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# TAPERED HEAD FACETS OF ZINC OXIDE NANORODS

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## ABSTRACT

Tapered head facets of ZnO nanorods are unique morphologies that offer potential applications in photoconductivity, chemical sensing, UV photodetection and optoelectronic display. Enhanced photoresponse could be due to large concentrations of intrinsic structural defects such as oxygen vacancies and zinc interstitials that are detected from visible PL emission. From our CFCOM gas synthesis technique, we have grown ZnO nanorods with tapered head facets at a rapid rate of 100nm/s in just 15s whereby the quenching stage could be crucial in retaining the tapered heads. Unstable tapered facets such as planes of $\{20\bar{2}5\}$, $\{10\bar{1}3\}$, $\{10\bar{1}4\}$ and $\{10\bar{1}5\}$ could be a contributing factor in the rapid growth rate of CFCOM ZnO rods due to their faster growth rates and high surface energies. Simulations of ZnO heads that we report can be used as a guideline for identification of tapered tips of ZnO nanostructures.

## INTRODUCTION

Due to sharp tips, tapered head of ZnO nanorods find promising applications in electron field emission by providing adequate brightness for flat panel display [1]. Thin nanorods with narrow tapered heads normally possess high levels of structural defects and surface recombination due to large surface-to-volume ratio [2]. Green-yellow emission is commonly attributed to these intrinsic structural defects that consist of singly-ionized and doubly-ionised oxygen vacancies while red emission, also known as metallic emission, is due to impurities especially interstitials of zinc [3,4]. High levels of oxygen vacancies at ZnO tapered head can greatly enhance photoconductivity response making ZnO rods excellent candidate for gas nanosensors [5].

It is known that unstable crystal planes of ZnO are normally the ones with high-order indexes such as $\{10\bar{1}4\}$, $\{20\bar{2}3\}$ and $\{10\bar{1}4\}$; and unstable crystal planes are expected to have faster growth rates and lower crystallinity if compared to that of stable crystal planes including $\{10\bar{1}0\}$ and $(10\bar{1}1)$ [6]. With the exception of $\pm(0001)$ plane facets, stable crystal facets have low growth rates and they readily appear in gas phase synthesis such as vapor-solid and vapor-liquid-solid processes [7]. ZnO is a II-VI compound semiconductor possessing a hexagonal wurtzite structure (space group $P6_3mc$) with lattice constants a=0.32495nm and c=0.52069nm. It has a wide direct bandgap of 3.37eV and a large exciton binding energy of 60meV making ZnO an excellent material for LEDs and UV lasing [1-4]. ZnO readily grows to form one-dimensional nanostructures with fast growth directions, $\langle 01\bar{1}0\rangle$, $\langle 2\bar{1}\bar{1}0\rangle$ and $\pm[0001]$, whereby the first two growth directions tend to produce nonpolar surfaces with lower energy than that of the $\pm(0001)$ polar facets [8].

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## EXPERIMENTAL DETAILS

The experiment is performed using a novel gas phase synthesis that we recently develop using a factory ZnO furnace and it is known as catalyst-free combust-oxidized mesh (CFCOM) process [9]. Figure 1a shows the furnace in operation. Pressurized zinc vapor is contained inside a graphite crucible heated to 1230-1270ºC temperature range that results in an estimated vapor pressure of 0.2-1.1MPa [10]. Once the lid of the crucible orifice is removed, the pressure difference causes the zinc vapor to purge out through the orifice at a high velocity of 8-12m/s (calculated). Due to dangerous open-flame radiation, safety measures are taken when placing a stainless steel mesh sieve about 10mm above the crucible orifice where hot zinc vapor flows. For the 150x160mm mesh sieve (Figure. 1b), a Tyler mesh 20 is used with 0.85mm sieve opening and 0.5mm wire diameter. After 10s of capturing time, the stainless steel sieve is then removed from the furnace and allowed to quench in normal ambient atmosphere. The whitish ZnO powder trapped on the mesh is removed from the mesh sieve by gently tapping on the sieve. Some zinc metal deposits at the center. The morphology of the as-grown nanoparticles is analyzed with LEOSupra50VP field emission scanning electron microscope (FESEM) equipped with energy dispersive spectrometer (EDS), PhillipsCM12 transmission electron microscope (TEM), SiemensD5000 x-ray diffractometer (XRD) and Jobin Yvon Horiba HR800UV photoluminescence spectroscopy unit. EDS measurement is made under 15kV incident electron energy.

