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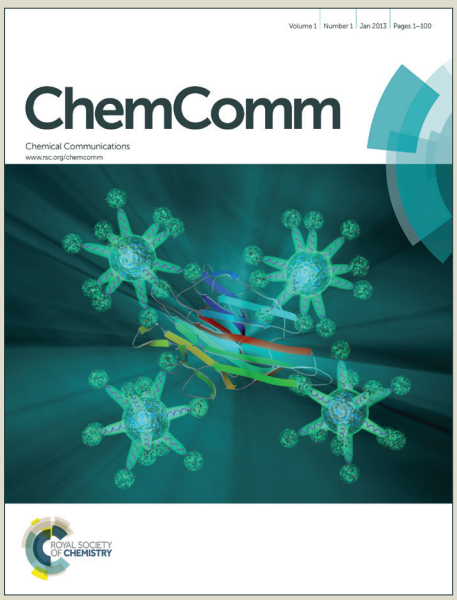

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A Solution-phase Approach to Cd_3P_2 Nanowires: Synthesis and Characterization

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Single-crystalline Cd_3P_2 nanowires (NWs) have been synthesized via solution–liquid–solid (SLS) mechanism. The lengths of the resulting nanowires can be effectively tuned in the range of 180 nm and 5 μm, and the photodetectors made of the Cd_3P_2 nanowires exhibited a pronounced photoresponse with high stability and reproducibility.

One-dimensional semiconductor nanowires (NWs) have raised considerable research interests due to their high aspect ratio and dimensional-dependent physical and electronic properties. They exhibit two quantum confined directions, while provide a natural pathway for charge carrier transport along the unconfined direction. This unique feature makes them suitable as building blocks of electronic devices. For instance, in photovoltaic cells, high-aspect-ratio nanowires have the potential for enhancement of electron transport in contrast to nanoparticles(NPs) , thereby leading to superior device performance.[1,2] Moreover, it is pivotal to control the synthesis of semiconductor nanowires for exploiting their applications, such as photodetectors.[3-7]

Cadmium phosphide (Cd_3P_2) is featured of a small direct band gap (0.55 eV), a large exciton Bohr radius (18 nm), a relatively high dielectric constant (5.8), and a small effective mass of the electron.[8-10] A number of papers have reported the synthesis of Cd_3P_2 nanostructures and their potential applications in optoelectronics.[11-14] However, the synthesis of Cd_3P_2 NWs has been rarely reported to date. To the best of our knowledge, the only one report on Cd_3P_2 nanowires synthesis was most recently described by Fan et al., wherein Cd_3P_2 NWs were prepared using InP as P precursor and Cd foil as the source of Cd at temperature as high as 900 °C via a chemical vapor deposition (CVD) process [15].

Currently, several efficient approaches have been developed to grow high-quality semiconductor NWs, e.g., nanochannel template growth,[16-18] vapor-liquid-solid (VLS) growth,[19-22] supercritical-fluid-liquid–solid (SFLS) growth,[23] and SLS growth.[24,25] Among them, the solution approaches seeded by low-melt metal catalyst offer appealing properties, including relatively low growth temperatures (generally < 400 °C),[26,27] high-crystalline structure, and tunable length. However, synthesis of nanowires by solution approach is limited by growth solvents as well as precursors. Thus the semiconductor nanowires prepared by solution catalytic approach are much fewer than those via VLS growth, which is usually performed at high temperatures (e.g., > 700 °C). In this work，we exploited the SLS approach to grow single-crystalline Cd_3P_2 nanowires using Bi nanoparticles as catalysts at temperature of only 290 °C. The length of the resulting nanowires can be tuned in the range of 180 nm ~ 5 μm by varying the ratio of Bi NPs/ Cd_3P_2 precursors while their diameter was kept basically unchanged at ~ 16nm. Experiments further show that the Cd_3P_2 nanowires exhibit absorption spanning visible-to-near-infrared range, and the photodetectors made of these nanowires shows a pronounced photoresponse with high stability and reproducibility, and their sensitivity enhances with the decrease of light wavelength.

