Single-Crystalline Branched Zinc Phosphide Nanostructures: Synthesis, Properties, and Optoelectronic Devices

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ABSTRACT

Hierarchical tree-shaped nanostructures, nanobelts, and nanowires of Zn₃P₂ were synthesized in a thermal assisted laser ablation process. All nanostructures are tetragonal phased Zn₃P₂ with excellent crystallinity and are free from an oxidization layer according to electron microscopy and X-ray diffraction analyses. Optical measurement revealed a strong absorption from the ultraviolet to near-infrared regions. Optoelectronic devices fabricated using individual nanowires demonstrate a high sensitivity and rapid response to impinging light. A crossed heterojunction of n-type ZnO nanowire and a p-type Zn₃P₂ nanowire has been characterized, and it offers a great potential for a high efficient spatial resolved photon detector.

Being a novel optoelectronic material, Zn₃P₂ has the following advantages over some other materials. It has a direct band gap in the range of 1.4–1.6 eV, which is the optimum range for solar energy conversion. The large optical absorption coefficient (> 10⁴ cm⁻¹) and a long minority diffusion length (~13 μm) of Zn₃P₂ permit high current collection efficiency. In addition, the constituent materials are abundant and cheap and would allow the large scale deployment of such devices as solar cells, infrared (IR) and ultraviolet (UV) sensors, lasers, and light polarization step indicators. In order to investigate the potential applications of Zn₃P₂, several kinds of heterojunctions have been designed, such as InP/Zn₃P₂, Mg/Zn₃P₂, Zn₃P₂/ZnSe, ITO/ Zn₃P₂, and ZnO/Zn₃P₂. However, the majority of research on Zn₃P₂ has been limited to thin films, and very little work has been done in the nanoscale range except for very few reports on the synthesis of Zn₃P₂ nanoparticles and on the synthesis of nanotriquets with an unavoidable ZnO layer coated on the surface. Because of the large excitonic radii, Zn₃P₂ is expected to exhibit pronounced quantum size effect, which has been observed for Zn₃P₂ nanoparticles. To the best of our knowledge, the electric property and photoresponse of Zn₃P₂ nanostructures, and heterojunctions made from Zn₃P₂ nanostructures, have not been reported thus far.

In this paper we report for the first time the synthesis of single crystalline tree-shape Zn₃P₂ structure arrays, nanowires, and nanobelts. The morphology and crystal structure were determined by electron microscopy and analytical techniques. In addition, the optical property of the synthesized nanostructures has been measured through photoluminescence (PL). Furthermore, we also present the crossed heterojunction made using a ZnO nanowire and a Zn₃P₂ nanowire. Optoelectronic measurements of single Zn₃P₂ nanowire and the crossed heterojunction indicate that Zn₃P₂ was very sensitive to light and the heterojunction exhibits enhanced performance, which implies that the Zn₃P₂ nanostructures have promising applications in optoelectronics.

Various nanostructures have been synthesized with thermal evaporation or laser ablation methods. Combining the two techniques, Zn₃P₂ structures were synthesized using a thermal-assisted pulsed laser ablation (TAPLA) process in a single-zone horizontal tube furnace, which is shown schematically in Figure 1. The two ends of the tube were closed and water-cooled to ensure a stable synthesis environment inside. A mixture of 0.8 g of ZnO and 0.12 g of graphite powder was placed in the middle of the tube. In order to transport the source vapor and reduce possible oxidization during the synthesis, N₂ was introduced from one end of the tube at a flow rate of 25 sccm during the entire synthesis process. A cylindrical target containing Zn₃P₂, ZnO, and Zn (in ratios of 2:1:1 by weight) was placed downstream. A single crystalline (111) Si wafer was placed in front of the target, serving as a collecting substrate. In order to minimize the residual oxygen, the tube was first evacuated to 10⁻²}
mbar and held for 2−3 h before the introduction of N₂ and maintained at a constant pressure of 200 mbar thereafter. The furnace was then heated up at a rate of 50 °C/min to the desired peak temperature of 1100 °C and held for another 20 min before slowly cooling down. Once the temperature exceeded 900 °C, a Compendex Series Excimer 102 laser (248 nm, 10 Hz, 30 kV, ~300 mJ) started to generate pulsed laser energy and kept shining a laser spot, 1 mm wide and 5 mm long, on the target during the synthesis until the furnace was cooled down to 900 °C.