(a)

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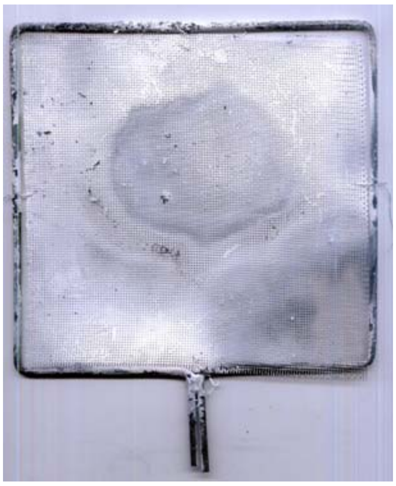

(b)

Figure 1: (a) ZnO industrial furnaces, (b) steel mesh after experiment.

## RESULTS AND DISCUSSION

The FESEM micrograph in Figure 2a shows a cluster of ZnO nanorods synthesized in our experiment using CFCOM technique that only last about 15s. Judging from the longest rods, the ZnO nanostructures grew at an amazing rate of 100nm/s which could be the fastest synthesis approach for ZnO rods. The characteristic hexagonal $(0001)$ facet is clearly seen in the upper inset where the wurtzite ZnO rod is bounded by six-sided $\{10\bar{1}0\}$ facets. Some of the rods exhibit a tapered appearance at the head or tip, as shown in the lower inset, where the tapered facets could be $\{10\bar{1}3\}$ surfaces. As posted in Figure. 2b, ZnO rods can have a *roundlike* tip that is made up of two pairs of tapered facets that are $\{10\bar{1}1\}$ and $\{10\bar{1}3\}$. Unstable tapered facets such as $\{10\bar{1}3\}$and $\{10\bar{1}4\}$ possess high surface energies and they readily grow in high temperature (high energy) conditions [6,7] that are offered in our CFCOM process. Once these tapered heads are formed, the tapering is retained by the quenching stage that suppresses further ZnO growth.
EDS analysis confirms that the ZnO rods consist of only Zn and O whereby the relative atomic % ratio of oxygen and zinc (O/Zn ratio) has a value of 1.36 that is a typical value for hexagonal structures based on our previous work [11-13]. The polycrystalline nature of CFCOM ZnO is evident from the XRD and TEM-SAED data (Figure. 3a and 3b) that highlight strong characteristic diffraction peaks of wurtzite ZnO occurring at 32.0º, 34.2º and 36.6º that correspond to $(10\bar{1}0)$, $(0002)$ and $(10\bar{1}1)$ surface planes.

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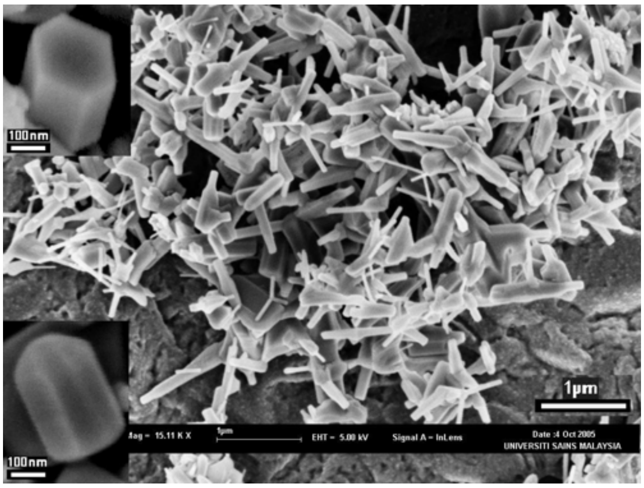
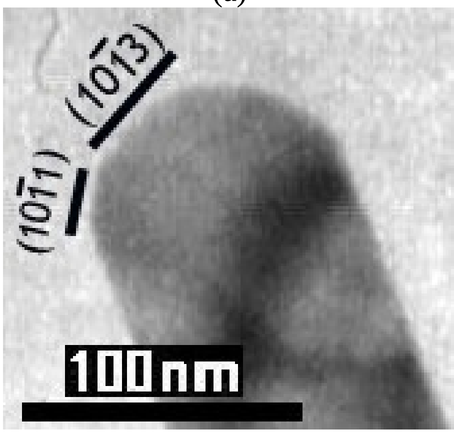