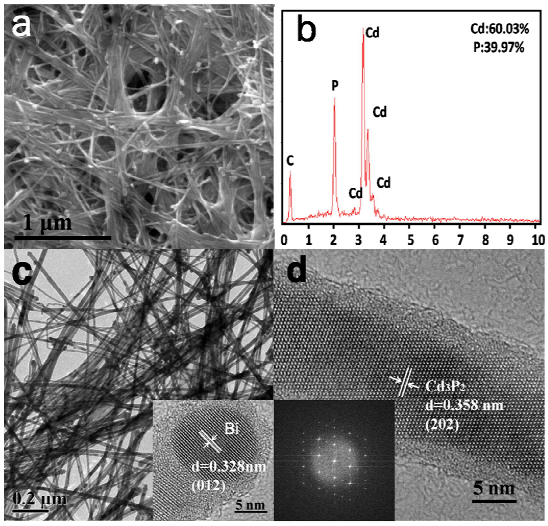

Fig.1. a) SEM image, b) EDX spectrum and c) TEM image of an ensemble of randomly aligned Cd_3P_2 nanowires. (Inset shows the HRTEM image of a Bi NP at the wire tip). d) HRTEM image of a part of the Cd_3P_2 nanowire. (Inset shows the FFT of the image). These images have obtained in the Cd_3P_2 nanowires prepared with Cd/P molar ratio of 6/1.

Fig. 1a shows the scanning electron microscopy (SEM) images of the ensemble of randomly aligned Cd_3P_2 nanowires that were

prepared with Cd/P molar ratio of 6/1 in the synthesis precursor. The nanowires show lengths up to 5 μm with relative uniform diameter. EDX linked with SEM was performed to reveal the chemical composition of the Cd_3P_2 NWs, as presented in Fig. 1b. The atomic ratio of Cd/P measured in the products is very close to the ideal composition of 3/2 for Cd_3P_2 materials, indicative of the formation of well stoichiometric product. The TEM image in Fig. 1c displays smooth nanowires with a mean diameter of ~15.9 nm, which correlates to the size of monodisperse Bi-nanoparticle catalysts (13.3 nm±1.2). A Bi catalyst nanoparticle attached to the wire tip was clearly revealed: the catalyst nanoparticle appears darker in the image because of Z contrast: $Z_{Bi} > Z_{Cd} > Z_p$ as shown in the inset of Fig. 1c. Furthermore, it reveals a d-spacing of 0.328 nm, as the (012) plane of rhombohedral Bi. To further study the growth of the Cd_3P_2 nanowires, the microstructures of the Cd_3P_2 nanowires were analyzed by high-resolution TEM (HRTEM). Fig. 1d shows a single Cd_3P_2 nanowire with a d-spacing of 0.358 nm, well-matched the (202) plane of tetragonal Cd_3P_2. These results confirm that the Cd_3P_2 nanowires were formed via the SLS mechanism,[24] and the growth direction of the Cd_3P_2 nanowires is perpendicular to the (202) lattice plane. The fast Fourier transform (FFT) of the image (inset of Fig. 1d) further confirms this preferential growth direction of the nanowires. The sharp diffraction maxima in the FFT demonstrate the single crystalline nature of the crystal. More HRTEM images of a number of individual Cd_3P_2 NWs are shown in Fig. S1, ESI†, confirming this conclusion.

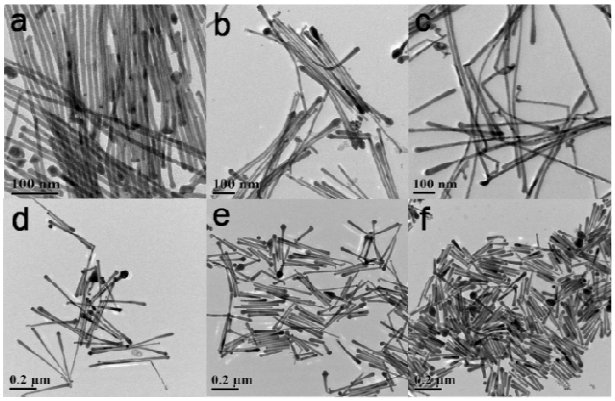

Fig. 2. TEM images of the Cd_3P_2 NWs synthesized with different Cd/P molar ratios of (a) 4/1, (b) 8/1, (c) 10/1 and different amount of (d) 2.0 μmol, (e) 4.0 μmol, and (f) 6.0 μmol of Bi nanoparticle catalysts.

