the HMT is hard to decompose to produce HCHO, especially at the higher pH. Rising temperature is necessary to accelerate the decomposition of HMT, but turn the hydroxymethylation reaction to the Mannich reaction.



Scheme S1. The hydroxymethylation of amine groups

(2) Mannich reaction to produce the Schiff base

The Mannich reaction occurs as reported in the paper.

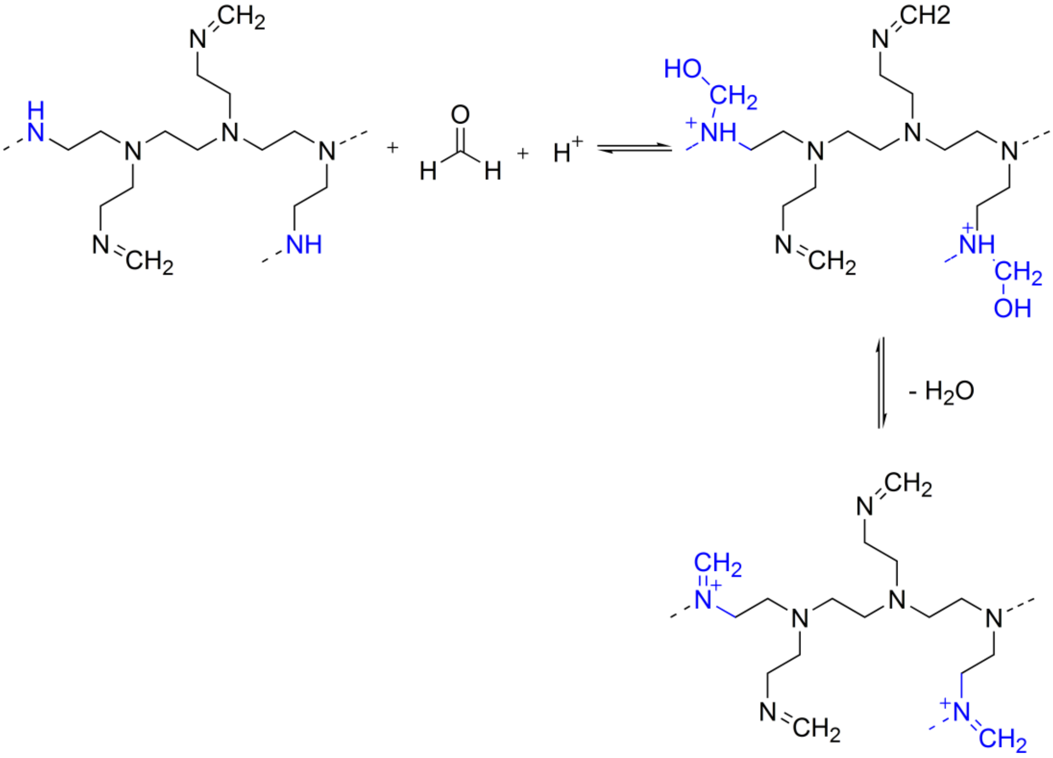


Scheme S2. Mannich reaction between –NH_2 and HCHO.

(3) Reaction producing the quaternary ammonium salt

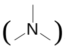
The Schiff base formed above might further react with HCHO to produce quaternary ammonium salts. However, all these hydroxymethyl (-CH_2-OH) connected with the N atom could not stabilize at high temperature above 90 °C. As shown in Scheme 2 and 3, the hydroxymethyl on methylamine groups (-NH-CH_2-OH) would dehydrate to form the imine (N=CH_2) groups (Scheme

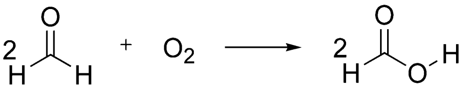
2). And the hydroxymethyl on secondary amine groups (-$^{+}$NH-CH$_2$-OH) would become the quaternary ammonium salt (-$^{+}$N=CH$_2$) groups (Scheme 3). These two groups are chromophores which result in the color changing of the solution. For these two reactions, the later one generally proceeds in a weak acid condition and consume H^{+}, which may increase the pH of the solution. As described in our manuscript, the pH of the solution dropped slightly during the hydrothermal process. Therefore, we are sure that color changing mainly comes from the reaction between HCHO and –NH$_2$ but not between HCHO and -NH-. Although the later reaction does not cause the color change, the chelating ability of PEI will be decreased, which also supports our growth mechanisms.

