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J. Phys. Chem. C, Just Accepted Manuscript • DOI: 10.1021/acs.jpcc.5b03702 • Publication Date (Web): 12 Jun 2015

Downloaded from http://pubs.acs.org on June 16, 2015

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A Novel Method for Continuous Synthesis of ZnO Tetrapods

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Abstract

In this work we propose a novel continuous method for zinc oxide tetrapods (ZnO-Ts) synthesis based on the combustion of micron-sized Zn particles in the air atmosphere. A stable geometry of produced ZnO-T structures in a wide synthesis temperature range in gram quantities was obtained. Stable growth conditions were determined by self-sustainable combustion around the Zn particle, as it was supported by thermodynamic analysis. ZnO-Ts had a high crystallinity and an average leg diameter of 15 ± 5 nm, length of 200 ± 100 nm. A practical application of ZnO-Ts decorated by Au nanoparticles and attached with DNA strands is investigated. The applicability of the synthesized ZnO-Ts for fast and efficient scintillation was also demonstrated, as ZnO-Ts showed an increased yield of the fast component of luminescence.

Keywords: ZnO tetrapods, continuous growth method, combustion, Au nanoparticles, scintillators.
1. Introduction

Zinc oxide (ZnO) is a direct wide band gap (3.37 eV) semiconductor material with a large exciton binding energy (60 meV). It has gained significant attention because of unique optical, piezoelectric and magnetic properties, as well as capability of band gap tuning. Non-catalytically grown ZnO nanostructures can be observed in various morphologies such as nanowires, nanobelts, and tetrapods. The latter has promising applications in solar cells, lasers, field emitters, UV and gas sensors. Decorating ZnO-Ts with Au nanoparticles allows to further enhance their properties, and to utilize them in many other applications, such as selective CO catalysis and Schottky barrier solar cells.

The most common method for the fabrication of zinc oxide tetrapods (ZnO-Ts) is a vapor phase synthesis. ZnO-Ts can be produced in the lab scale by a hydrothermal process, from the mixture of ZnO and C, in a chemical vapor transport and deposition system. Moreover, ZnO-Ts can be synthesized from Zn powder and collected from reactor walls or filtered at the outlet of the reactor. Direct synthesis of ZnO-Ts from the metal vapor has obvious advantages of low temperature process and high yield. However, for the mass production the technique should allow continuous synthesis, in which products can be unceasingly obtained without interrupting the process. Additionally, to make use of the fascinating 1D properties, the diameter of ZnO-T “legs” should be controlled and kept below 20 nm to fulfill the requirements for quantum confinement. It was shown for ZnO nanowires that smaller diameter gives higher sensitivity. Qiu and Yang demonstrated that ZnO-Ts with 17 nm diameter “legs” exhibited over double sensitivity to humidity compared to those with 100 nm. Moreover, decreasing the diameter of ZnO-Ts results in the blue shift in photoluminescence.

The process control during the vapor phase synthesis is quite challenging, especially the concentration gradient and flow rate of reagents fluctuates in the reactor during the synthesis because of unevenness in the flow. To increase mixing inside the reactor flow restrictors or...
baffles\textsuperscript{21} are used. However, the process becomes more complicated, fine control of zinc precursor flow is needed, moreover small diameter ZnO-Ts are hard to obtain.

A flame synthesis\textsuperscript{22,23} gives a certain advantage of simplicity and possibility to obtain a high yield continuous synthesis. The ZnO-T growth rates are very high, however, the lack of controllability over the reaction parameters, and also an introduction of other combustible materials during the synthesis raise concerns of the product purity\textsuperscript{24}.

In this work, we introduce a novel method for the continuous high yield production of ZnO-Ts with small sizes. For this purpose we designed and constructed a vertical flow reactor to be able to observe and to control the processes inside the reactor, to distinguish main factors affecting the formation of ZnO-Ts and to synthesize the final product with the controlled geometry and at high rates. In order to enhance their optical properties and propose novel applications, we successfully decorated ZnO-Ts with Au nanoparticles using DNA strands. One of the potential applications of the ZnO tetrapod structures was demonstrated in fast and efficient scintillators.

