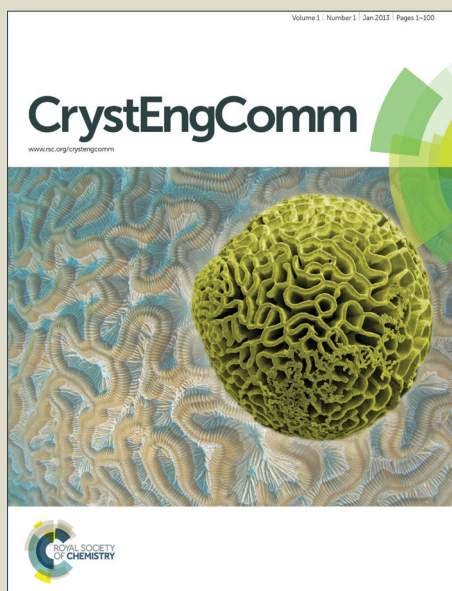


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COMMUNICATION

Synthesis and characterization of single-crystalline graphitic C₃N₄ nanocones

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th October 2014,
Accepted 00th 2014

DOI: 10.1039/x0xx00000x

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Single-crystalline g-C₃N₄ nanocones (g-CNNCs) were successfully synthesized on nickel-covered silicon (100) substrates supported on a graphite frame by a novel plasma sputtering reaction deposition method. The g-CNNCs have the characteristic photoluminescence-peak of g-C₃N₄ and the longitudinal resistivity belonging to semiconductor, which make them have many potential applications.

At the end of the last century, Cohen et al. predicted empirically that β -C₃N₄ might have exceptional hardness even higher than diamond.¹ Afterwards, Teter et al. used the first-principle calculations to further predict several allotropes of C₃N₄, such as α -C₃N₄, β -C₃N₄, cubic C₃N₄ and graphitic C₃N₄ (g-C₃N₄).² In recent years, g-C₃N₄ has become a research hot in the field of material science due to many potential applications induced by its special electronic structure and excellent chemical and thermal stabilities (resulted by its layered covalent C-N-bonding structure).³ The g-C₃N₄ has been prepared by polymer polymerization method and used as photocatalysis to acquire hydrogen from water.⁴⁻¹⁰ However, the g-C₃N₄ powders prepared by the polymer polymerization method usually include the intermediate organic products and need to be purified, which limited their performance. Meanwhile, the small grain size makes it difficult to measure some basic physical parameters of g-C₃N₄, such as resistivity. So, the search for the experimental methods preparing single-crystalline g-C₃N₄ crystals is important to fully develop the properties of this material in the possible applications.

For the preparation of the g-C₃N₄, the traditional methods, such as chemical vapor deposition, physical vapor deposition method etc., were dogged by the difficulty to dissociate the stable N₂ which often resulted in disordered and carbon-rich materials.¹¹⁻¹⁵ In this article, an abnormal glow discharge plasma sputtering reaction deposition (PSRD) method is used to synthesize single-crystalline g-C₃N₄ nanocones (g-CNNCs) in the mixed inlet gas of CH₄, N₂ and H₂. The abnormal glow discharge has been known to be able to produce high concentration nitrogen atoms.¹⁶ In the PSRD method, the g-CNNCs were synthesized under the joint actions of the H⁺-sputtering on the graphite frame to generate the C atoms, the H⁺ etching on the growing graphite, amorphous C and amorphous CN_x structures, and the reaction between the active N atoms and sputtered C atoms. The H⁺ stream with energy of about 350 eV can also strengthen the sharpening effect on the growing nanocones. The PSRD method not

only has a new mechanism in syntheses of the g-CNNCs, but the synthesized g-CNNCs also have good crystallinity and perfectly conical shape which will be conducive to improve their performance and may provide possibilities to discover some new applications.

There are two steps in preparation of g-CNNCs by PSRD. In the first step, 100 nm thick Ni films (as catalyst) were deposited on scratched Si (100) substrates by pulsed laser deposition under 1×10^{-3} Pa. The wavelength, pulse energy, repetition of the used Nd:YAG laser were 532 nm, 50 mJ and 10 Hz, respectively. In the second step, g-CNNCs were fabricated on the Ni-coated Si substrates by PSRD. In this step, the Ni-covered Si substrates were put on a graphite supporter (as cathode), which is right below the tip of the cone-shaped anode.¹⁶ The DC plasma source generated reactive plasma just above the substrates through the abnormal glow discharge with the CH₄, N₂ and H₂ mixed gas inlet [H₂:N₂ = 1:10, CH₄/(N₂+H₂) = 150] under a total pressure of 850 Pa. The discharge voltage and current were 350 V and 180–200 mA, respectively.