The influence of precursors was studied to optimize the Cd_3P_2 nanowire growth. Fig. 2 shows the TEM images of the Cd_3P_2 nanowires prepared with the different ratios of Cd/P. It is apparent that the ratios of the precursors play an important role in affecting the quality of the resulting nanowires. Fig. 2 shows that high quality Cd_3P_2 nanowires with smooth surface and relative uniform diameters can be obtained when Cd/P ratios were at 4/1 (Fig. 2a) and 6/1 (Fig. 1c). As Cd/P ratios continued to increase, the NWs would be curve or dendritic as shown in Fig. 2b (Cd/P=8:1) and Fig. 2c (Cd/P=10:1). It is hence appropriate to keep the Cd/P ratio in the range of 4/1~ 6/1 to obtain high quality Cd_3P_2 nanowires in this study. Further study on Cd_3P_2 nanowires were therefore focused on the sample prepared with Cd/P ratio of 6/1. Interestingly, further study show that the lengths of the Cd_3P_2 nanowires can be effectively tuned by varying the amount of Bi nanoparticle catalysts used in the reaction: Nanowires with length over 5 μm can be obtained under condition that 1.2 μmol of Bi nanoparticle catalysts was involved in the reaction (shown in Fig. 1). However, the length of the Cd_3P_2 nanowires can be rapidly reduced to ~ 450 nm if the amount of Bi NP catalyst was increased to 2.0 μmol (Fig. 2d), and further decreased to ~ 230 nm (Fig. 2e) and 180 nm (Fig. 2f) when 4.0 μmol and 6.0 μmol of Bi NP catalysts were used, respectively. This is in line with the fact that, a decrease of the amount of Bi nanoparticle catalysts employed in the synthesis generally led to an increase of nanowire lengths for the SLS grown nanowires.[28] In addition we have attempted to tune the diameters of the Cd_3P_2 nanowires by varying the sizes of Bi catalysts. However, it was found that all of the resulting Cd_3P_2 shows similar diameters in the range of 13 nm to 17 nm shown in (Fig. S2, ESI†).

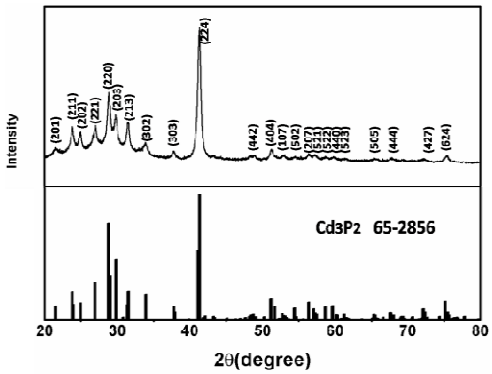

Fig. 3. XRD patterns for the Cd_3P_2 nanowires.

Fig. 3 shows a typical XRD pattern for the Cd_3P_2 nanowires with length of ~ 5 μm. The peak broadening is characteristic of a material at nanoscale. The NWs exhibits a number of well-resolved reflection peaks that can be indexed to the (221)，(220), (203), (213) and (224) planes of Cd_3P_2 structure, respectively (JCPDS No. 65-2856). Therefore, pure phase Cd_3P_2 nanowires were successfully synthesized with high-crystalline structures by the solution-solid-liquid mechanism via the Bi NP catalytic role.

The UV/Vis/NIR absorbance spectra of the colloidal Cd_3P_2 nanowires suspensions were measured to study the optical properties. The Cd_3P_2 nanowires absorbed light across the near-infrared to the entire visible spectrum (Fig. S3, ESI†), thus making suspensions

