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Communication

Effect of thickness on the photophysics and charge carrier kinetics of graphitic carbon nitride nanoflakes

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ABSTRACT

We investigated the thickness effect on the photophysics and charge carrier kinetics of graphitic carbon nitride nanoflakes (g-CNN) by using ultraviolet visible diffuse reflectance spectroscopy, atomic force microscopy, femtosecond transient absorption spectroscopy, and picosecond time-correlated single photon counting measurement. For the first time, we found that g-CNN displays a layer-dependent indirect bandgap and layer-dependent charge carrier kinetics.

Graphitic carbon nitride (g-CN) has attracted considerable attention since the pioneering work reported by Wang and coworkers in 2009 [1]. g-CN has been successfully used in a wide range of photocatalytic applications such as water splitting [2–6], carbon dioxide reduction [7–10], pollutant degradation [11–13], and bacterial disinfection [14,15]. There are numerous studies related to g-CN on how to optimize its photocatalytic performance under solar light irradiation [16–22]. However, the origin of its photocatalytic activity, particularly the charge transport process of g-CN is seldom reported. Up to date, there are only a few transient absorption spectroscopy studies on g-CN in literatures to address its charge carrier kinetics [23,24]. This is in particular due to the fact that it is difficult to produce a g-CN sample having near-optical quality [25].

In the recent, we investigated the charge carrier kinetics of g-CN nanoflakes (g-CNN) with few layers by using femtosecond transient absorption spectroscopy [26]. We found a new and positive absorption band appears in its femtosecond transient absorption spectrum, which could be attributed to the absorption of the electronic excited state (or the photogenerated electron/hole pair) of g-CNN after light excitation. In combination with the result obtained from a picosecond time-resolved fluorescence measurement, we proposed a kinetic scheme to understand the photophysics and charge carrier kinetics of g-CNN after light excitation. But there still remains unanswered question, for example, the difference in the ultraviolet visible diffuse reflectance spectrum (UVDRS) between g-CNN and bulk g-CN.

Herein, we prepared g-CNN sample with various layers through controlling the heating reflux time of bulk g-CN in tetraethylammonium hydroxide ($N(CH_2CH_3)_4OH$) aqueous solution and studied their photophysics and charge carrier kinetics by using UVDRS, atomic force microscopy (AFM), picosecond time-correlated single photon counting, and femtosecond transient absorption spectroscopy. We found that the indirect bandgap for g-CNN with few layers is larger than that for g-CNN with most layers. We also found that the charge carrier kinetics for g-CNN with few layers is slower than that for g-CN with most layers.

The g-CN sample was synthesized according to the procedure described by Thomas and coworkers [27]. Briefly, 10 g dicyandiamide (DCDA) was put into a close crucible and was heated to a designed temperature of 650 °C with a 2.3 °C/min ramp rate, where it was held for 4 h. After cooling to room temperature, the product was milled into a fine powder in an agate mortar for further characterization and measurement. The g-CNN sample was produced according to the method reported by Panasiuk and coworkers [28]. Briefly, 0.10 g bulk g-CN was mixed with 10.00 mL 1.36 mol/L $N(CH_2CH_3)_4OH$ aqueous solution and kept for a certain time at boiling temperature (about 100 °C) with magnetic stirring and using a reflux condenser to avoid water evaporation.

The UVDRS of g-CNN was recorded on a Shimadzu UV-3600 spectrophotometer equipped with a diffuse reflectance accessory, where its absorption spectrum was referenced to $BaSO_4$. The AFM image of g-CNN was recorded on a Bruker Dimension Icon

