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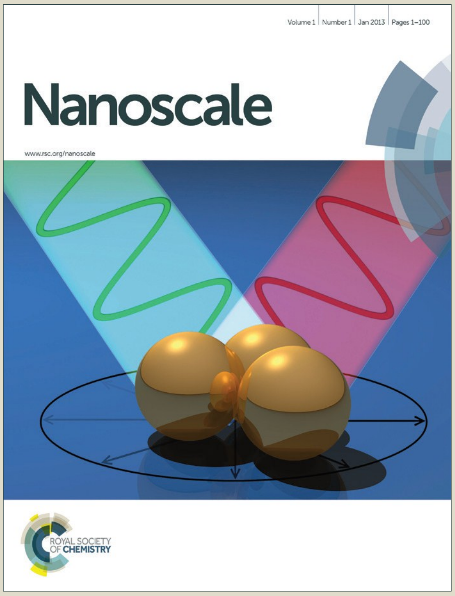

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Unexpected Photoluminescence property from one-dimensional molecular chains

Ye Yuan, Mingguang Yao*, Shuanglong Chen, Shijie Liu, Xigui Yang, Weiwei Zhang, Zhen Yao, Ran Liu, Bo Liu, Bingbing Liu*

Unlike bulk iodine, iodine molecular chains formed inside one dimensional (1D) nanochannels of $AlPO_4$-5 (AFI) single crystal show an unexpected PL behavior. Thanks to its unique 1D structure, the PL exhibits obvious polarization both in the excitation and emission, by changing the angle between the c-axis of the channels and polarization direction of incident laser. As pressure increases, the PL intensity increases obviously due to the population increase of $(I_2)_n$ chains upon compression. In contrast, the breaking of $(I_2)_n$ chain at high temperature leads to the decrease of PL intensity. Our theoretical calculation further point out that the PL may arise from the intrinsic band structure of $(I_2)_n$ chains.

Introduction

Atomic/molecular chains are expected to exhibit novel quantum effect and physical properties due to the unique structure, which thus may have potential applications in various fields.[1] Manipulating the atomic chains at an atomic level has been recently demonstrated in the atomic chain of gold, which was synthesized under high vacuum through an electron beam technique. The obtained gold chains have coaxial helical multishell (HMS) structure and exhibit quantized conductance.[1-4] Besides gold atomic chains, the atomic/molecular nanochains constructed by other atoms/molecules have also been reported, such as Se, Br_2, and I_2, *etc*.[5-10] These nanochains have been prepared by using various templates, such as zeolite and carbon nanotubes.[5-7] Basically, the synthesis of naonchains by this method has been developed and more attention has been now paid to the characterization and structural manipulation of the nanochains by the application of external interactions.[11,12] Furthermore, investigations on the properties such as optical and electronic properties of the nanochains have been considered as important topics for the potential applications, while less progress have been made on this aspect.

Among the studied nanochains, diatomic molecule iodine has been found to form unique 1D molecular chains in the nanochannels of carbon nanotubes and zeolite crystals, which has been attracting great research interest recently.[6,13] Polarized Raman measurements on $(I_2)_n$ chains show that the 1D neutral chains ($(I_2)_n$) formed are constructed by well aligned iodine molecules which are parallel to the z-axis of the nanochannels.[13] Upon compression, Yao *et al.* discovered that the randomly orientated individual iodine molecules may rotate into a direction parallel to the nanochannels, leading to the elongation of the $(I_2)_n$ chains and increase of the chain population.[11] Similar transformation has also been observed in the confined iodine in the 1D elliptical channels of $AlPO_4$-11 (AFL) under pressure.[14] Here, we report an unexpected photoluminescence from the 1D $(I_2)_n$ chain confined in AFI nanochannels, which is quite different from the non-photoluminescence in the bulk iodine crystals. Upon compression, the PL increases obviously, due to the nanochain population increase. Such unexpected discovery inspires us that more novel properties could be discovered in the atomic/molecular nanochain system compared with the corresponding bulk counterpart.

