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Synthesis and characterization of single-crystalline graphitic C$_3$N$_4$ nanocones

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Single-crystalline g-C$_3$N$_4$ 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-C$_3$N$_4$ 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-C$_3$N$_4$ might have exceptional hardness even higher than diamond. Afterwards, Teter et al. used the first-principle calculations to further predict several allotropes of C$_3$N$_4$, such as α-C$_3$N$_4$, β-C$_3$N$_4$, cubic C$_3$N$_4$ and graphitic C$_3$N$_4$ (g-C$_3$N$_4$). In recent years, g-C$_3$N$_4$ 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). The g-C$_3$N$_4$ has been prepared by polymer polymerization method and used as photocatalysis to acquire hydrogen from water. However, the g-C$_3$N$_4$ 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-C$_3$N$_4$, such as resistivity. So, the search for the experimental methods preparing single-crystalline g-C$_3$N$_4$ crystals is important to fully develop the properties of this material in the possible applications.

For the preparation of the g-C$_3$N$_4$, the traditional methods, such as chemical vapor deposition, physical vapor deposition method etc., were dogged by the difficulty to dissociate the stable N$_2$ which often resulted in disordered and carbon-rich materials. In this article, an abnormal glow discharge plasma sputtering reaction deposition (PSRD) method is used to synthesize single-crystalline g-C$_3$N$_4$ nanocones (g-CNNCs) in the mixed inlet gas of CH$_4$, N$_2$ and H$_2$. The abnormal glow discharge has been known to be able to produce high concentration nitrogen atoms. 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 CNTs, 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. The DC plasma source generated reactive plasma just above the substrates through the abnormal glow discharge with the CH$_4$, N$_2$ and H$_2$ mixed gas inlet [H$_2$:N$_2$ = 1:10, CH$_4$/(N$_2$+H$_2$) = 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 µm) but different cone-angles (about 10º and 18º, 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-C$_3$N$_4$ 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$_\alpha$ radiation. Because XRD was measured in an area of 0.16 mm$^2$, 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-C$_3$N$_4$, respectively (Fig. 3). According to the FWHM of g-C$_3$N$_4$-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 47.7° is attributed to the 022 peaks of cubic silicon (c-Si), and three strong peaks at 32.15°, 56.31° and 61.63° accord well with the 301, 222, and 127 peaks of monoclinic silicon oxide. The three strong peaks should come from the silicon oxide layer of the substrate for these peaks also appear in the bare silicon substrates and their intensities have no significant change after the growth of the g-CNNCs (Fig. S2, ESI†). Consider that the g-C$_3$N$_4$ planes are parallel to the substrate surface, the in-plane structure of the g-C$_3$N$_4$ planes 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-C$_3$N$_4$-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-C$_3$N$_4$ is 0.681 nm which is well consistent with the d-value in the SAED patterns. This lattice spacing is exactly equal to the stacking distance of the hexagonal graphite planes (Fig. S2, ESI†). Considering that the g-C$_3$N$_4$-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 the hexagonal graphite planes (Fig. S2, ESI†). Considering that the tri-s-triazine structure is more stable in the two possible allotropes of g-C$_3$N$_4$ (i.e. triazine and tri-s-triazine structures), we inferred that the graphite 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 conditions.
results show that the as-synthesized g-CN NCs are single-crystalline structure with the [001] growth orientation. The PL spectra demonstrate the characteristic peak of g-CN at corresponding to the band gap of 2.73 eV. The resistivity of the as-synthesized g-CN NCs 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..

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Notes and references

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