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microscope. The femtosecond transient absorption study of g-CNN was performed on a home-made femtosecond transient absorption spectroscopy setup [29]. Briefly, the outputs of a Spectra Physics 1 kHz amplified Ti:sapphire laser were used to pump an optical parametric amplifier (OPA) and to generate the white light continuum. The outputs of the OPA were used as the pump pulses, and the white light continuum generated by a spinning fused silica disk were used as the probe pulses. The timing between the pump and probe pulses was controlled by a Newport M-ILS250CC motorized translation stage. The time resolution of this apparatus was about 150 fs. The fluorescence lifetime of g-CNN was measured using a home-made time correlated single photon counting apparatus [30]. Briefly, the outputs of an OPA pumped by a Spectra Physics 1 kHz amplified Ti:sapphire laser were used as excitation sources. The emission was collected and sent into a Princeton Instruments SP2358 monochromator and detected with a Hamamatsu R3809U-50 MCP-PMT. Next the signal from the R3809U-50 MCP-PMT was amplified by a Becher & Hickl GmbH HFAC-26 preamplifier. Then the output of the HFAC-26 preamplifier and the output of a fast PicoQuant TDA 200 photodiode were connected to a Becher & Hickl GmbH SPC-130 module, respectively, as the start and stop pulses. The instrumental response function of this setup was about 70 ps.

Fig. 1A shows the normalized UVDRS of g-CNN prepared with different heating reflux time of bulk g-CN in 1.36 mol/L N $(CH_2CH_3)_4OH$ aqueous solution, respectively. The symbol g-CNN-x stands for the sample prepared with x minutes heating reflux time of bulk g-CN in 1.36 mol/L N$(CH_2CH_3)_4OH$ aqueous solution. It is clear that the absorption band edge of g-CNN shifts to blue as the increasing the reflux time of bulk g-CN in N$(CH_2CH_3)_4OH$ aqueous solution. The sample g-CNN-240 has a shorter wavelength absorption band edge while the sample g-CNN-20 has a longer wavelength absorption band edge. From the Tauc plot shown in Fig. 1B, we determined that the indirect bandgap for g-CNN-20, g-CNN-60, and g-CNN-240 is about 2.60, 3.08, and 3.31 eV, respectively. It is obvious that the indirect bandgap for g-CNN-240 is about 0.70 eV larger than that for g-CNN-20.

It is reported that the interlayer interaction/coupling in 2-dimensional layer material (2DLM) can dramatically affect its band structure so as to exhibiting distinct layer-dependent electronic and optical properties [31–38]. Many few-layered 2DLMs such as black phosphorus [32], MoS_2 [33–36], WS_2 [37], and PtS_2 [38] have showed layer-dependent bandgaps. The g-CNN is also a 2DLM which should also display a layer-dependent bandgap. To confirm this suggestion, we performed the AFM measurements for g-CNN-20 and g-CNN-240. Fig. 2A displays the AFM image of g-CNN-20. Fig. 2B shows the AFM image of g-CNN-240. Fig. 2C shows the height profiles of g-CNN-20 measured along the lines marked on Fig. 2A. Fig. 2D shows the height profiles of g-CNN-240 measured along the lines marked on Fig. 2B. Fig. 2E displays the height

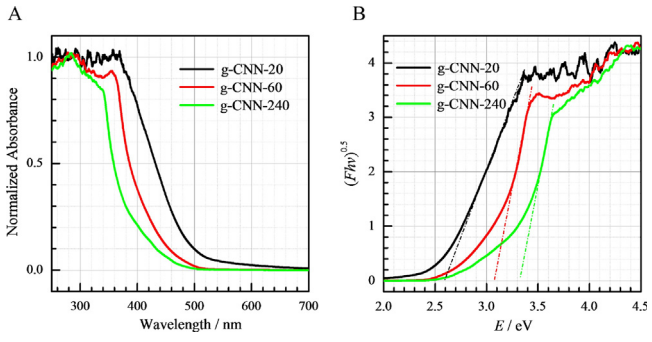

Fig. 1. (A) Normalized UVDRS of g-CNN-20, g-CNN-60 and g-CNN-240, respectively; (B) Tauc plot of g-CNN-20, g-CNN-60 and g-CNN-240, respectively.