2. Results and discussion

2.1 Non-catalytic growth of ZnO-Ts

The non-catalytic growth of tetrapod structures of ZnO\textsuperscript{5} as well as other II-IV semiconductors\textsuperscript{25}, follows first the formation of zinc blende nuclei, from which consequently wurtzite legs start to grow\textsuperscript{26,27}. The growth mechanism in the vapor phase is shown schematically in Figure 1. In the first stage Zn particle heats up and melts since the surrounding temperature is higher than the Zn melting point (420 °C). Zn starts to evaporate and reacts with surrounding O\textsubscript{2} forming supersaturated ZnO vapor. ZnO nucleus is formed as a result of homogeneous vapor nucleation. Since the Zn and O\textsubscript{2} is further supplied the growth of the crystal is followed. This stage is critical as the rate of Zn and O\textsubscript{2} supply to the surface of the growing crystal controls the geometry. Highly anisotropic shape formation requires a kinetic growth regime, when the rate of the supply of molecules to the surface is greater than their diffusion on the surface\textsuperscript{25,28}. Consequently to
obtain ZnO-Ts, it is important to keep high Zn vapor pressure and by mixing with O\textsubscript{2} to get the preferential growth at most reactive sites. Low Zn vapor pressure and the mixing rate will result in thermodynamically controlled process. In this case ZnO molecules, arriving at the surface of growing crystal have much time to diffuse to thermodynamically favorable positions, therefore spherical nanocrystals are formed.

From SEM and TEM images (Figure 2) we observe the structure of the product. From TEM observation we found that ZnO-Ts consisted of 4 “legs” with an average diameter of 15 ± 5 nm and the length of 200 ± 100 nm. The process of ZnO-T growth was mostly controlled by oxidation reactions in the vicinity of the surface of the Zn particles, while the temperature of the reactor walls mostly affected only heating of the Zn powder in the air to overcome the energy barrier for the self-sustaining combustion. The critical temperature for ZnO-T synthesis in our reactor was 720 °C. At lower temperatures rapid and self-sustaining combustion of Zn particles did not start, which could be caused by low Zn vapor pressure in the vicinity of the particle surface and low O\textsubscript{2} splitting rate.

X-ray diffraction measurements (Figure 3 (A)) showed that ZnO-Ts had only wurtzite structure with lattice constants of $a = b = 0.324$ nm and $c = 0.519$ nm. To show the structural advantage of ZnO-Ts over other ZnO nanostructure, we prepared powder of ZnO nanoparticles for comparison. ZnO nanoparticles were prepared by oxidation of zinc nitrate salt Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O as it was shown in our earlier work\textsuperscript{29}. ZnO nanoparticles and ZnO-Ts have the same structure, just in case of ZnO nanoparticles peaks are wider, as they consist of thin layers and contain many defects. The diameter of tetrapod nucleus (zinc-blende phase) is about a fourth of the leg diameter\textsuperscript{26}. therefore the wurtzite mass is at least $10^6$ times larger than the mass of the zinc-blende. Consequently, the latter could not be detected, as it is about four orders of magnitude lower than the XRD detection limit.

UV-vis-NIR absorption measurements of ZnO-Ts (Figure 3 (B)) synthesized at various reactor temperatures (from 720 to 900 °C) showed emission peaks centered at around 375 nm and only with a slight change in the inclination of the spectra, as ZnO-Ts prepared at higher
temperatures tend to have lower absorption at higher wavelengths. From our previous work\(^4\) it is known that the change of the inclination of the spectra originates from slight differences in ZnO-Ts “leg” geometry. This confirms that the conditions for the growth of the ZnO-Ts are regulated mostly by the process of the particle combustion and not by reactor temperature as it is seen for the vapor phase reactors\(^4\), where a temperature change by 50 °C had a tremendous effect on the structure of the product. For this reason the temperature inconsistency due to recirculation, has much lower effect on the geometry of the ZnO-Ts in our reactor. Therefore, it was found that the temperature has a small effect on the size of ZnO-Ts in the range of 720 – 900 °C. The highest yield of ZnO-Ts was obtained in the range from 750 to 850 °C (Figure 3 (C)).