The morphologies of the g-CNNCs synthesized at different discharge currents and periods were observed by field emission scanning electron microscopy (FESEM, Hitachi S-4800). It could be found from Fig. 1a that the nickel layer has started to melt and fragment into very small separated spheres with the diameters of 20–40 nm under the heating of the discharge plasma at the discharge current of 180 mA for only 3 min. It was thought that these small nickel spheres provide the nuclei for the formation of incipient nanocones. In Fig. 1b, the incipient g-CNNCs with the base-diameters of 300–400 nm have been grown after the 10 min discharge. As the discharge period increases to 25 min, the g-CNNCs have grown up and their conical shapes become better (Fig. 1c). Figs. 1d and 1e give the surface morphologies of the g-CNNCs synthesized for 45 min discharge at the discharge currents of 180 and 200 mA, respectively. It could be seen from Figs. 1d and 1e that both the g-CNNCs are vertically arranged and closely distributed and have perfect and consistent conical-shapes. It could be estimated that the both g-CNNCs have similar heights (about 2–3 μ m) but different cone-angles (about 10° and 18°, respectively). The decrement of the cone-angle of the g-CNNCs with the increment of the discharge current may be due to the enhancement of the sharpening effect on the growing g-CNNCs. Besides, the thickness of Ni film have profound influence on the growth of the g-CNNCs. Too much or too little of the nickel deposition time will lead to the failed cone-shape of the grown g-CNNCs (Fig. S1, ESI†).

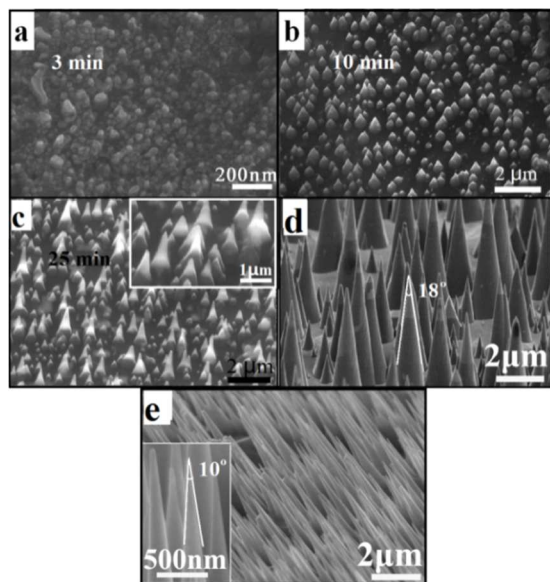


Fig. 1 FESEM micrographs of the g-CNNCs prepared at the discharge current of 180 mA for different discharge periods of (a) 3, (b) 10, (c) 25, and (d) 45 min, respectively. The g-CNNCs prepared at the discharge current of 200 mA for 45 min discharge period is shown in subgraph (e).

To define the structure of the synthesized g-CNNCs, transmission electron microscopy (TEM, JEOL2010) and selected-area electron diffraction (SAED), micro-area electron diffraction (MAED) fitted within the JEOL2010 were carried out. The TEM image of a g-CNNC synthesized at the discharge current of 180 mA for 45 min is shown in Fig. 2. For TEM observation, the as-synthesized g-CNNCs were directly scraped off from the sample surface and transferred onto the copper grid covered by an about 10 nm-thick carbon thin film. The g-CNNC in Fig. 2a has a perfect cone-shape like those shown in Fig. 1d and most of its body is covered by a dark carbon/nickel layer scraped off from the sample surface in the TEM-sample preparation. Figs. 2b and 2c give the SAED patterns at the body and tip of the g-CNNC, respectively. The SAED patterns in Figs. 2b and 2c show that both the tip and body of the g-CNNC are of a single-crystalline structure which is consistent well with hexagonal g-C₃N₄ on the lattice constants and the corresponding angles between the Miller indexes. All the above SAED patterns appear to have the same zone axis along the [010] direction and cone axis along the [001] orientation (the electron incident direction is vertical to cone axis orientation). Meanwhile, the amplified morphology of the tip and the MAED patterns at different places along its cone axis are measured (Fig. 2d). All the above MAED patterns also appear to have the same zone axis along [010] orientation.

