Long wavelength emissions of periodic yard-glass shaped boron nitride nanotubes

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Extraordinary and stable long wavelength emission (centered at ~685 nm) from the yard-glass shaped boron nitride nanotubes (YG-BNNTs) was observed in their cathodoluminescence and photoluminescence spectroscopy. The mechanism for this near-red light emission at ~685 nm is attributed to the periodical nature of the BNNT units with regular lattice defects. The visible-light emission from YG-BNNTs indicates that this material has great potential for applications as nano-optical and/or nano-optoelectronic devices in nanoscale surgery and spectroscopy. © 2009 American Institute of Physics. [DOI: 10.1063/1.3069278]

One-dimensional nanomaterials have been investigated for the use in nanoscale optoelectronic and photonic applications such as nanoscale surgery and spectroscopy because of their capability for efficient transport of carriers.1 Semicon-ductor nanomaterials are fluorescent with fluorescence efficiencies of as high as 80%, thus they are promising for use in nanosized light sources, laser, light emitting display devices, and medical diagnosis devices.2 The band gaps of III-V nitride nanomaterials range from 1.9 eV for wurtzite structured InN to 6.2 eV for cubic structured BN, making them well suitable for optoelectronic and photonic applications throughout visible into ultraviolet regions. BN nanostructures also have super thermal3 and chemical stabilities,4 which make them ideal nanosized luminescent materials.

Through band gap engineering (including doping and/or introducing lattice defects), it is possible to achieve red, green, and blue emissions from BN nanostructures. Particularly, the visible light emission is vital for nondestructive biological assays and medical imaging purpose.5 Intrinsic cathodoluminescence (CL) of boron nitride nanotubes (BNNTs) without any doping has been investigated and near-UV light emission was observed.6 A broad and tunable visible light emission from Eu-doped BNNTs excited by electrons7 and from Cu-doped BNNTs8 as well as visible photoluminescence (PL) emission from Si-doped BNNTs,9 have been reported. However, these methods introduce foreign elements and the resultant emissions are relatively low. Therefore, it is a great challenge to achieve strong visible-light emission, particularly long wavelength emission, in BN nanostructures.

In this letter, we demonstrate an observation of extraordinary, stable, and long wavelength emission from yard-glass (YG) shaped BNNTs filled with Fe nanoparticles. This strong emission is attributed to the periodical nature of the BNNT units with regular lattice defects. The YG-BNNTs with strong long wavelength emission can be used as nanosized light emission diodes.

Periodically Fe-filled YG-BNNTs were grown by catalytic decomposition of ammonia at a temperature of 1300 °C using a floating catalyst method. The detailed growth method and their structural characteristics can be found in Ref. 10. In order to compare the structural characteristics between the periodically Fe-filled YG-BNNTs and conventional bamboo-structured (BS) BNNTs,11 transmission electron microscopy (TEM) has been employed. Figures 1(a) and 1(b) are typical TEM images of YG-BNNT and BS-BNNT samples. YG-BNNT is a BNNT connected by uniform YG units (in terms of their shape and size) with iron particles periodically filled in their knollike nodes. To determine the fine structures of YG-BNNTs and BS-BNNTs, high resolution TEM was employed to view different locations of a typical YG unit [as marked in Fig. 1(a)] and a bamboo BNNT [as marked in Fig. 1(b)]. Figures 1(c)–1(j) reveal that YG-BNNTs and bamboo BNNTs are highly crystalline and their in-plane [(1010) planes] lattice spacing [Figs. 1(e) and 1(j)] is ~0.22 nm. Moreover, both of them display gradual disappearance of BN layers at the outer surface toward the open end, leading to a wedge-shaped open end. Both the wall and knob are well crystallized with the identical lattice spacing of ~0.33 nm [corresponding to the d002 spacing in bulk hexagonal (h-) BN]. The most distinct characteristic that should be emphasized is that their joints are totally different, as shown in Figs. 1(d) and 1(h). Compared to the sequent connection of BS-BNNTs, which BN layers cover the sequent knob, the connection of YG-BNNTs is in an inserted mode that has lattice defects as marked by a circle. Moreover, lattice stress should exist in the bended structures.