2.2 Stability of ZnO-T growth conditions

The ZnO-T growth shows stability at the reactor temperature range from 720 to 900 °C, which in fact are between the melting point ($T_m = 420 \, ^\circ\text{C}$) and boiling point ($T_b = 907 \, ^\circ\text{C}$) of Zn, wherefore after the heating stage Zn particle can be described as a liquid droplet. The temperature at the surface of Zn particle is higher than in the reactor because of the combustion process around the particle. This was confirmed from the brightness of the halo around the particle made by a high speed camera (Figure 1(C) and supporting Movie S1). Zn particle combustion follows certain steps:

1) heating of Zn particle to the reactor temperature;
2) melting of Zn particles;
3) evaporation of Zn;
4) exothermal reaction between Zn vapor and oxygen in the vicinity of Zn particles;
5) Zn particle temperature increase up to the boiling point;
6) a steady state combustion of the boiling Zn particle;
7) growth ZnO-Ts.
It is worth noting that some stages occur simultaneously and not necessarily in the order given above. Further growth of ZnO-Ts from Zn oxidation products was described in section 2.1.

The combustion zone is formed in the close proximity to the surface of the spherical drop, as it is shown schematically in Figure 1 (B). The heat transfer from the combustion zone will be mainly determined by thermal conductivity and radiation. Droplet evaporation is driven by a heat flux, $q$, from the combustion zone to the particle. Zn vapor diffuses from the surface of the droplet to the combustion zone and reacts with oxygen diffused from the surrounding ambient. Here, these components react chemically, which is accompanied by formation of supersaturated ZnO vapor and heat release. From the combustion zone, heat flux, $Q$, is transferred to the ambient air.

At the equilibrium conditions in the combustion zone, heat release rate from the oxidation process equals to the rate of the heat transfer to the surroundings (to the particle and outside of the particle):

$$\rho \lambda_f (\text{-d}v/\text{d}t) = 4\pi R^2 Q + 4\pi r^2 q, \quad Q = \sigma T^4 + \chi' (T - T_0)/l_0, \quad q = \sigma T^4 + \chi (T - T_b)/l_b,$$

(1)

where $\rho$ is the density of Zn droplet; $\lambda_f$ is a specific heat of ZnO formation from solid Zn; $v = 4\pi r^3/3$ is a volume of the droplet with radius, $r$, at time $t$; $R$ is an external radius of the combustion zone; $\sigma$ is the Stefan-Boltzmann’s constant; $T$ is the combustion zone temperature; $T_0$ is the temperature of surrounding gas; $l_0$ is the length of the transition layer between zones with temperatures of $T_0$ and $T$; $T_b$ is the boiling point of Zn; $l_b$ is the length of the transition layer between zones with temperature of $T_b$ and $T$; $\chi$ and $\chi'$ are thermal conductivities of the vapor-gas mixture in the respective layers between particle and combustion and combustion and surrounding atmosphere.

Heat balance of the Zn droplet evaporation due to the heat, transferred from the combustion zone, can be expressed as:

$$\rho (\lambda_b + c(T_b - T_0)) (-\text{d}v/\text{d}t) = 4\pi r^2 q$$

or taking into account that $c(T_b - T_0) \ll \lambda_b$ at the experimental reactor temperatures we obtain

$$j = q/m_Zn \lambda_b, \quad j = (\rho/m_Zn) (-\text{d}r/\text{d}t),$$

(2)
where $\lambda_b$ is the specific heat of Zn boiling (1756 kJ kg\(^{-1}\)); $c$ is the specific heat capacity of Zn (0.388 kJ kg\(^{-1}\) K\(^{-1}\)); $m_{Zn}$ is the mass of a Zn atom; $j$ is the Zn vapor flux from the droplet.

