Investigation of reaction conditions on morphology and optical properties of Zinc Oxide Nanorods

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Abstract. Zinc oxide nanoparticles (ZnO NPs) were synthesized by precipitation method in the presence of various polymers. Rod shaped ZnO NPs (length ~ 1 micron) were obtained at 70 °C in a reaction medium containing 10-20 mM of zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O), 0.05-0.1 mg/ml of polyethylenimine (PEI) and 20 mM of hexamethylenetetramine (HMT). Properties of ZnO NPs were characterized by fluorescence, UV-visible spectroscopy, atomic force and transmission electron microscopy.

1. Introduction
Due to the fact that the properties of nanoparticles (NPs) are strongly dependent on their size and shape the synthesis of rodlike metal and semiconductor NPs is of interest [1-3]. Spherical metal NPs are characterized by only one plasmon resonance, whereas by extending a particle in one dimension a second lower energy resonance band in the longitudinal direction takes place. In general, the number of surface plasmon resonance peaks increases for particles having aspect ratios (length/diameter, L/D) larger than 1 [4, 5]. The crystal grows faster in only one direction or anisotropic growth is required for the formation of nanorods and nanowires. So, in the synthesis of metal and semiconducting NPs, control over the shape and size is one of the important and challenging tasks. Nanocomposite films containing rod-like NPs with unique optical properties are suitable for use in optoelectronic devices [6-9].

In connection with these findings, the synthesis of rod-like NPs of ZnO, which is a wide band gap semiconductor with large excitation energy and an important functional material with near electric conductivity, optical transparency and piezoelectricity have attracted considerable attention. ZnO is a promising material for electronic and optoelectronic applications such as solar cells, liquid crystal displays, gas sensors, surface acoustic wave devices etc. The emission properties of ZnO NPs in the visible region depend on their synthetic method. Now various techniques have been developed for the preparation of ZnO nanorods such as ZnO vapor phase deposition methods, metalorganic chemical vapor deposition, hydrothermal method and so on [10-14]. But these methods require severe reaction conditions, such as high temperature or accurate gas concentration, flow rate or scarce raw materials or complex process, and so on. Therefore, the synthesis of ZnO NPs by deposition method (precipitation) from an aqueous solution is simpler and more accessible.
2. Experimental procedure
All the chemical materials used in these experiments were purchased from Sigma-Aldrich and used without any further purification. To obtain ZnO NPs, an aqueous solution of Zn(NO$_3$)$_2$.6H$_2$O and a polymer were mixed and the resulting solution was cooled for 5 minutes in an ice bath. A solution of hexamethylenetetramine (HMT, C$_6$H$_{12}$N$_4$, 20 mM) was added dropwise to the cooled aqueous solution of 0.1 mg/mL polymer and 20 mM Zn(NO$_3$)$_2$.6H$_2$O with vigorous stirring by a magnetic stirrer. Then, the resulting ZnO gel was placed in a water bath heated to 70 °C and maintained under these conditions with stirring for 4 hours. The obtained ZnO particles were stored at room temperature in the light.

Samples containing rod or spherical ZnO particles were separated by centrifugation. The resulting ZnO precipitates were resuspended in ethanol and then were washed 3 times with the same solvent while being centrifuged for 10 min at 5000 rev/min. Samples were dried at room temperature to remove excess ethanol.

Size and shape of ZnO particles were evaluated using optical microscope Planar MB (Belarus), atomic force microscope Nanoscope-3D («Veeca», USA) and transmission electron microscope JEM-100CX II (JEOL, Japan). The absorption and fluorescence spectra of ZnO NPs were recorded by spectrofluorimeter CM 2203 («SOLAR», Belarus).