When the synthesis process was completed, dark yellowish fuzzy material was found around the laser ablated pit on the target and on the surface of the substrate. The morphology of the as synthesized materials was examined using a LEO 1530 field emission scanning electron microscope (SEM) and the composition of Zn and P was first confirmed with energy dispersive spectrometry (EDS) attached to SEM. The morphology of the as synthesized materials was examined using a LEO 1530 field emission scanning electron microscope (SEM) and the composition of Zn and P was first confirmed with energy dispersive spectrometry (EDS) attached to SEM.

Figure 2 shows typical SEM images of the as synthesized Zn₃P₂ nanostructures and analysis results using EDS and XRD. A top view of the as synthesized nanostructures on a Si substrate is present in Figure 2a and its inset, which shows that those hierarchical nanostructures take a 6-fold symmetry. The tree shape is further revealed in the side view of Zn₃P₂ nanostructures in Figure 2b, which is the as synthesized product from the target lying on a conductive carbon tape for SEM imaging. The constituent branches of those tree-shape structures can be as long as several tens of micrometers. The diameter of those branches is in the range of 10 nm to a few hundred nm. Generally the branches at the root of the central trunk are larger than those at the top part of the trunk. A single branch is uniform and gradually gets smaller toward its tip. When the branches grow longer, some Zn₃P₂ nanobelts are also formed, as shown in Figure 2c. The thickness is in the range of 100 nm to several hundred nm, but the same nanobelt has a very uniform thickness throughout the entire belt. In comparison, the widths vary dramatically, even within a single nanobelt. As can be seen from Figure 2c, some nanobelts can be as wide as 10 μm at the root and get noticeably narrower toward the tip. Smaller nanobelts have also been observed, as shown in the inset in Figure 2c with a width around 100 nm. Considering their superlong length, those nanobelts are still overall very uniform. Besides those hierarchical nanostructures and derivative nanobelts, numerous Zn₃P₂ nanowires (NWs) with diameters up to 100 nm have also been found on the surface of the Si substrates. EDS analysis in both SEM and transmission electron microscopy (TEM) modes gave the same result for all nanostructures reported in this paper, including tree-shaped nanostructures, nanowires, and nanobelts. A typical spectrum in Figure 2d, which was taken from a Zn₃P₂ branch during TEM analysis, indicates the presence of Zn and P originating from the sample grid, and O peaks from oxidation of the nanostructure.

X-ray diffraction characterization in Figure 2e, performed using a PANalytical X-Pert Pro MRD with Cu Kα radiation, confirms that the phase of the nanostructures is tetragonal Zn₃P₂ (JCPDS Card No. 65-2854) with lattice constants 

\[ a = 8.095 \text{ Å} \quad \text{and} \quad c = 11.47 \text{ Å} \]

XRD analysis indicates that the synthesized nanostructures are single-phased Zn₃P₂ with very good crystallinity. No Zn, ZnO, or any other phases are detectable. Zn₃P₂ nanostructures were further examined using a Hitachi HF-2000 (FEG) transmission electron microscope, as shown in Figure 3. Figure 3a presents a TEM image of a part of a Zn₃P₂ nanostructure with selected area electron diffraction (SAED) patterns recorded from the circled areas labeled b−g and shown in Figure 3b−g, respectively. All of the branches in Figure 3a are in the same plane, and the angle between them is about 60°. As expected, all of the SAED patterns from different locations are along the same
zone axis, [021]. Additionally, in-plane rotations are found for some of the SAED patterns, indicating the existence of twin structures when forming the branches. More detailed analysis will be reported separately. Figure 3h presents a TEM image of a Zn$_3$P$_2$ nanobelt with the same SAED as that of nanostructures in Figure 3a, which is reasonable because nanobelts always grow from those nanostructures, based on SEM observation. According to those SAED patterns, we conclude that the central wire in Figure 3a and the nanobelts in Figure 3h have a growth front of (012). The top and bottom branches in Figure 3a have growth fronts of (312), (312), or the opposite directions. Secondary branches can also grow from grown branches, as indicated by arrowheads in Figure 3a. The high-resolution TEM image in Figure 3i, taken from the circled area in Figure 3h, illustrated the nearly perfect single-crystalline arrangement of atoms in the nanowires. Amorphous materials are scarcely seen on the surface. In addition, no ZnO layer has ever been seen on the surface of those Zn$_3$P$_2$ nanostructures. Electron microscopy and XRD data demonstrate that perfectly crystalline Zn$_3$P$_2$ nanostructures free from an oxidation layer can be obtained. Because no catalyst was introduced during the synthesis and no catalyst was found at the tip or bottom of the grown nanostructures, the nanostructures were formed by a vapor-solid (VS) process. The ZnO and graphite in the middle of the tube follow a carbon-thermal evaporation process as follows:

$$\text{ZnO(s)} + \text{C(s)} \leftrightarrow \text{Zn(v)} + \text{CO(v)} \quad (1)$$