(a)

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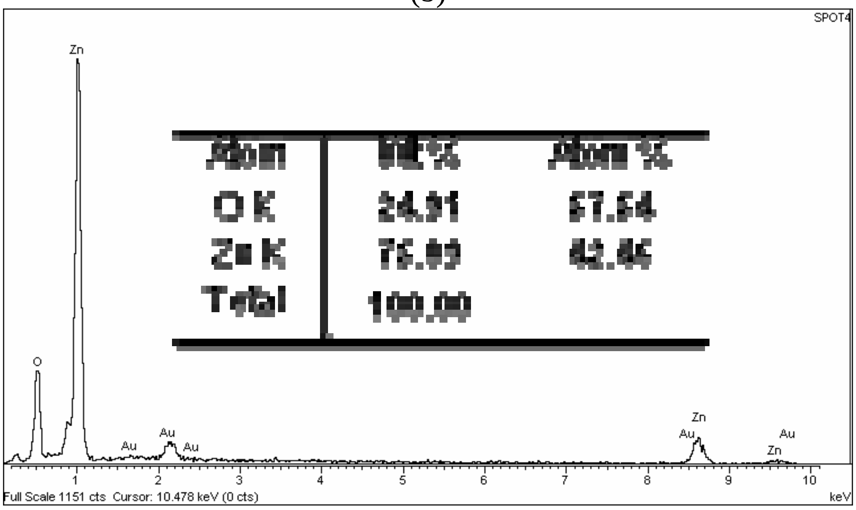


(c)

Figure 2: (a) A cluster of ZnO nanorods , showing hexagonal $(0001)$ surface, (upper inset) and tapered head with $\{10\bar{1}3\}$ head cap (lower inset), (b) tapered head with two sets of facets making it look round, and (c) EDS spectrum.

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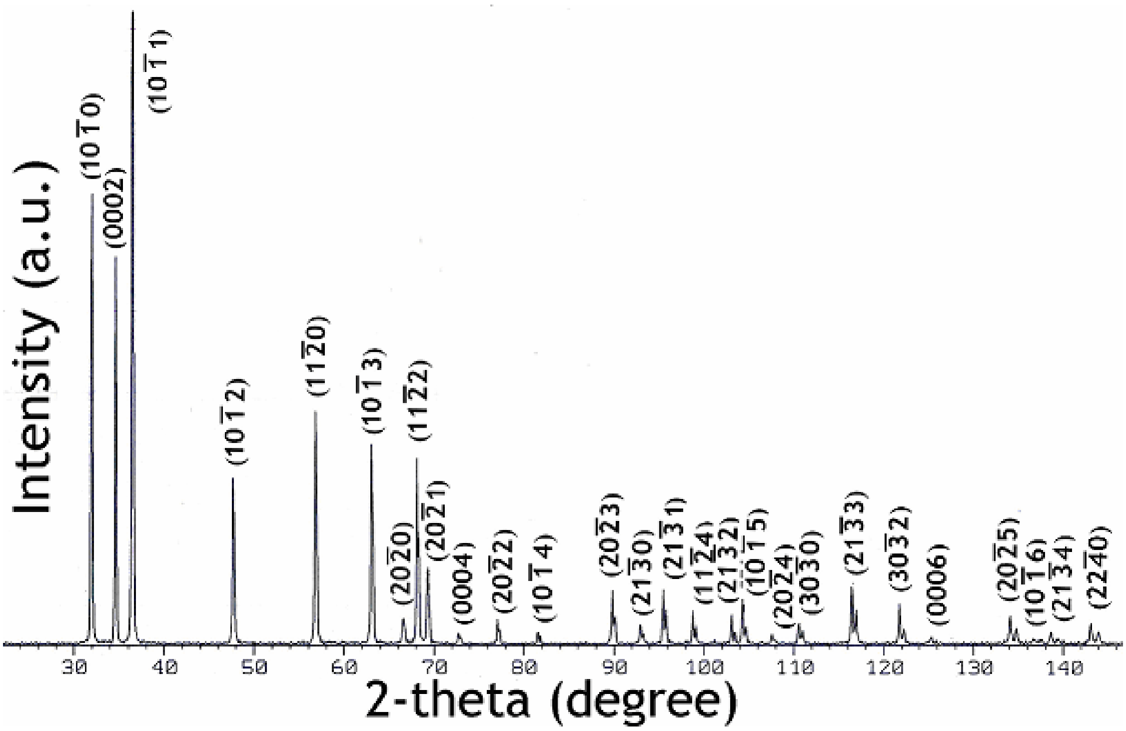
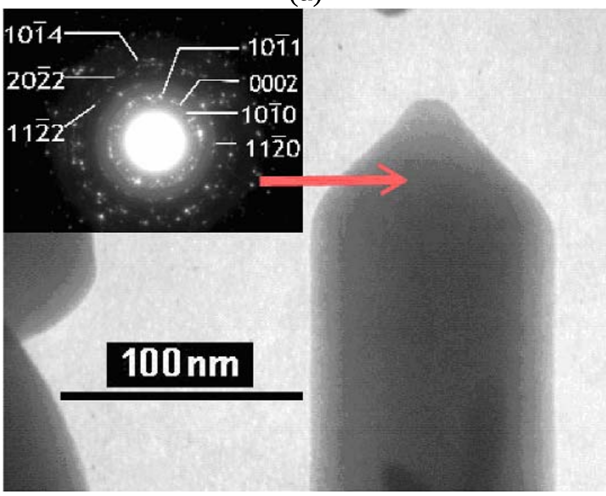