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which can be attributed to the curvature-induced peak is similar to that of bulk counterphase BN vibrational mode within BN plane. This temperature. Figure 2 features were analyzed from Raman spectra at room temperature. Figure 2(a) is a typical Raman spectrum of YG-BNNTs, in which the dominant peak centered at 1366 cm$^{-1}$, but shifts toward lower wave number, which can be attributed to the curvature-induced $E_{2g}$ mode close to that observed in chemical vapor deposited $h$-BN (16–30 cm$^{-1}$). C-doped BNNTs (18 cm$^{-1}$), and Si-doped BNNTs (28 cm$^{-1}$), which are characterized by a large amount of defects. Therefore, the peak broadening can be attributed to lattice defects observed in YG-BNNTs [refer to Fig. 1(d)]. To further confirm the lattice phonon vibrations, Fourier transform infrared spectroscopy (FTIR) characterization was carried out. A typical result is presented in Fig. 2(b), showing strong vibrations with a dipole moment at 798 and at 1366 cm$^{-1}$ with a pronounced shoulder at 1540 cm$^{-1}$, which can be indexed to the $A_{2u}$ (BN vibration out-of-plane polarization) and $E_{1u}$ (BN vibration in-plane polarization) modes, respectively. Since BN is a polar material with N being slightly negative charged and B being slightly positive charged, the long-range characteristics of the Coulomb potential give rise to a macroscopic electric field $E$ for longitudinal phonons. Such a phenomenon can result in splitting at the longitudinal optical (LO) and transverse optical (TO) modes. Therefore, in pyrolytic $h$-BN, the $A_{2u}$ mode splits into $A_{2u}$ (TO) and $A_{2u}$ (LO), with a shoulder at 767 cm$^{-1}$ and a peak at 783 cm$^{-1}$, while the $E_{1u}$ (TO) and $E_{1u}$ (LO) modes are located at 1367 and 1510 cm$^{-1}$. For the as-prepared YG-BNNTs, the $E_{2u}$ is shifted to 798 cm$^{-1}$ without any peak splitting, which is slightly lower than the reported polycrystalline $h$-BN (Ref. 19) but close to multi-walled BN nanotubes. This can be explained by the existence of lattice defects in the YG-BNNTs that is responsible for the softening of infrared responses and their TO modes. Otherwise, the position ($E_{1u}$) at 1366 cm$^{-1}$ is close to the in-plane $E_{1u}$ (TO) mode observed in the pyro-

FIG. 1. Typical TEM images of YG-BNNTs (a) and conventional BS-BNNTs (b). Detailed atomic structures of locations of [(c)–(f)] a YG unit [as marked in (a)] and [(g)–(j)] a bamboo BNNT [as marked in (b)].

To evaluate their optoelectronic characteristic, phonon features were analyzed from Raman spectra at room temperature. Figure 2(a) is a typical Raman spectrum of YG-BNNTs, in which the dominant peak centered at 1364 cm$^{-1}$ can be attributed to the $E_{2g}$ mode, the so-called counterphase BN vibrational mode within BN plane. This peak is similar to that of bulk $h$-BN in the range of 1366–1370 cm$^{-1}$, but shifts toward lower wave number, which can be attributed to the curvature-induced $E_{2g}$ mode close to that observed in chemical vapor deposited $h$-BN (16–30 cm$^{-1}$). C-doped BNNTs (18 cm$^{-1}$), and Si-doped BNNTs (28 cm$^{-1}$), which are characterized by a large amount of defects. Therefore, the peak broadening can be attributed to lattice defects observed in YG-BNNTs [refer to Fig. 1(d)]. To further confirm the lattice phonon vibrations, Fourier transform infrared spectroscopy (FTIR) characterization was carried out. A typical result is presented in Fig. 2(b), showing strong vibrations with a dipole moment at 798 and at 1366 cm$^{-1}$ with a pronounced shoulder at 1540 cm$^{-1}$, which can be indexed to the $A_{2u}$ (BN vibration out-of-plane polarization) and $E_{1u}$ (BN vibration in-plane polarization) modes, respectively. Since BN is a polar material with N being slightly negative charged and B being slightly positive charged, the long-range characteristics of the Coulomb potential give rise to a macroscopic electric field $E$ for longitudinal phonons. Such a phenomenon can result in splitting at the longitudinal optical (LO) and transverse optical (TO) modes. Therefore, in pyrolytic $h$-BN, the $A_{2u}$ mode splits into $A_{2u}$ (TO) and $A_{2u}$ (LO), with a shoulder at 767 cm$^{-1}$ and a peak at 783 cm$^{-1}$, while the $E_{1u}$ (TO) and $E_{1u}$ (LO) modes are located at 1367 and 1510 cm$^{-1}$. For the as-prepared YG-BNNTs, the $E_{2u}$ is shifted to 798 cm$^{-1}$ without any peak splitting, which is slightly lower than the reported polycrystalline $h$-BN (Ref. 19) but close to multi-walled BN nanotubes. This can be explained by the existence of lattice defects in the YG-BNNTs that is responsible for the softening of infrared responses and their TO modes. Otherwise, the position ($E_{1u}$) at 1366 cm$^{-1}$ is close to the in-plane $E_{1u}$ (TO) mode observed in the pyro-