Zn vapor was transferred by N$_2$ carrying gas downward to the reaction area around the target. Being a mixture of Zn$_3$P$_2$, ZnO, and Zn, the target releases vapors mainly composed of Zn, P, and O ions under the laser ablation that provides enough energy to break the Zn−P and Zn−O bonds. The O ions were mainly taken by oxidizing the carbon and CO, making it possible for the Zn and P ions to join, resulting in the growth of Zn$_3$P$_2$ nanowires. The Zn$_3$P$_2$ wires grow along [021] and later are followed by the growth of side branches, as shown schematically in Figure 4. Figure 4a illustrates a Zn$_3$P$_2$ wire along [021] with three sets of side surfaces (012), (312), and (312). A continuous supply of Zn and P results in the growth of the side branches from the

**Figure 3.** A detailed crystal structure analysis with TEM. (a) Low-magnification TEM image of Zn$_3$P$_2$ structure with SAED patterns from circled areas labeled b−g and shown in panels b−g, respectively. The arrowheads indicate secondary branch growth. (h) TEM image of Zn$_3$P$_2$ nanowires with SAED from the circled area and (i) a high-resolution TEM image.

**Figure 4.** (a) Growth of a Zn$_3$P$_2$ nanowire along [021]. (b) Branch growth from the central wire. (c) Formation of tree-shaped Zn$_3$P$_2$ nanostructure as a result of continuous growth of side branches and secondary branches.
central wire, as shown in Figure 4b. The side growth with 6-fold symmetry results from the fact that the angles between the side surfaces in Figure 4a are 120°. When the central wire and the side branches grow longer, new branches will grow from the central wire and even secondary branches also grow from the side branches, which is illustrated in Figure 4c and can be found in Figure 2a.

The optical performance of Zn$_3$P$_2$ nanostructures is very interesting. Figure 5 shows a reflection spectrum from 1 to 2 eV (Figure 5(a)) and photoluminescence (PL) spectrum under the excitation of 326 nm at room temperature (Figure 5(b)). From the reflectance spectrum it can be seen that energies below 1.4 eV are almost totally reflected by the Zn$_3$P$_2$ nanostructures without absorption, while a distinct edge was found at approximately 1.4 eV, indicating a strong absorption of higher energies. The corresponding PL spectrum provides direct evidence of this distinct absorption edge, at which a broad peak of 1.4–1.7 eV can be found. The broad spectrum found in PL likely results from the free exciton emission near the band edge, namely, acceptor-bound excitons.

In addition, single Zn$_3$P$_2$ nanostructures were prepared for the investigation of photoconductivity under the illumination of different wavelengths of light or a white LED lamp, as shown in Figure 6a. To characterize the $I$–$V$ characteristics of single NW, we placed a Zn$_3$P$_2$ NW between two Au electrodes via a dielectrophoresis (DEP) technique and deposited Pt by focused ion beam (FIB) microscopy as the top electrode to improve the contact. An ohmic contact can be obtained between Au and Zn$_3$P$_2$. In addition, Pt/Zn$_3$P$_2$ also forms an Ohmic contact because Pt has a greater work function (5.7 eV) than p-type Zn$_3$P$_2$ (5.06 eV) despite the possible presence ofGa dopants during the Pt deposition process. The ohmic contact was also proved by the linear behavior in later $I$–$V$ measurement of the device. The representative nanodevice is schematically illustrated in the upper inset of Figure 6a and the corresponding SEM image of the nanodevice is inset in Figure 6a. A LabView program was used to control the two-terminal $I$–$V$ testing process. The linear $I$–$V$ characteristic without illumination of light (blue line) confirms the ohmic contact between the electrodes and Zn$_3$P$_2$ NW, and a resistance about 3.63 $\times$ 10$^9$ Ω is derived. The resistivity of Zn$_3$P$_2$ NW was calculated about 5.6 $\times$ 10$^2$ Ω cm with the length and the diameter as 35 μm and 232 nm, respectively, based on the SEM characterization. The dark resistance here is higher than that of its thin film counterpart (2–3 $\times$ 10$^5$) possibly due to the contact resistance. On the other hand, under the illumination of light at a wavelength of 532 nm (green color with power <5 mW), 680 nm (red color with power <5 mW), or continuous wavelength from a white LED lamp, the resistance decreased significantly due to excess electron–hole pairs (EHPs) excited by the illuminating light, which has an energy larger than the band gap of Zn$_3$P$_2$. In addition, the desorption of the contaminants from the surface due to the illumination increased the conductivity as well. It is reasonable to expect that the shorter wavelength results in higher photoconductivity because the light with higher energy can create more electron–hole pairs inside the NW. In addition, the excess energy ($h\nu - E_g$) created phonons in the lattice and raised the temperature, resulting in larger electron and hole mobility and contributing a higher conductivity. The on/off ratio, which is defined as the current under the illumination over the dark current, is presented in Figure 6b as a function of the illuminated time, indicating high sensitivity of Zn$_3$P$_2$ NW to the illumination of different wavelength of light. The response time for all of the light is considerably less than 1 s with the on/off ratio being about 3 for red light (680 nm), 4–5 for green light (532 nm), and 2–3 for white light from a LED lamp.