Experimental section

1. Experimental Methodology. $AlPO_4$-5 single crystal was prepared by a hydrothermal method. The as-prepared crystals were calcined at 600°C in O_2 atmosphere for 48 hours to remove the DIPA molecules in the channels thoroughly.[15,16] The iodine@AFI crystal was obtained by using a vapor-phase diffusion method. In brief, the empty AFI crystal and iodine powder were sealed in a Y-shaped quartz tube under vacuum (10^{-3} Pa). Then, the tube was heated at 400°C for 48 hours. By washing with ethanol and exposing to the air for several days, we obtained iodine filled AFI single crystal (iodine@AFI). Raman and PL measurements were performed using a micro-Raman system (Renishaw inVia) with a 514.5 nm Ar^+ laser as the excitation source. As the 514.5 nm laser is linearly polarized light, the PL for excitation polarization was measured by rotating the sample from parallel to perpendicular to the polarization direction of incident laser. The emission polarization was measured by VV configuration (polarization of excitation laser light and detection of Raman scattering are parallel) and VH configuration (polarization of excitation laser light and detection of Raman scattering are perpendicular),

State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, P.R. China.
E-mail: liubb@jlu.edu.cn; TEL: 86-431-85168256, E-mail: yaomg@jlu.edu.cn

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respectively. A diamond-anvil-cell (DAC) was used to create high pressure. The sample was loaded on the diamond cullet surface. Silicon oil and a tiny ruby were used as the pressure transmission medium and for pressure calibration, respectively. In the comparison experiments to study the vapored iodine molecules, we firstly sealed iodine crystals in a quartz tube under high vacuum and then heated the tube to 100^{o}C which is high enough to sublimate iodine and form vapored iodine gas. In situ PL and Raman measurements were carried out at this high temperature.

2. Theoretical Methodology. In the theoretical simulation, the band structure was calculated by using HSE06 method, which has been performed using the projector augmented wave (PAW)[17] method as implemented in the Vienna ab initio simulation package (VASP).[18,19] The plane wave energy cutoff was set to 228.34 eV. And the smallest allowed spacing between k-points is 0.23 Å^{-1}. The supercell is 1×4×1 and 4 iodine molecules were added inside to form the iodine molecular chains. As the van der Wasls radius of iodine molecule (6.8 Å) is smaller than the diameter of AFI 1D nanochannels (7.3 Å) and the $(I_2)_n$ nanochains have no charge transfer to the channel walls, the influence of AFI framework has not been taken into account and the band structure of $(I_2)_n$ chain under vacuum is calculated.

Results and discussion

Figure 1 (A) shows the Raman spectra of undoped AFI single crystal and iodine@AFI crystal with different doping concentration. The weak Raman activity of undoped AFI single crystal proves that AFI is a good template to study the behavior of iodine confined in the 1D nanochannels. For iodine@AFI crystals, the Raman mode at 165cm^{-1} can be clearly observed in the spectrum of the high concentration doped sample, which are from $(I_2)_n$ chains.[13] In contrast, the Raman mode at 165 cm^{-1} is absent in the low concentration doped sample, which suggests that few $(I_2)_n$ chains are formed in the channels. Furthermore, we carried out the Energy Dispersive Spectroscopy (EDS) analyses on the iodine@AFI samples to roughly estimate the mass percentages of iodine in the samples. The mass percentage of iodine in iodine@AFI sample with high doping concentration is about 11.9%, while it is only ~5.1% in the low concentration sample. These results are comparable to those reported in the previous literature.[12] The PL spectrum collected at room temperature from iodine@AFI single crystal with high doping concentration is shown in Figure 1 (B). A broad and intense emission band is observed in the range from 550nm to 900nm with peak centered at 750nm (1.66eV). In sharp contrast, bulk iodine crystal, undoped AFI and iodine@AFI with low doping concentration do not show any visible photoluminescence in this energy range. And we also measured the PL spectra of vapored iodine molecules. Like previous reports, sharp and discrete emission peaks are observed which are very different from that of iodine@AFI crystals. It is worth mentioning that we can safely exclude the influence from DIPA molecules, since the DIPA molecules have been carefully removed from the as-prepared AFI single crystal. In addition, defect such as oxygen vacancy may be created during the heating treatment process. As the synthesis conditions for both the low concentration doped sample and the high concentration doped sample are the same, defects if present in both samples, the low concentration doped sample should also exhibit obvious PL. However, no PL was observed in the low concentration doped sample. We thus could also exclude the defect as the PL origin in the high concentration doped sample. Therefore, the PL should be from the $(I_2)_n$ chains confined in the nanochannels.