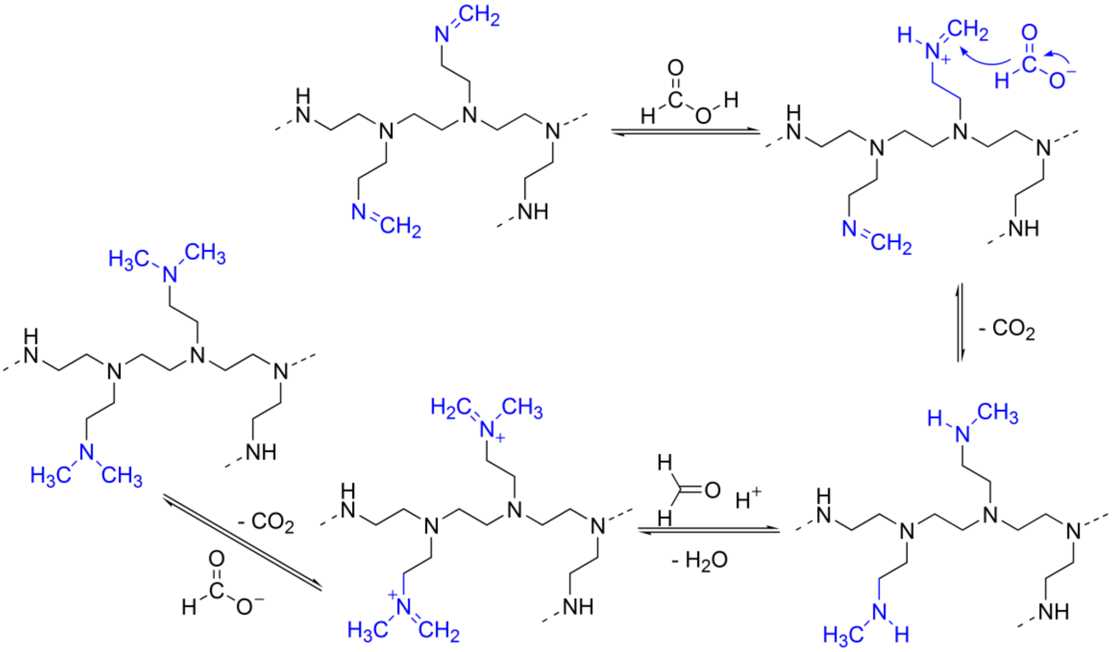


Scheme S3. Mannich reaction between -NH- and HCHO.

(4) Methylation of amine groups

It is known that the formaldehyde could be oxidized into formic acid, as shown in Scheme 4. Then the formed formic acid will react with –N=CH$_2$ groups produced above, forming the methyl (-CH$_3$) on the N atom, which is called the Eschweiler-Clarke reaction. When the formaldehyde and formic acid were enough in the solution, all of the methylamine (-NH$_2$) and secondary amine (-NH-) groups would be converted to tertiary amine (). According to Scheme 4, the reaction needs O$_2$ in the solution. But in our experiment, the oxidized of formaldehyde is suppressed because of the sealed container. So this reaction does not play the dominant role during the hydrothermal growth of ZnO nanorods.





Scheme S4. Eschweiler-Clarke reaction of imine（C=N）groups

In the above discussion, we list four possible reactions between PEI and HCHO. Among these, HCHO comes from the decomposition of HMT, and the decomposition rate relates to the temperature and the solution pH. The first reaction (hydroxymethylation of amine groups) usually occurs at the low temperature, which prevents the HMT decomposition at the high pH. A high temperature for promoting HMT decomposition transforms the 1st reaction to the 2nd reaction (Mannich reaction). The 3rd reaction can only occur at the acid solution, and the 4th reaction needs O_2. Both reactions are not possible in our present growth solution. In conclusion, the 2nd reaction producing Schiff base is the most possible in the growth solution. The Schiff base is responsible for the color change of the solution, which also weakens the chelating ability of PEI. The low chelating ability can release Zn^{2+} to support the hydrothermal growth of ZnO nanorods.