At the steady-state combustion condition, the vapor flux, $j$, defined by Equation (2), equals the equilibrium vaporization flux, $j_{eq}$, at the boiling point:

$$j = j_{eq}. \quad (3)$$

The equilibrium vaporization flux, $j_{eq}$, from the droplet surface (to the surrounding atmosphere) can be expressed in the framework of the gas kinetics theory as\(^{30}\)

$$j_{eq} = j_s (1 - n_L/n_s)(1 + \alpha V_{Zn} L/4D), \quad (4)$$

where $j_s = an_s V_{Zn} / 4$ is the equilibrium vaporization flux from the droplet surface (to vacuum) at the boiling point; $n_s = p_s / kT_b$ is the saturated (equilibrium) vapor number concentration; $n_L$ is the vapor number concentration at the distance $L$ from the drop surface; $p_s$ is the saturated vapor pressure at $T_b$; $\alpha$ is the accommodation factor; $V_{Zn} = (8R_g T_b/\pi M_{Zn})^{1/2}$ is the mean atom velocity at the temperature of $T_b$; $D$ is the Zn diffusion coefficient in air; $M_{Zn}$ is Zn molar mass; $k$ is the Boltzmann’s constant; $R_g$ is the universal gas constant.

At $D = V_{Zn} l/3$, $\alpha = 1$, $L \approx l$, and $n_L = n_s/2$ (assuming that a Zn atom scatters on air molecule to the backwards direction with a 0.5 probability of passing the mean free path, $l$) Equation (4) can be expressed as $j = p_s / (7(\pi m_{Zn} k T_b / 2)^{1/2})$. Therefore, Equation (2) becomes

$$p_{s, b}/[7(\pi R_g T_b / 2M_{Zn})^{1/2}] = \sigma T^4 + 10R_g T_n (T - T_b) (R_g / \pi M_g (T+T_b))^{1/2} / 3v_n. \quad (5)$$

Here we assume that $p_s = p_n$ at boiling point ($p_n$ is normal pressure), $\chi / l_b = C_v V / 3v_{mod}$ at $l_b \sim l$, where $C_v = 5R_g / 2$ is the mole heat capacity at the constant volume of the gas layer between zones with temperatures of $T_b$ and $T$; $v_{mod} = v_n (T+T_b) / 2T_n$ is the mole volume of the gas layer between zones with temperatures of $T_b$ and $T$ at the average temperature $(T+T_b) / 2$; $v_n = 0.0224$ m\(^3\)/mol is the mole volume of the gas at normal conditions ($T_n = 273$ K, $p_n = 101325$ Pa), $M_g$ and $V = \ldots$
\[ 2(R_g(T+T_b)/\pi M_g)^{1/2} \] are respectively molar mass and mean velocity of the gas molecules in the layer between zones with temperatures of \( T_b \) and \( T \).

Calculation according to Equation (5) for \( M_g = 0.029 \text{ kg/mol} \) gives the temperature of the particle combustion of \( T = 2390 \text{ K} \). It is worth noting that the heat transfer by radiation will be negligible compared to the heat transfer by thermal conductivity at this temperature. According to Equation (2) we can estimate the combustion time as

\[ \tau = 7r \rho (\pi R_g T_b/2 M_{Zn})^{1/2}/p_n. \] (6)

We obtain \( \tau = 22 \text{ ms} \) for a Zn particle with the radius of \( r = 100 \mu \text{m} \) and density of \( \rho = 6660 \text{ kg/m}^3 \). The combustion time is in a good agreement with experimental values observed by the high speed camera in our reactor (Figure 1 (C) and supporting Movie S1).

The system of Equations (1), (2) and (3) contains three unknown values: \( R, T \) and \( dr/dt \) (or \( \tau \)). As can be seen only Equation (1) depends on the reactor temperature, \( T_0 \), as \( Q \sim (T- T_0) \), and this dependence at the combustion temperature is weak. By other words, we obtain conditions for self-sustainable steady-state combustion, where the combustion parameters weakly depend on the reactor temperature.