In order to verify that the PL origin is from $(I_2)_n$ chain, we annealed the high concentration doped iodine@AFI crystal at 400^{o}C for 12 hours. After such high temperature annealing the $(I_2)_n$ chains dissociate into iodine molecules and most of the iodine molecules diffuses out of the AFI nanochannels. The optical images of iodine@AFI crystal before and after annealing are shown in Figure 1 (C) and (D). The color of iodine@AFI crystals changes from dark red to light pink after annealing, suggesting a significant decrease of the iodine doping concentration. This has been further confirmed by our Raman measurements. As shown in the Raman spectra (Figure 1 (C)), the vibration of $(I_2)_n$ chains decreases significantly in the intensity and individual I_2 molecules also weakens obviously after the annealing. Accompanying with the reduction of $(I_2)_n$ chains, the photoluminescence of iodine@AFI crystals decreases remarkably after the annealing (Figure 1 (D)). This strongly supports that the PL arises from $(I_2)_n$ chains formed in the channels.

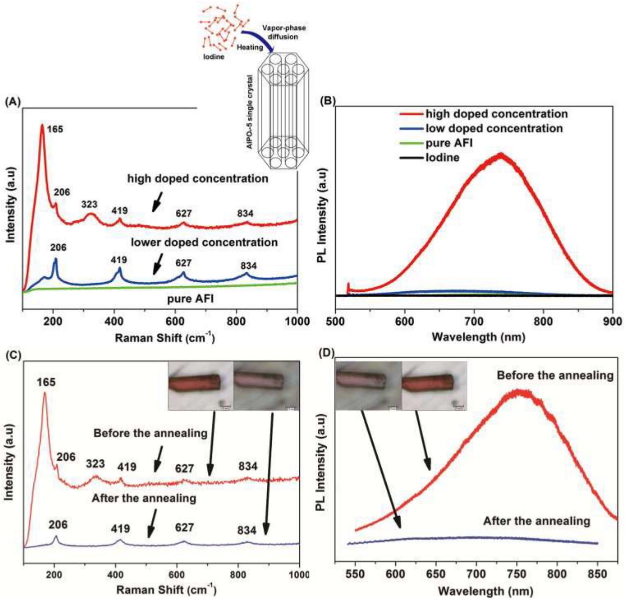

Figure 1 (A) Raman spectra of the iodine@AFI crystal with high doping concentration and low doping concentration, as well as pristine AFI crystals; (B) the corresponding PL spectra of those samples; (C) Raman spectra and (D) PL spectra of an iodine@AFI crystal before and after the annealing. The insets are the optical images of the corresponding iodine@AFI crystal before and after the annealing.