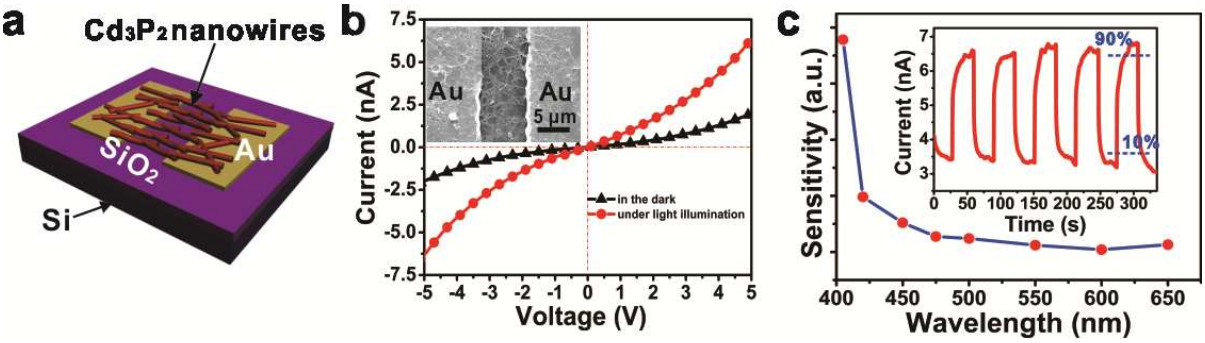

Fig. 4. (a) Schematic illustration of the photodetector fabricated from the Cd_3P_2 nanowire network. (b) *I-V* curves of the photodetector measured in the dark and under light illumination (405 nm, 7.5 mw/cm²), respectively. Inset shows the SEM image of a typical device. (c) Wavelength-dependent sensitivity of the photodetector. Photoresponse of the photodetector to pulsed light is shown in the inset.

brownish black color. The indirect optical band gap (inset of Fig. S3, ESI†) of the typical Cd_3P_2 nanowires were determined at 0.78 eV,which is a little larger than that of the bulk materials, probably attributed to size quantum effect or surface effect. To study the optoelectronic properties of the Cd_3P_2 nanowires, the transient photocurrent response was first tested by a photoelectrochemical cell. A Cd_3P_2 nanowire film was prepared by spray-casting a nanowire suspension in hexane onto FTO substrate. The film was then annealed at 150 ^oC for subsequent measurement under illumination with a Xenon lamp. As shown in Fig. S4, ESI†, when tuning on the light, the current increased quickly. Oppositely, the current decreased when the light tuned off, indicative of their sensitivity to light irradiation. Moreover, when the potential was enlarged, the response would be increased. This clearly demonstrates n-type semiconducting behavior for the resulting Cd_3P_2 nanowires in this study.

To gain more insight into the optoelectronic properties of the Cd_3P_2 nanowires, photodetectors based on the Cd_3P_2 nanowire network were fabricated by directly drop-casting the nanowires on pre-prepared Au electrode pairs on SiO_2 (300 nm)/Si substrate. Schematic illustration and SEM image of the photodetector are shown in Fig. 4a and inset of Fig. 4b, respectively. From the current versus voltage (*I-V*) curves of a typical device measured in the dark condition and under light illumination (405 nm, 7.5 mw/cm^2) (Fig. 4b), one can see that the photodetector shows a pronounced photoresponse. The photocurrent from Cd_3P_2 NWs in this work is significantly lower than that of PCBAME/Cd_3P_2 hybrid NWs prepared via CVD at high temperature.[15] It is known that the organic oleic acid (OA) are indispensable to the growth of Cd_3P_2 NWs in this study by colloidal chemistry, while they can form an insulating layer to suppress injection or extraction of charge carriers from the NWs. We have conducted ligand exchange to improve the conductivity of the NWs by removing the insulating OA layer with hydrazine hydrate.[29] However, it is impossible to completely remove the organic ligand by such ligand exchange strategy. Therefore, the device performance of the colloidal nanowires is still worse than that of CVD-grown bare nanowires. Additionally, the device can be reversibly switched between low-and high-resistivity states when the light is switched on and off repeatedly (inset of Fig. 4c), revealing the high stability and reproducibility of the photodetector. The response time and recovery time, defined as the time intervals from 10% to 90% of the difference between maximum and minimum current, are deduced to be 7.2 s and 4.9 s, respectively. Fig. 4c shows the wavelength-dependent sensitivity of the photodetector. Notably, the device exhibits high sensitivity to the short-wavelength light, and the sensitivity enhances with the decrease of light wavelength.

In summary, high quality Cd_3P_2 nanowires have been synthesized using Bi nanoparticles as seeded catalyst via SLS mechanism at only 290 ^oC. The lengths of nanowires can be varied in the range of 180 nm ~ 5 μm by changing the synthetic parameters. Experiments demonstrate that the as-prepared Cd_3P_2 NWs are single-crystalline structured materials with light absorption across visible-to-near-infrared ranges. Photoelectrochemical measurement reveals they are n-type semiconductor and are sensitive to light irradiation. Moreover, photodetectors made of these nanowires exhibit the high sensitivity to short-wavelength light, confirming the great potential of Cd_3P_2 nanowires in high-performance optoelectronic devices.

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Note and references

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Electronic supplementary information (ESI) available: detailed experimental, TEM, UV-Visible absorption spectra and Transient photocurrent response. See DOI: 10.1039/ x0xx00000x /

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