Hence on the basis of our model we can conclude that over the critical temperature, needed to initiate the combustion, the reactor temperature (in the range 720-900 \( ^\circ \text{C} \)) does not have significant effect on the combustion and consequently on ZnO-T growth conditions, which is evident from the experimental results, showing ZnO-T growth stability in a wide range of the reactor temperatures.

### 2.3 ZnO-T decoration with Au nanoparticles using DNA

ZnO-T powder is porous and therefore is attractive for applications with a need of high surface ratio. ZnO nanostructures are decorated with Au nanoparticles (Au NPs) in solar cells for
the light absorption enhancement\textsuperscript{31}, for photodetection improvement\textsuperscript{32}, for tailoring the photoluminescence properties\textsuperscript{33}, or for photoelectrochemical water splitting\textsuperscript{34}. For high efficiency and stability it is of great importance that Au NPs are immobilized on the surface and do not form agglomerates.

Oligonucleotides are of great interest because of the potential use of the programmability of DNA to organize nanocrystals in space. In this work we used DNA stranded Au NPs to immobilize the NPs on the ZnO-Ts’ surface and to enhance light absorption. Au NP attachment to ZnO-T surface was examined by pressurized washing of the structures and observed by means of SEM. The changes in the light absorption of the obtained structures were tested by UV-vis-NIR spectroscopy.

Au NPs with DNA make a stronger bonding with ZnO-T, therefore stay attached after pressurized washing as it is shown in Figure 4 (C) and (D) compared to the Au NPs without DNA. Au NPs without DNA tend to form aggregates, whereas Au NPs with DNA uniformly cover the whole surface of ZnO-Ts. This is achieved as DNA is covalently bonded to Au NPs and at the same time DNA forms an electrostatic interaction with ZnO-Ts surface\textsuperscript{35}. Moreover, a DNA molecule attached to a Au NP stabilizes it and does not allow to aggregate.

Figure 4 (A) shows the UV-vis absorption spectra of ZnO-T and Au NPs with DNA. It is known that for Au NPs with sizes ranging from 5 to 20 nm in diameter, the electrons are trapped and therefore show a characteristic collective oscillation frequency of the plasmon resonance, giving rise to the plasmon resonance band at around 520 nm for pure Au\textsuperscript{36}. The exact absorption position varies with particle morphology and particle surface coating. In our case the Au particles are covered with DNA and therefore show plasmon absorption at 538 nm (Figure 4 (A)), a 18 nm red-shift from that of the pure Au particles.

The characteristic gold plasmon peak of the ZnO-Ts with Au NPs is apparently red-shifted and broadened; this results from the size, structure and the interaction between Au and the metal oxide, and it is also apparent for Fe$_3$O$_4$\textsuperscript{37}. Previous studies show that excess electrons on the Au
particles can cause the plasmon absorption shift to shorter wavelength; whereas electron deficiency will shift the absorption to longer wavelength\textsuperscript{36}. The red shift of the surface plasmon spectra indicates that the interface communication between Au and ZnO-Ts results in deficient electron population on Au\textsuperscript{38}.

2.4 ZnO-T for scintillation elements

Radiation detection, medical imaging and high energy physics fields have demonstrated an interest in ZnO for a scintillator application due to its sub-nanosecond decay times and potentially high light output, when employed as a high energy radiation detector\textsuperscript{39,40}.

The comparison of X-ray excited luminescence is shown in Figure 5 (A). Two emission bands are observed: shortwave (near the absorption edge) and the long-wavelength (green) band. Shortwave band resulting from the donor-bound excitons has a maximum peak at 383 - 389 nm and a constant scintillation decay of 0.7 ns\textsuperscript{41}. Luminescence mechanism of green emission band of ZnO, despite the huge number of studies is still a matter of debate. Basically, zinc vacancy\textsuperscript{42} and oxygen vacancies\textsuperscript{43} are considered to be responsible for the green luminescence.