FIG. 2. (a) Raman spectrum and (b) FTIR spectrum of YG-BNNTs. (c) CL spectra of a single YG-BNNT and BS-BNNT, collected at an accelerating voltage of 5 kV and a current of 1.2 nA. (d) PL spectra of YG-BNNTs and BS-BNNTs, collected under $T$ $=300$ K and a laser with excitation at 325 nm.
lytic h-BN (1367 cm\(^{-1}\)),\(^\text{17}\) the polycrystalline bulk h-BN (1377 cm\(^{-1}\)),\(^\text{19}\) and pure BNNTs (1367 cm\(^{-1}\) (Ref. 15) or 1372 cm\(^{-1}\)),\(^\text{10}\) but lower than that in h-BN monolayers epitaxially deposited on metal surfaces (1395 cm\(^{-1}\)),\(^\text{20}\) which should be attributed to the curvature of BN layers in the closed end of YG-BNNTs.

CL spectrum of the synthesized YG-BNNTs was measured in comparison with that of BS-BNNTs [Fig. 2(c)] at the room temperature. Compared with a single emission at \(\sim 352\) nm from the BS-BNNTs, the spectrum of YG-BNNTs is composed of three relatively strong emissions centered at 352, 440, and 685 nm. The peaks centered at 352 nm (corresponding to 3.52 eV) and 440 nm (corresponding to 2.82 eV) are typical for BN nanostructures,\(^\text{6,18,23}\) or multi-walled cylindrical BNNTs,\(^\text{23}\) which are excited by high-energy electrons. These ultraviolet light emissions were very stable for a long irradiation time of 10 min. It is of interest to note that the emission at 685 nm (corresponding to 1.80 eV) is the strongest one among the three emissions. The band structures of BNNTs were investigated both theoretically and experimentally.\(^\text{24}\) It was reported that the electronic structures of BNNTs can be tuned between 1 and 5.8 eV by the direct band gap,\(^\text{8,23}\) radiative transitions,\(^\text{6,18,23}\) excitonic effects,\(^\text{9}\) and doping/replacement.\(^\text{7}\) The broad low-energy emissions in the 500–600 nm range are often considered to be due to defects and the B and/or N vacancies.\(^\text{10}\) Moreover, visible emissions at 490 and 550 nm were observed due to Si doping\(^\text{10}\) and Eu doping in BS-BNNTs,\(^\text{7}\) respectively. Taking all these analyses into account, the emission at 685 nm should have a different emission mechanism, which may be attributed to the specific structures of YG-BNNTs, although there is a possibility that the BNNTs were doped by Fe. Since no Fe was detected in YG-BNNTs from electron-energy-loss spectroscopy analysis and the intensity of the 685 nm emission is significantly strong, we can rule out the possibility that this long wavelength emission is caused by Fe doping. As evidenced in Figs. 1(d) and 1(h), the YG-BNNTs have the inserting connection mode which gesticates lattice defects to induce this emission at 685 nm. This long wavelength emission will be important for the optoelectronic applications in scatheless biological essay and medical analysis, and also indicates that the light emission from near-UV to near-red light range can be tuned by structural engineering (introducing defects), not by doping.

To further evaluate their optoelectronic properties, the PL spectra, excited at 325 nm (\(\sim 3.81\) eV) and 300 K of a concentrated ensemble of the YG-BNNTs and Bamboo BNNTs were analyzed at a macroscopic scale [Fig. 2(d)]. The PL spectrum of YG-BNNTs is composed of three individual luminescence emissions centered at \(\sim 352, \sim 470,\) and \(\sim 680\) nm, which are well consistent with the CL observations. On the contrary, only one peak centered at \(\sim 352\) nm with a shoulder at \(\sim 450\) nm is observed in BS-BNNTs. From these comparisons, it can be concluded that the PL regions at \(\sim 350–470\) nm can be attributed to the intrinsic emission from BS-BNNTs, which have a large number of bent BN layers and associated defects similar to the cup-shaped BN layers in the BS nanotubes. The near-red emission centered at \(\sim 680\) nm can be attributed to lattice defects in the periodical structures and their inserting connection mode. Figure 2(d) demonstrates again that the introduction of structural defects is feasible to tune light emission from the near-UV to near-red light range.

In conclusion, a stable long wavelength emission centered at 685 nm from the YG-BNNTs filled with Fe nanoparticles was observed. This near-red light emission is originated from structural defects existing in the unique periodical structures, which are different from the doped BNNTs, and indicates that it is feasible to achieve visible light emission from the periodical structure of BNNTs without doping. The strong near-red light emission is expected to have extensive applications in optoelectronics and medical diagnosis.

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