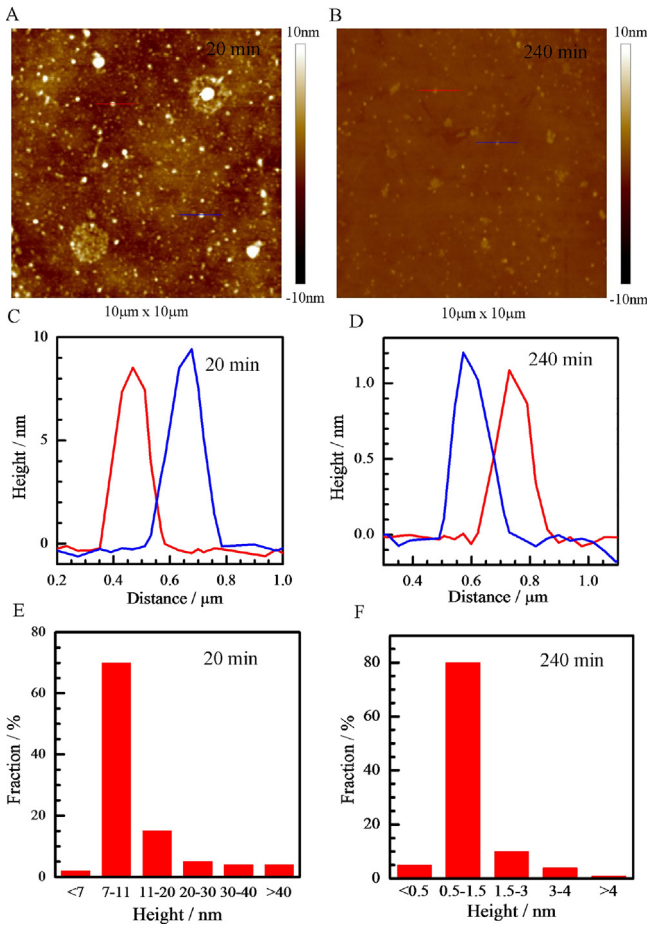

Fig. 2. (A) AFM image of g-CNN-20; (B) AFM image of g-CNN-240; (C) Height profiles of g-CNN-20 measured along the lines marked on A; (D) Height profiles of g-CNN-240 measured along the lines marked on B; (E) Height distributions of g-CNN-20 evaluated from A; (F) Height distributions of g-CNN-240 evaluated from B.

distributions of g-CNN-20 evaluated from the AFM image shown in Fig. 2A. Fig. 2F displays the height distributions of g-CNN-240 evaluated from the AFM image shown in Fig. 2B.

With the data shown in Fig. 2C, we determined that the average thickness for g-CNN-20 is 9 ± 2 nm and that the lateral size for g-CNN-20 is 240 ± 30 nm in diameter. With the data shown in Fig. 2D, we determined that the average thickness for g-CNN-240 is 1.0 ± 0.4 nm and that that the lateral size for g-CNN-240 is 230 ± 20 nm in diameter. The thickness of g-CNN-20 is distinctly thicker than that of g-CNN-240. With the reported thickness for a single-layered g-CNN [28], we derived that the CN layer number for g-CNN-20 is about 20 and that the CN layer number for g-CNN-240 is around 2. The CN layer number for g-CNN-20 is distinctly larger than that for g-CNN-240. These results clearly demonstrated that the interlayer interaction plays an important role on the photophysics of g-CNN. Besides, our results also suggested that the g-CNN with few layers has a larger indirect bandgap and that the g-CNN with most layers has a smaller indirect bandgap, which is well consistent with the literature's report where Zhao and coworkers [38] found that few-layered PtS_2 has a layer-dependent indirect bandgap from 1.6 eV of monolayer to 0.25 eV of bulk. To our knowledge, this is the first report to address that g-CNN has a layer-dependent bandgap.

To deep understand the photophysics of g-CNN, we further performed the femtosecond transient absorption spectroscopy measurements on g-CNN-20 and g-CNN-240, as shown in Fig. 3. Fig. 3A displays the femtosecond transient absorption spectra of g-

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