In the spectrum of the ZnO layered nanoparticles a green luminescence component with a maximum at 525-560 nm is observed, but the exciton peak is absent, whereas ZnO-T spectrum has two peaks: a higher intensity exciton peak with a maximum at 389 nm and green component peak at around 540 nm. The suppression of green luminescence earlier was done by ZnO doping\textsuperscript{40}, nonetheless, our work shows that it can be also achieved by controlling the structure of ZnO.

3. Conclusion

In summary, we have designed and constructed a vertical flow reactor for the synthesis of zinc oxide tetrapods, on the basis of combustion of Zn powder suspended in the air. This method was applied for the continuous mass production of ZnO-Ts. SEM and TEM observations of the product showed that high crystallinity ZnO-T structure consisted of 4 “legs” with an average
diameter of $15 \pm 5$ nm and the length of $200 \pm 100$ nm. Our method allowed us to produce gram quantities of pure ZnO-Ts, at the highest yield at 750-850 °C. In this temperature range the size of ZnO-Ts was not affected by the reactor temperature, which was explained by self-sustainable combustion.

In order to enhance optical properties, ZnO-Ts were decorated with Au NPs, strong attachment using DNA strands was achieved. Structures of ZnO-Ts with Au NPs, attached through DNA, show plasmon absorption at 538 nm. Fast and efficient scintillation without doping was also shown. The suppression of green luminescence was achieved by controlling the structure of ZnO-Ts.

4. Experimental section

4.1 Material preparation

ZnO-Ts were synthesized by a vapor phase oxidation of Zn powder in an air atmosphere. No catalysts were used at any stage of synthesis or Zn powder preparation. To produce ZnO-T structure of nanometer size, a few experimental parameters have to be carefully controlled: Zn vapor at relatively high concentration must be quickly mixed with O$_2$, whereas the growth time should be kept minimal to avoid the thickening of the ZnO-T legs. To fulfill these parameter requirements we designed and built the reactor based on the combustion of Zn micron-sized particles in an open reactor in the air atmosphere. These allowed us to rapidly evaporate Zn, to oxidize Zn vapor by surrounding air oxygen and to form small diameter ZnO-Ts by supersaturated ZnO vapor condensation.

The synthesis reactor consisted of a vertical quartz tube with a 30 mm diameter inserted into a furnace with a length of 600 mm, a powder feeder and the product collection system. A vertical orientation of the reactor is needed for free fall of the Zn powder, and also to minimize recirculation associated with the buoyancy forces. Zn powder ($\geq$99.999 % purity, particle size $<10$ µm) was fed from the top of the reactor. Zn powder was continuously introduced into the heated reactor using a
homemade vibrational powder feeder with a feeding rate optimized at 0.42 g/min. The air entrained powder stream was introduced into the reactor to provide conditions for its rapid heating and oxidation. This method provides the conditions for high Zn vapor pressure and high mixing rate with O2. An air was sucked at the top of reactor from surrounding atmosphere, the vacuum was adjusted to the flow rate of 2.0 L min⁻¹. Cyclone was used to separate heavy particles and agglomerates. Produced tetrapods were collected downstream of the reactor on a nitrocellulose filter.

DNA attachment to Au nanoparticles was done by reducing the disulfide bond in the thiol modified oligonucleotides to monothiol using tris(2-carboxyethyl)phosphine (TCEP 20 mM, 1 h) in water. The oligonucleotides were purified using size exclusion columns (G-25, GE Healthcare) to get rid of the small molecules. Monothiol modified oligonucleotides and phosphinated AuNPs were then incubated with DNA to Au molar ratio more than 200:1 in 0.5 TBE buffer (89 mM Tris, 89 mM boric acid, 2 mM EDTA (Ethylenediaminetetraacetic acid), pH 8.0) containing 50 mM NaCl for 40 hours at room temperature to make sure the AuNPs were fully covered by thiolated DNA. AuNP-DNA conjugates were washed with 0.5 × TBE buffer in (Millipore, Billerica, MA) to get rid of the extra oligonucleotides. The concentration of these AuNP-DNA conjugates was estimated from the optical absorbance at 520 nm.