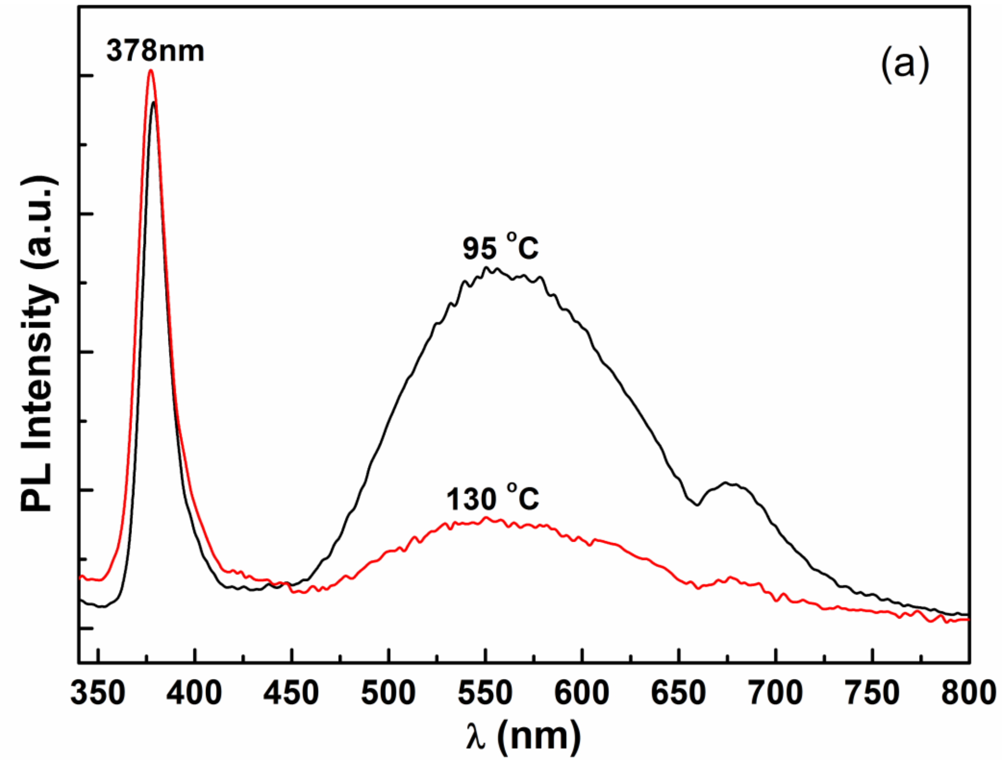


Figure S1. PL spectra of the as-grown ZnO nanorod arrys at 95 °C and 130 °C, respectively.

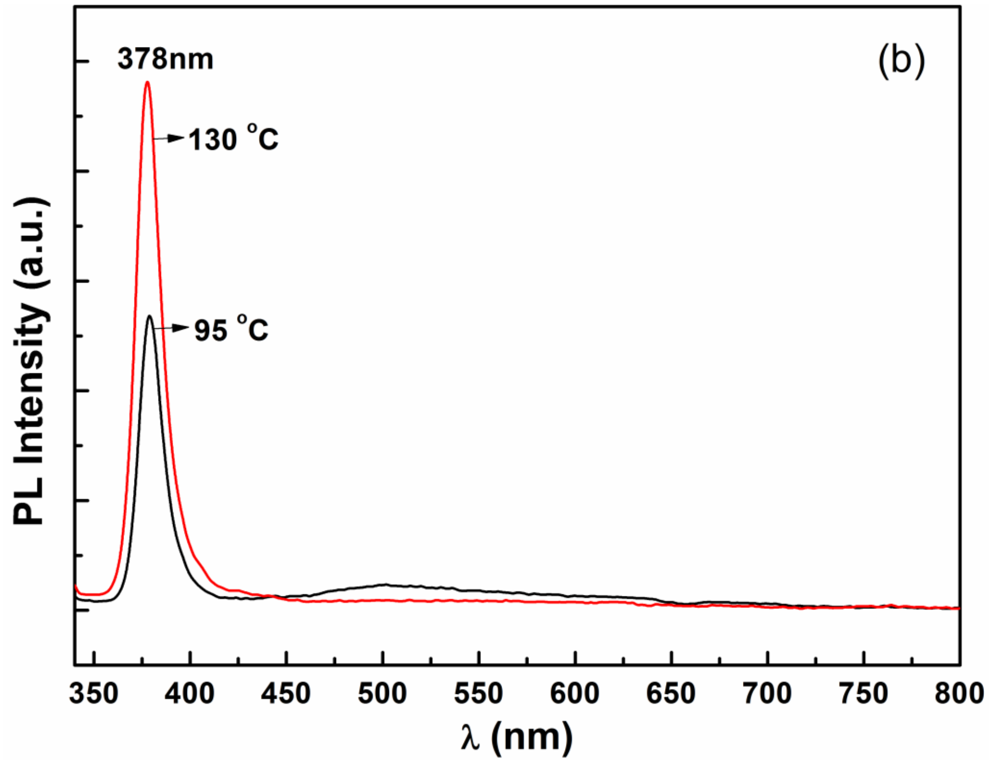


Figure S2. PL spectra of the ZnO nanorod arrys grown at 95 °C and 130 °C, respectively, and annealed in Ar atmosphere at 350 °C for 30 min.