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In previous studies, $(I_2)_n$ chain exhibits clear polarization behaviors in optical measurements, because of its unique one-dimensional structure. Recently, Ye *et al* reported the polarized Raman scattering of iodine@AFI crystal, which identified the stable one-dimensional $(I_2)_n$ chains and showed that the orientation is parallel to the axis of AFI channels.[13] Figure 2 (A) shows the anisotropy of PL signal when polarization of excited laser light varies from parallel to perpendicular to the axis of channels. And the PL intensities decreased dramatically from parallel to perpendicular to the channel axis. From this result, we can deduce the absorption dipoles are parallel to the axis of the channel.[22] Figure 2 (B) and (C) show the polarization of emission. The PL intensity in a VV configuration decreased monotonically as the angle θ between the c-axis of the channels and polarization direction of incident laser increases from θ=0° to θ=90°. On the other hand, the VH configuration increased firstly then decreased from θ=0° to θ=90°. According to the polarization of emitted light, we can state the emitted light from iodine@AFI crystal is linearly polarized light and its polarization orientation is parallel to the channels of AFI crystal. Therefore, the emission dipoles are also parallel to the channels of AFI crystal. These phenomena can be well explained by the unique one-dimensional configuration of the $(I_2)_n$ chains. Furthermore, the anisotropy of PL further excludes the possibility that the PL arises from defects of AFI crystal, because defects should be isotropic to exciting laser. It is noted that photoluminescence polarization has also been observed in other similar 1D nanomaterials, such as CdSe, GaP and LnP nanorods.[23-25] Two main mechanisms were proposed to explain these phenomena.[26] The first one is the quantum size effects,[27-32] and the other is the huge difference in dielectric constants between the nanowires and their surroundings.[33,34]

The thermal variation of iodine nanostructures confined inside the channels of AFI crystal has also been reported. $(I_2)_n$ chains may dissociate and transform to iodine molecules upon heating.[14] An obvious change in the Raman intensity of $(I_2)_n$ chain was found in the temperature range of 60-80°C. It is thus natural to expect that the PL intensity may also decrease visibly in a similar heating process. We therefore measured the PL spectra of high concentration doped sample in the temperature range of 25-115°C. The results are shown in Figure 3 (A). The inset shows the integrated PL intensities as a function of temperature. It is obvious that the PL intensity decreases dramatically from 55°C to 85°C, which corresponds to the dissociation of $(I_2)_n$ chains described above. This temperature range is very close to that for the structural transformation of $(I_2)_n$ chains reported by Ye *et al*. Therefore, we propose that $(I_2)_n$ chains are broken down at high temperature, which leads to the weakening of PL in $(I_2)_n$ chains.

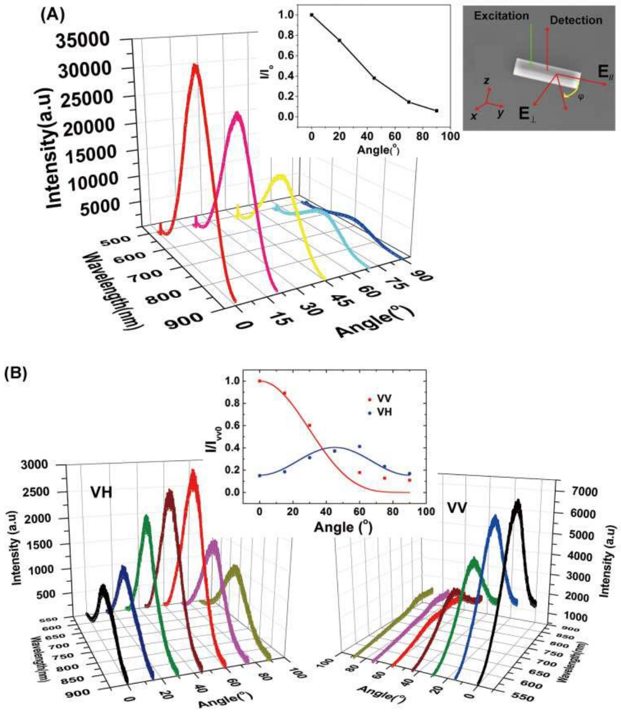

Figure 2 (A) PL spectra for excitation polarization of iodine@AFI crystal. The inset shows the integrated PL intensity as a function of the angle θ. Polarized PL spectra for VV and VH configuration are shown in (B) and (C), respectively. The inset shows the integrated polarized PL intensity as a function of the angle θ.