(a)




(b)

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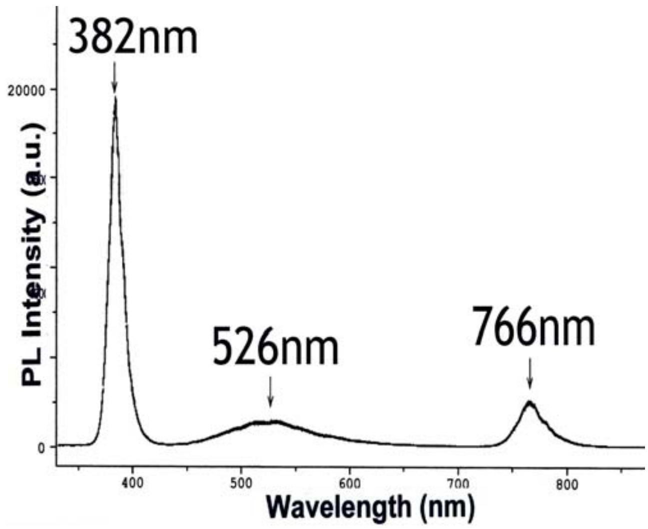


(c)

Figure: 3 (a) XRD spectrum, (b) TEM-SAED on nanorod head, and (c) PL spectrum.

CFCOM ZnO nanorods exhibit defect-induced excitonic photoluminescence in the green (526nm) and red (766nm) regions of the PL spectrum, as posted in Figure. 3c. These intrinsic optical properties are attributed to oxygen vacancies (green emission) and zinc interstitials (red emission) [1,2,4,9]. Oxygen vacancies on ZnO surfaces, especially tapered head surfaces, offer unique applications in chemical sensing and photoconductivity due to the surface states that are chemically and electrically active [1]. Rods with long tips or with tapered facets of $\{20\bar{2}1\}$ and $\{30\bar{3}2\}$ can offer superior nanosensing due their larger surface-area-to-volume ratio and higher head aspect ratio. Furthermore, they can be used for UV photodetection and optical switching considering their prominent UV peak emission at 382nm [2,3]. The enhanced intensity of UV luminescence could be induced by a large density of states as a result of high concentration of defect-bound excitons [2]. Unstable crystal planes such as $\{10\bar{1}4\}$ and $\{10\bar{1}6\}$ facets can degrade optical response and also worsen crystallinity due to their high surface energies [14].