In order to collect the structure information of the collective g-CNNCs, the samples were further characterized by X-ray diffraction (XRD, D8 ADVANCE and DAVINCI DESIGN) using Cu K α radiation. Because XRD was measured in an area of 0.16 mm², its patterns could reflect the crystalline structures of the g-CNNCs in a certain area. In the XRD pattern of the g-CNNCs synthesized at the discharge current of 180 mA for 45 min, there are three apparent peaks at 27.3°, 54.6° and 61.2° which are attributed to the 002, 004 and 203 peaks of the g-C₃N₄, respectively (Fig. 3). According to the FWHM of g-C₃N₄-002 peak, the average grain size of g-CNNCs is calculated to be 101.2 nm by the Debye Scherrer formula, which is smaller than the actual ones due to the existence of defects. Besides, a weak peak at 47.70° is attributed to the 022 peaks of cubic silicon

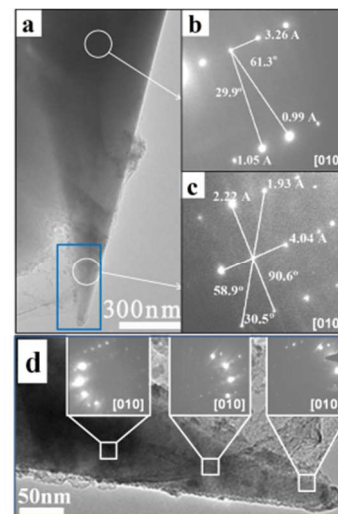


Fig. 2 (a) TEM micrograph of the top of the nanocone grown at the CH₄/(N₂+H₂) ratio of 1/150, the corresponding SAED patterns taken from (b) bodies and (c) tops, and (d) MAED patterns taken from different places along the cone axis.

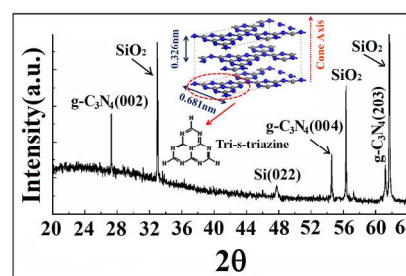


Fig. 3 XRD patterns of the g-CNNCs and the tri-s-triazine network structure of the g-C₃N₄ plane.

(c-Si), and three strong peaks at 32.15°, 56.31° and 61.63° accord well with the 301, 222, and $\bar{1}27$ peaks of monoclinic silicon oxide. The three strong peaks should come from the silicon oxide layer of the substrate and their intensities have no significant change after the growth of the g-CNNCs (Fig. S2, ESI†).¹⁷ Because the graphitic (001) planes of the g-CNNCs are parallel to the substrate surface, the in-plane structure of the graphitic planes (one of their related peaks is at around 13° and the corresponding lattice spacing of the g-C₃N₄ is 0.681 nm) cannot be reflected in our XRD pattern (because there are no peaks in the range of 10-20°, this range is not shown in Fig. 3). The emergence of g-C₃N₄-203 peak may be due to the inclination of the partial nanocones in the lateral region (Fig. S3, ESI†). Meanwhile, it can be calculated that the corresponding lattice spacing of the g-C₃N₄-002 is 0.327 nm, which is well consistent with the d-value in the SAED patterns. This lattice spacing is exactly equal to the stacking distance of graphitic planes with tri-s-triazine structure reported by Thomas et al. and Wang et al.^{18,19} Considering that the tri-s-triazine structure is more stable in the two possible allotropes of g-C₃N₄ (i.e. triazine and tri-s-triazine structures),¹⁹ we inferred that the graphitic planes of the synthesized g-CNNCs are of tri-s-triazine network structure (Fig. 3).

Understanding the photoluminescence (PL) characteristic of the g-CNNCs is necessary to evaluate their photocatalysis and photoelectric properties. PL spectroscopy was measured at room

temperature by a miniature fiber optic spectrometer (USB 2000+) using a He-Cd laser (325 nm, 30 mW) as exciting light source. Fig. 4a shows the PL spectra of the g-CNNCs synthesized at the discharge current of 180 mA for 45 min and the only nickel-covered Si substrate, respectively. In Fig. 4a, there is a notable emission peak centered at 454 nm (corresponding to the band gap of 2.73 eV) with a FWHM of 50 nm, which is in good agreement with the band gap of g-C₃N₄ spheres with tri-s-triazine structure (2.7 eV) synthesized by Wang et al.⁴ It has been known that the c-Si is of an indirect band gap and will not produce photoluminescence, so there is no peak in the PL spectrum of Si substrate. The above phenomena also indicate that the synthesized g-CNNCs is of good g-C₃N₄ crystallinity.