In our previous study, we show that high pressure is a powerful tool to tune the arrangements of the iodine species confined in the nanochannels. To explore the effect of high pressure on the PL of the $(I_2)_n$ chains, we performed high pressure PL measurements on iodine@AFI. As shown in Figure 3 (B), the PL intensity increases obviously from ambient pressure to 1.1GPa and then decreases with pressure increasing further. Such pressure-induced PL enhancement is obviously different from the most observations that the PL of a material usually decreases dramatically upon compression to high pressure.[35] In our recent high pressure studies, we revealed that the population of $(I_2)_n$ chains increases upon compression.[11] In particular, the Raman intensity of $(I_2)_n$ chains increased from ambient pressure to 2.72GPa and then decreased at higher pressure, which is caused by the formation of $(I_2)_n$ chain due to the assembly of individual I_2 molecules (vapor-like) upon compression. Therefore, it is reasonable that the population increase of $(I_2)_n$ chains results in the corresponding PL enhancement. As pressure increases further, no obvious population increase of the iodine chains can be observed,[11] and instead the interaction enhancement between the iodine chains and the hosting AFI due to the compression of AFI channels plays role on the PL decrease of the confined iodine. Thus, PL decreases rapidly at higher pressure. All these changes can be easily understood by the scene that the PL arises from the $(I_2)_n$ chains. In addition, the

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PL center shows clear redshift as the pressure increases and this will be discussed in the following paragraph.

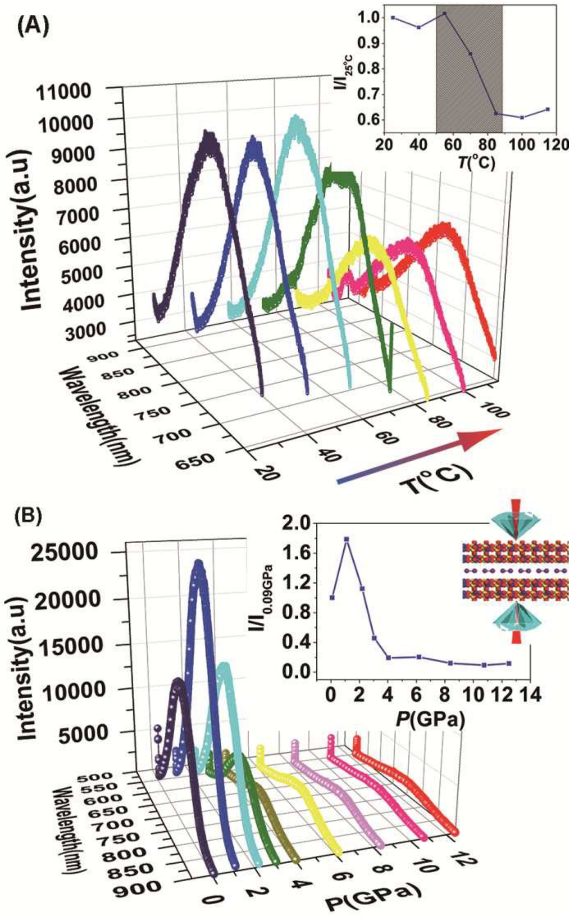

Figure 3 (A) PL spectra of iodine@AFI at different temperature. Inset shows the integrated PL intensity as a function of temperature. (B) The PL spectra of iodine@AFI crystal at high pressure. Inset shows the integrated PL intensity as a function of pressure.