Figure. 6 illustrates several simulations of tapered head facets of ZnO and their corresponding XRD relative intensities of Figure. 3a. The six head simulations show how a real tapered head would look if the growth conditions are perfect, and they can be used as a guide for the identification of tapered crystal planes of ZnO. Lower index planes such as $\{10\bar{1}1\}$ and $\{10\bar{1}2\}$ are stable crystal facets with lower growth rates and they can readily grow in a wider range of growth temperature. However, unstable crystal planes that have faster growth rates can only exist in high-energy and high-temperature growth environment similar to our CFCOM approach. We may postulate that the rapid growth rate of CFCOM rods (100nm/s) could be accelerated by unstable crystal facets of higher indexes that include surfaces of $\{20\bar{2}3\}$, $\{20\bar{2}4\}$, $\{20\bar{2}5\}$, $\{10\bar{1}3\}$, $\{10\bar{1}4\}$, $\{10\bar{1}5\}$ and $\{10\bar{1}6\}$, as posted in the XRD spectrum in Figure. 3a.

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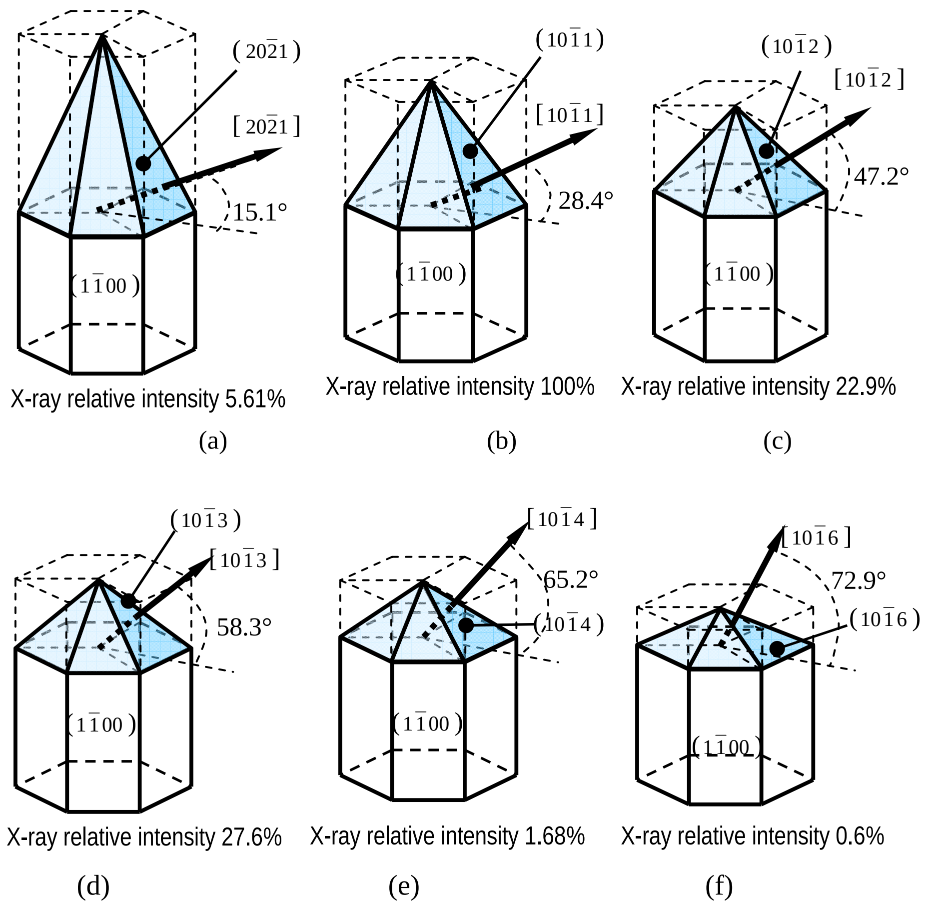


Figure 4: Simulation of tapered head facets of ZnO nanorods illustrating surfaces of (a) $\{20\bar{2}1\}$, (b) $\{10\bar{1}1\}$, (c) $\{10\bar{1}2\}$, (d) $\{10\bar{1}3\}$, (e) $\{10\bar{1}4\}$, and (f) $\{10\bar{1}6\}$

## CONCLUSION

We have reported a novel gas synthesis approach , CFCOM process, that is capable to produce ZnO nanorods at a rapid rate of 100nm/s in just 15s. These unique rods has tapered head facets that have potential applications in electron field emission, photoconductivity, chemical sensing and photodetection. The impact of unstable tapered facets has been discussed in terms of their faster growth rates and degrading influence on ZnO optical properties. Tapered head simulations that we presented can be a useful tool in nanomaterial research.

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