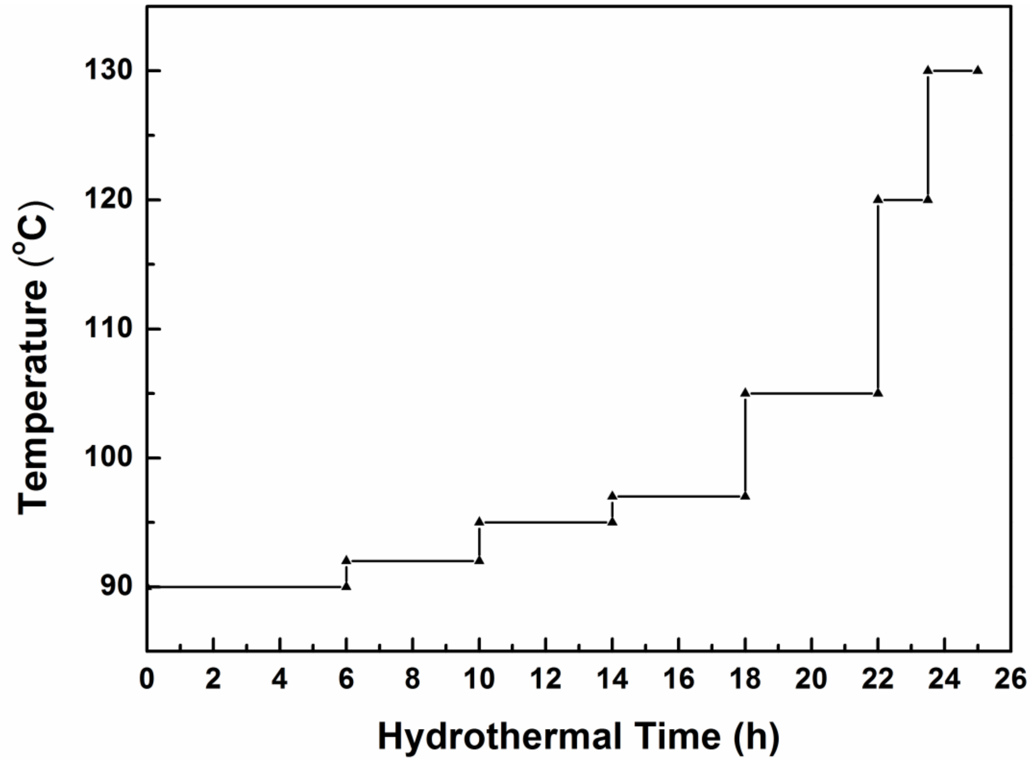


Figure S3. The stepping rising temperature progress from 90 °C to 130 °C.

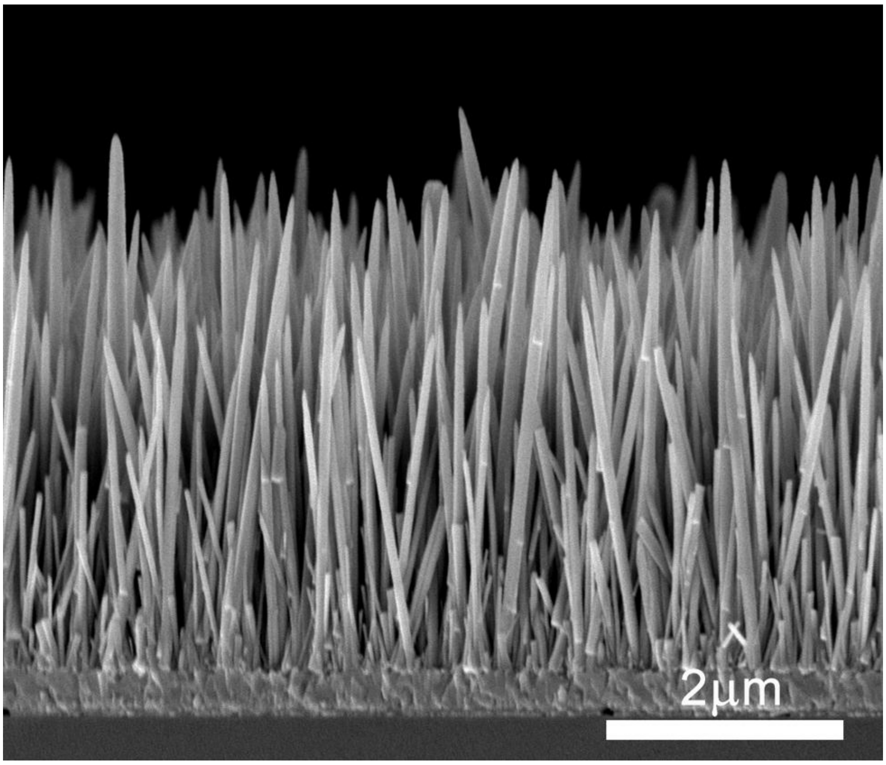


Figure S4. FESEM image of ZnO nonowires grown from the solution of 0.05 M $Zn(NO_3)_2 \cdot 6H_2O$, 0.06M HMT and 0.003 M PEI at 130 ºC.