3. Results and discussion
The ZnO nanorods were synthesized by reaction of Zn(NO$_3$)$_2$ and HMT in the presence of a polymer as a structure-modifying agent. The formation of ZnO nanorods in the condition of HMT is depicted by reactions 1–4.

\[
\begin{align*}
\text{Zn(NO}_3\text{)_2} & \rightarrow \text{Zn}^{2+} + 2(\text{NO}_3^-) \quad (1) \\
\text{C}_6\text{H}_4\text{N}_4 + 6\text{H}_2\text{O} & \rightarrow 6\text{HCHO} + 4\text{NH}_3 \\
\text{NH}_3 + \text{H}_2\text{O} & \rightarrow \text{NH}_4^+ + \text{OH} \\
\text{Zn}^{2+} + 2\text{OH}^- & \rightarrow \text{ZnO}\downarrow + \text{H}_2\text{O} \quad (4)
\end{align*}
\]

The effects of various polymers on the synthesis of ZnO were investigated. The most effective additive for the synthesis of rod-like ZnO particles is PEI and the least is PVP-40 (Table 1 and Figure).

Table 1. Characteristics of absorption and fluorescence spectra (1 cm quartz cuvette) of ZnO suspension, obtained in the presence of different polymers

| polymers | $\lambda_{\text{max}}$, nm | $D_{\text{max}}$ | $\lambda_{\text{exc}}$, nm | $\lambda_{\text{fl}}$, nm | $I_{\text{max}}$, rel.unit |
|---------|----------------|-------------|----------------|----------------|----------------|
| Polyethyleneimine (PEI), ~60 kDa | 301 | 1.51 | 353 | 630 | 0.40 |
| Poly(diallyldimethylammonium chloride), 100-200 kDa | 367 | 1.30 | 352 | 614 | 1.45 |
| Poly(allylamine hydrochloride), ~17 kDa | 302 | 0.78 | 352 | 616 | 0.41 |
| Poly(allylamine hydrochloride), ~70 kDa | 359 | 1.22 | 354 | 616 | 0.41 |
| Polyvinylpyrrolidone (PVP-40), 40 kDa | 359 | 1.22 | 354 | 616 | 0.41 |
| Polyvinylpyrrolidone, 24 kDa | 360 | 1.33 | 350 | 629 | 0.45 |
| Polyvinylpyrrolidone, 70 kDa | 360 | 1.33 | 350 | 629 | 0.45 |
| Polyvinylpyrrolidone, 100 kDa | 360 | 1.33 | 350 | 629 | 0.45 |

Note: the reaction medium containing 0.1 mg/mL polymer, 20 mM Zn(NO$_3$)$_2$.6H$_2$O and 20 mM HMT.

$\lambda_{\text{exc}}$ and $\lambda_{\text{fl}}$: Maximum excitation and fluorescence, respectively.
In the reaction medium, containing 10 and 20 mM Zn(NO$_3$)$_2$, when the magnification is 400 times rod-like ZnO particles can be revealed by using optical microscope (Planar MB). However, their number decreases at concentrations Zn(NO$_3$)$_2$ 30 and 50 mM, but the length of the particles increases. In the presence of 70 and 100 mM Zn(NO$_3$)$_2$ mainly spherical particles are formed. Fluorescent properties of the particles depend on the concentration of Zn(NO$_3$)$_2$ (Table 2). With increasing concentration from 10 to 30 mM, the fluorescence intensity of the particles decreases. However, at higher concentrations of Zn(NO$_3$)$_2$ fluorescence samples are practically unchanged (Table 2). Thus, the presence of more than 20 mM zinc nitrate in the medium of synthesis is inexpedient, since it does not increase the content of the rod-like particles, but only affects their dimensions. In a medium containing more than 70 mM of Zn(NO$_3$)$_2$ substantially spherical particles are formed.