Having shorter response time and higher on/off ratio than that of single NW, the p–n photodiode is an alternative form of photoconductor and can be constructed with crossed nanowires. By combination with wide band gap materials, such as ZnO, SnO$_2$, and ZnS, the whole range of light from
ultraviolet to the near-infrared can be effectively absorbed by this kind of photodiode, which is beneficial for terrestrial application of solar cell. We report the performance of a prototype nanoscale photodiode based on the crossed structure of a p-type Zn$_3$P$_2$ NW with an n-type ZnO NW. In order to form the required nano-heterojunction, we aligned a Zn$_3$P$_2$ NW between two Au electrodes via the DEP technique and fixed it with Pt metal via a FIB, which can improve the contact. After that, a ZnO NW was aligned perpendicular to Zn$_3$P$_2$ NW by DEP technique and connected to another pair of Au electrodes via Pt deposition by FIB microscopy. The final structure and schematic diagram are illustrated in insets of Figure 8a. The composition of the two NWs is confirmed with EDS and an ohmic contact is achieved individually for (Au, Pt)/Zn$_3$P$_2$ NW and is consistent with previous reports.\(^2\) The nano-heterojunction can be considered as an abrupt N+P junction, in which the depletion region is almost located at the Zn$_3$P$_2$ side, which have been calculated for the thin film case.\(^3\) The N+P junction characteristic is revealed by the rectification behavior of the I–V measurement in Figure 8a. At high forward bias, some of the minority carriers can diffuse and recombine in the depletion region, resulting in the recombination current. Considering the contribution of diffusion and recombination currents under forward bias, a simple I–V behavior can be empirically given by \(J \approx J_0 \exp \left(\frac{eV}{nkT}\right)\) (2)


where \(J_0\) is the saturated current, \(n\) is an ideality factor, \(k\) is Boltzmann’s constant, and \(T\) is the absolute temperature, respectively. When the I–V curve is dominated by an ideal diffusion current, \(n = 1\); whereas when the I–V curve is dominated by a recombination current, \(n = 2\). Otherwise, when \(n\) has a value between 1 and 2, both mechanisms are at play. However, the ideality factor \(n > 2\) is received in the present study by fitting the plot of \(\ln(J/J_0)\) as a function of forward bias, which likely results from the high contact resistance at both the interfaces of (Pt, Au)/ZnO NW and (Au, Pt)/Zn$_3$P$_2$ NW and is consistent with previous reports.\(^2\) In order to distinctly display the I–V behavior of the photodiode under the illumination of different wavelength lights, we reversed the polarity of the input voltage compared with the one in Figure 8a. The I–V curves for the photodiode under reverse bias and in the dark and under the illumination of light with wavelength of 532 or 680 nm are presented in Figure 8b, showing apparent current enhancement by the light. The increase of the current results from the generation of electron–hole pairs inside the depletion region and nearby under the excitation of the light and can be given by

\[I_{ph} = I_n + I_p = q\Delta n v_n + q\Delta p v_p \]  (3)

where \(I_{ph}\) is the total photocurrent density, \(I_n\) and \(I_p\) are the photocurrents caused by electrons and holes, \(q\), \(\Delta n\), \(\Delta p\), \(v_n\), and \(v_p\) represent electronic charge, the concentration of generated electrons and holes, and average drift velocities of electrons and holes within the specific depletion field, respectively. The concentration of the generated electron–hole pairs and the resultant current as well increase with the increase of the energy and intensity of incoming light, which explains why red light causes less current enhancement than

**Figure 7.** (a) The ideal energy diagram for ZnO/Zn$_3$P$_2$ heterojunction. (b) The individual position and length for neutral n- and p-regions as well as the depletion region without applied bias and under reverse bias, respectively.
green light while the dim white light produces the least enhancement. In addition, the lights have greater effect on reverse biased photodiode than forward biased photodiode, which is consistent with the fact that the photoexcited electron–hole pairs can significantly influence the concentration of minority carriers, which dominate the current through a reverse biased diode. The influence of the lights on the reverse biased photodiode is illustrated explicitly in Figure 8b with logarithmic scale and with the on/off ratio plot shown inset. Interestingly, all of the current from the illumination of light shows a similar trend: significantly greater than dark current under low reverse bias and more and more comparable to dark current under higher reverse bias.