Having knowledge of the electrical properties of the g-CNNCs is also important for the development of their applications. So far, there has not yet been an effective experimental measurement for the resistance of g-C₃N₄. Comparing with the g-C₃N₄ powder, the vertically arranged g-CNNCs are more feasible for the current-voltage (I-V) measurement.²⁰ Here, the longitudinal resistances of the as-synthesized g-CNNCs were measured by Pt-cylinder-tip contact I-V method (the top surface of the Pt-cylinder-tip is 0.5 mm in diameter) using Power SourceMeter (Keithley 2420) (Fig. S4, ESI†). According to the distribution density of the g-CNNCs, the resistance (R) of a single g-CNNC can be gotten and its resistivity (ρ) can be calculated by the following equation (assuming the current direction is of radial distribution):

$$R = \frac{-\rho(r_1 - r_2)^2}{2\pi hr_1 r_2 \ln \cos \theta} \quad \left(\theta = \arctan \frac{r_2 - r_1}{h} \right)$$

Where h is the average height of the nanocones, r₁ and r₂ are the radius of the nanocone top and bottom, respectively. In order to verify the accuracy of the method, we performed the same tests on silicon nanocones (Si-NCs) synthesized by ion sputtering deposition (Fig. S5, ESI†). The I-V curves for the samples of g-CNNC and Si-NC are shown in Fig. 4b, and both of them are nearly consistent with linear characteristic. The resistivity of the measured g-C₃N₄ is calculated to be 3.32 Ω·m and that of Si-NC is 4.42×10³ Ω·m (the relevant test data of the two samples are listed in Table S1, ESI†). Although the calculation results can be affected by the estimation biases of diameter and distribution density, the magnitude of g-C₃N₄ resistivity should be reliable for the resistivity of Si-NC measured by the same method is also in the normal range (the standard resistivity of c-Si crystal 4×10³ Ω·m). It has been known that the g-C₃N₄ has graphite-similar layered structure. But the measured resistivity of g-C₃N₄ (belonging to the semiconductor level) is quite larger than that of graphite [the resistivity of graphite is only (8-13)×10⁻⁶ Ω·m]. The reason should be that the tri-s-triazine network structure of the graphitic planes of the g-C₃N₄ is constituted by the covalent C-N bonds and there are no free electrons for the charge transport.

In conclusion, vertically arranged g-CNNCs have been synthesized using the PSRD method at the discharge voltage and current of 350 V and 180–200 mA. The SEM, TEM and XRD

results show that the as-synthesized g-CNNCs are single-crystalline structure with the [001] growth orientation. The PL spectra demonstrate the characteristic peak of g-C₃N₄ corresponding to the band gap of 2.73 eV. The resistivity of the as-synthesized g-CNNCs measured by Pt-cylinder-tip contact method is about 3.32 Ω·m. This kind of material is promising to be applied in photocatalysis, biological sensors, photoelectric nanodevices, photovoltaic solar cells, etc..

This work is financially supported by the National Basic Research Program of China (973 Program, Grant No. 2012CB934303) and National Natural Science Foundation of China (Grant No.10875030).

Notes and references

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† Electronic Supplementary Information (ESI) available: Morphologies for different nickel deposition time, XRD patterns for g-CNNC sample and bare Si substrate, Inclined g-CNNCs, Electrical testing schematic diagram, Si-NCs, Electrical testing information. See DOI: 10.1039/c000000x/

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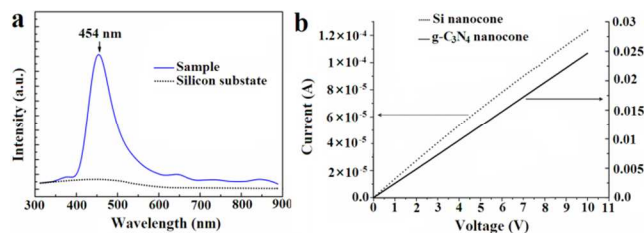


Fig. 4 (a) PL spectra of the g-CNNCs and Si substrate, and (b) the I-V curves for the Si-NCs and g-CNNCs.

Synthesis and characterization of single-crystalline graphitic C_3N_4 nanocones

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CrystEngComm, 2014

DOI: 10.1039/x0xx00000x, Communication

Single-crystalline g- C_3N_4 nanocones were successfully synthesized by a novel plasma sputtering reaction deposition method.