Figure. Images of ZnO particles: microscope field Planar MB (magnification 400 times) (1), the AFM Nanoscope-3D (2) and TEM JEM-100CX II (3 and 4). Scan Window 3.0×2.1 (1) and 4.8×3.3 (2) microns.)
Table 2. Characteristics of absorption and fluorescence spectra ZnO suspension, obtained at different concentrations of Zn(NO$_3$)$_2$.

| Zn(NO$_3$)$_2$, mM | $\lambda_{\text{max}}$, nm | D$_{\text{max}}$ | $\lambda_{\text{exc}}$, nm | $\lambda_{\text{fl}}$, nm | I$_{\text{max}}$, rel. units |
|-------------------|--------------------------|---------------|--------------------------|--------------------------|-----------------------------|
| 10                | 282                      | 1.92          | 356                      | 641                      | 1.36                        |
|                   | 369                      | 1.25          |                          |                          |                             |
| 20                | 294                      | 2.81          | 355                      | 632                      | 0.92                        |
|                   | 368                      | 2.11          |                          |                          |                             |
| 30                | 285                      | 2.21          | 358                      | 621                      | 0.75                        |
|                   | 369                      | 1.15          |                          |                          |                             |
| 50                | 303                      | 1.96          | 357                      | 637                      | 0.70                        |
|                   | 369                      | 1.15          |                          |                          |                             |
| 70                | 315                      | 3.34          | 358                      | 634                      | 0.70                        |
|                   | 370                      | 2.06          |                          |                          |                             |
| 100               | 318                      | 3.36          | 354                      | 631                      | 0.76                        |
|                   | 369                      | 2.34          |                          |                          |                             |

Note: except Zn(NO$_3$)$_2$, the reaction medium contained 0.1 mg/ml PEI and 20 mM HMT. $\lambda_{\text{exc}}$ and $\lambda_{\text{fl}}$: Maximum excitation and fluorescence, respectively.

Table 3. Characteristics of absorption and fluorescence spectra (1 cm quartz cuvette) ZnO suspension, obtained at different concentrations of PEI.

| PEI, mg/ml | $\lambda_{\text{max}}$, nm | D$_{\text{max}}$ | $\lambda_{\text{exc}}$, nm | $\lambda_{\text{fl}}$, nm | I$_{\text{max}}$, rel. unit |
|------------|--------------------------|---------------|--------------------------|--------------------------|-----------------------------|
| 0          | 303                      | 1.22          | 355                      | 627                      | 0.77                        |
|            | 362                      | 1.03          |                          |                          |                             |
| 0.05       | 304                      | 1.91          | 359                      | 618                      | 0.42                        |
|            | 368                      | 1.72          |                          |                          |                             |
| 0.10       | 303                      | 2.38          | 355                      | 626                      | 0.36                        |
|            | 366                      | 2.13          |                          |                          |                             |
| 0.15       | 302                      | 1.22          | 361                      | 619                      | 0.40                        |
|            | 363                      | 0.94          |                          |                          |                             |
| 0.20       | 303                      | 1.98          | 357                      | 622                      | 0.34                        |
|            | 366                      | 1.73          |                          |                          |                             |
| 0.30       | 302                      | 1.67          | 359                      | 614                      | 0.58                        |
|            | 367                      | 1.41          |                          |                          |                             |

Note: except to PEI, the reaction medium contained 20 mM Zn(NO$_3$)$_2$.6H$_2$O, and 20 mM HMT. $\lambda_{\text{exc}}$ and $\lambda_{\text{fl}}$: Maximum excitation and fluorescence, respectively.

If the medium containing 0.05 and 0.10 mg/ml of PEI, the maximum amount of particles are nanorod. These particles have intense fluorescence less than those obtained without PEI. In the presence of 0.15 mg/ml PEI less ZnO rod particles are formed than in the case of 0.05 and 0.10 mg/ml of resin, but they are longer. In the case of 0.2 and 0.3 mg/ml PEI rod-like particles are formed, but their number is minimal. A sample of the particles formed in the presence of 0.3 mg/ml PEI showed a maximum fluorescence at 514 nm when it is excited by light with a wavelength of 325 nm. When $\lambda_{\text{exc}}$ = 355-367 nm, all the particles fluoresce at 614-626 nm.

4. Conclusion

Rod-like zinc oxide was synthesized at 5-6 °C in an aqueous solution containing 0.05-0.10 mg/ml of PEI (~ 60 kDa), 10-20 mM Zn(NO$_3$)$_2$.6H$_2$O and 20 mM HMT, followed by aging at 70 °C for 4-6 hours.
5. References

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