In general, the reverse current is composed of the diffusion current in neutral regions and the generation current in the depletion regions. The reverse current, or reverse saturation current, comes from minority carriers in the neutral region, which diffuse toward and subsequent drift through the depletion region. On the other hand, the generation current comes from electron–hole pairs which are generated in the depletion region and drift toward neutral regions under the internal field. Thermal generated minority carriers and electron–hole pairs contribute to the dark current. In contrast, the impinging photon can generate substantial electron–hole pairs in both the depletion region and neutral region on the Zn3P2 side and considerably enhance the reverse current. At low reverse bias, photon-generated carriers are overwhelming over thermal generated carriers and result in a surprisingly high on/off ratio (∼102) in the inset of Figure 8b. However, thermal generated electron–hole pairs increase with increased bias and contribute more and more to the reverse current, as can also been seen in the dark current curve in Figure 8a. Accordingly, the on/off ratio should decrease with increased reverse bias, which confidently agrees with our result in the inset of Figure 8b. Despite of the decrease at high reverse bias, the on/off ratio can still reach 9–10, which is superior to other single NWs as photoconductors.28–31

Additionally, the photon response of the photodiode to different lights is shown in Figure 8c in which we applied a fixed reverse bias of 5 V and turned on and off green light (523 nm), red light (680 nm), and the white light lamp serially. Green light produces the highest (∼13) on/off ratio as expected. Interestingly, the dim white light also produces an on/off ratio (∼5) which is significantly greater than 1, indicating the high sensitivity of the photodiode to visible lights. Furthermore, the response time for all tested lights is below 1 s. The very nice performance of the diode may result from the following advantages. First of all, the top ZnO NW has a wide band gap and the light from infrared to violet can penetrate easily with minimum energy loss.32,33 Second, the depletion region is mostly located at the Zn3P2 NW side so that electron–hole pairs can be generated by a wide light range from 380 to 800 nm, and significant generation current enhancement results. Finally, the large minority diffusion length of Zn3P2 enables more photon-generated minority carriers in the neutral region to diffuse into the depletion region and results in a large on/off ratio and high sensitivity as well. The high sensitivity, quick response, and nanoscale size can benefit the ZnO/Zn3P2 nanoscale heterojunction as a candidate for a high efficient and spatial resolved photon detector.

In summary, we have synthesized tree-shaped Zn3P2 nanostructures, nanobelts, and nanowires in a thermal-assisted laser ablation process and proposed a possible growth process of those nanostructures. The photoluminescence spectrum of Zn3P2 nanostructures shows a broad emission centered at 770 nm with a slight blue shift with regard to that of the
bulk Zn$_3$P$_2$. A strong absorption from ultraviolet to near-infrared is apparent from the reflectivity measurement of those nanostructures. Taking advantage of the direct band gap of 1.5 eV, high absorption coefficient, large minority diffusion length, and high crystallinity free from oxidization, those nanostructures have potential applications in solar cell, broad range photodetectors, lasers, etc. Preliminary investigation on their application has been performed on the optoelectric measurement of a single Zn$_3$P$_2$ nanowire and a nanoscale photodiode.

The conductance of a single Zn$_3$P$_2$ nanowire shows high sensitivity to green light (523 nm), red light (680 nm), and white light and is very suitable as a photocoupler. Furthermore, we also constructed a nanoscale photodiode with crossed ZnO/Zn$_3$P$_2$ nanowires. The linear behavior of individual nanowires and the rectification behavior between ZnO and Zn$_3$P$_2$ revealed the formation of p–n heterojunction. Despite the absence of an antireflection coating or any other optimization, the photon diode gives rapid response and very high on/off ratio upon the illumination of light. Considering their small size, we expect Zn$_3$P$_2$ nanostructures and corresponding heterojunctions will play an important role in nano-optoelectronics.

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Supporting Information Available: EDS data and I–V measurement of individual constituent nanowires of the heterojunction. This material is available free of charge via the Internet at http://pubs.acs.org.

References

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