To give further insight on the origin and the transformations of the PL in iodine@AFI, we used a simple model to calculate the band gap of $(I_2)_n$ chains. Due to the fact that only weak van der Wasls interaction and the absence of charge transfer between the confined $(I_2)_n$ chains and the AFI framework, the influence of AFI framework on the electronic band gap of $(I_2)_n$ chains has not been considered in our calculation. Thus, $(I_2)_n$ chain has been constructed as an ideal one dimensional crystal with infinite length in vacuum. Since the $(I_2)_n$ chains formed in the nanochannels might have different lengths and thus exhibit slightly different intermolecular distance in the chains, we change the intermolecular distances in the $(I_2)_n$ chains and to explore the effect of intermolecular distance on the PL of the $(I_2)_n$ chains in the simulation. The effect of the orientation of the iodine molecules arranged in a chain on the PL has also been examined. The result indicates that the intermolecular distance affects the band gap significantly while the orientation of iodine molecules has little effect on the band gap. The closer the molecules in the $(I_2)_n$ chains the lower energy of the band gap, *i.e.*, the energy of the band gap decreases as the intermolecular distance decreases. Moreover, the iodine density in AFI channels should be inhomogeneous and $(I_2)_n$ chains with different lengths and intermolecular distance might exist inside the channels. Such formed chains thus have a relatively broad distribution in the band gap. These different $(I_2)_n$ chains contribute to the PL emission in experiment and thus exhibits a broad feature. Based on our calculation, the $(I_2)_n$ chains with intermolecular distance of around 3.5 Å give a PL peak at 1.78eV, which is close to the strongest emission energy in the photoluminescence bands observed in experiment. This indicates that the $(I_2)_n$ chains in our synthesized iodine@AFI mainly consist of the molecular chains with intermolecular distance of around 3.5 Å. Furthermore, the intermolecular distances of iodine molecules in the chains decreases upon compression, which leads to the decrease of the corresponding band gap under pressure. This well explains the pressure-induced redshift in PL energy of our $(I_2)_n$ chains (see Figure 3 (B)). As we know, vapor-like iodine molecules exhibit sharp and discrete fluorescence peaks due to the electron transition in iodine molecules.[20,21] When the iodine molecules assemble into $(I_2)_n$ chain in 1D nanochannels of AFI, which can be taken as a 1D crystal and possess a band structure. The electrons of the iodine molecule are localized inside the molecule due to the fact that the $(I_2)_n$ chain is a neutral molecular chain. The band structure of such a crystal thus can be estimated by a simple tight-binding approximation model, for which the iodine molecule is considered as a single cell unit. Subsequently, in $(I_2)_n$ chain, the single iodine molecular levels broaden into a band due to the interaction between the neighboring molecules, as well as the possible chain-AFI wall interactions, and thus $(I_2)_n$ chains exhibit different PL spectrum features compared with the vapored iodine. Particularly, the PL behavior from iodine $(I_2)_n$ chains exhibit obvious polarization effect, which is different from that of the vapored iodine molecules. In a word, the theoretical calculation supports that the PL arises from $(I_2)_n$ chains. The PL behavior in molecular nanochains will open new research area in both experiment and theory, which may also have practical application in photoelectric device.

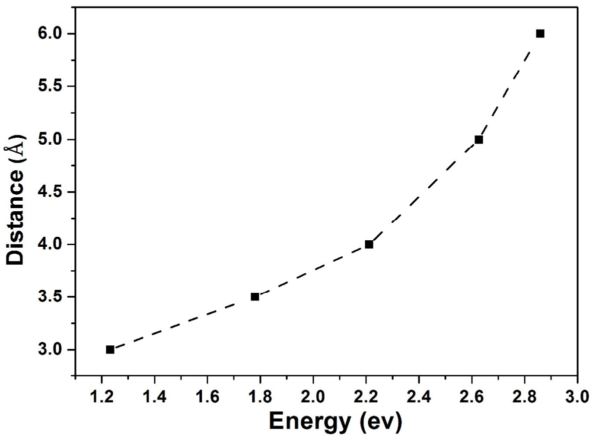

Figure 4 The band gap of $(I_2)_n$ chain as a function of intermolecular distance of the contained I_2 molecules.

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Conclusions

In summary, we observed a unexpected PL from $(I_2)_n$ chains confined in AFI nanochannels. The photoluminescence exhibits strong polarization due to the unique 1D structure of the formed chains. The PL intensity increased as the applied pressure increased, which can be well understood by the fact that the iodine molecules transform into $(I_2)_n$ chains upon compression. The PL intensity decreased when $(I_2)_n$ chains were broken by heating at high temperature. Our calculation suggests that the PL should arise from the intrinsic band structure of $(I_2)_n$ chains. Such unexpected discovery inspires us that more novel properties could be discovered in the atomic/molecular nanochain system compared with the corresponding bulk counterpart, which have the potential of providing new applications.

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