ZnO-Ts were collected on a cellulose filter, transferred to water solution and mixed with AuNPs without sonication, afterwards deposited on a Ag filter. The filter was located in a closed holder and washed with water and afterwards with a 2 µl suspension of AuNP-DNA. In order to examine the AuNP attachment to the ZnO-T surface pressurized washing was done. 1 min after AuNP deposition filter was washed under the pressure with 30 ml of water, dried under nitrogen and observed in SEM.

4.2 Characterization
The obtained structures were investigated by scanning and transmission electron microscopes (SEM JEOL JSM 7500F and TEM JEOL 2200FS with double aberration correctors). For the SEM investigations, the samples were attached to carbon tape and observed at the energy of 1–5 keV. For the TEM studies, the ZnO-Ts were transferred to a copper TEM grid by gently touching the filter with ZnO-Ts. An energy of the electron beam used for the TEM observation was 200 keV.

Absorbance was measured by UV-vis-NIR dual-beam spectrophotometer (Lambda 950, Perkin-Elmer). The process of the particle combustion in the furnace was photographed with a high speed camera Casio Exilim EX-FH25. The crystalline structure of the product was examined by an X-Ray Diffraction technique (Bruker D8 Advance). The X-ray excited luminescence (XRL) spectra were measured under steady state X-ray excitation (40 kV, 10 mA) with a FEU-106 PMT and a MDR-2 grating monochromator with 1200 grooves/mm. The spectra were corrected for the quantum efficiency of the photomultiplier and for the monochromator transmission.

Acknowledgements

The authors thank Dr. Ilya Anoshkin for his help with high speed camera photographing. This work was supported by Ministry of Education and Sciences of the Russian Federation (Project DOI: RFMEFI58114X0006). S.D.S. acknowledges the Ministry of Education and Sciences of the Russian Federation (project No 3.392.2014K).

Supporting Information Available: Full description of the material. This material is available free of charge via the Internet at http://pubs.acs.org.

References


Figures

Figure 1. Zinc oxide tetrapod (ZnO-T) growth from Zn particles: (A) schematics of the reactor, showing the development of Zn particle combustion, from heating of the Zn particle to the steady state combustion and ZnO-Ts formation; (B) combustion zone formed around a Zn particle in the surrounding air ambience; (C) high-speed camera photograph progression of burning Zn particle inside the reactor, with indicated time in ms; (D) growth mechanism of ZnO-Ts: Zn particle combustion followed by nucleation and growth. The critical stage to obtain tetrapod structure is to control the growth conditions in the kinetic regime. Structures shown are not to scale.
Figure 2. Electron microscopy images of ZnO-Ts: (A) SEM, scale bar is 200 nm; (B) and (C) HR-TEM, scale bars are 5 nm.
Figure 3. ZnO-T characterization: (A) X-ray diffraction shows wider peaks of ZnO nanoparticles comparing to ZnO-T; (B) UV-vis-NIR spectroscopy of ZnO-Ts synthesized at various temperatures; (C) ZnO-T yield of synthesis is highest in the range from 750 to 850 °C.
Figure 4. ZnO-Ts decorated with Au nanoparticles: (A) absorption spectra and (B) a photograph of ZnO-T, Au NP and their mixture solutions; (C), (D) SEM image of ZnO-Ts with Au NP, attached through DNA, scale bars are 20 nm.
Figure 5. Comparison of ZnO-Ts with ZnO layered nanoparticles: (A) X–ray excited luminescence of ZnO-Ts (solid line) and ZnO layered nanoparticles (dashed line); (B) SEM image of ZnO layered nanoparticles; scale bar is 500 nm. SEM image of ZnO-Ts, used for measurement, is shown in Figure 2 (A).