

# One-step growth and field emission properties of quiasaligned TiO<sub>2</sub> nanowire/carbon nanocone core-shell nanostructure arrays on Ti substrates

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Quasialigned nanoarrays consisting of TiO<sub>2</sub> nanowire cores and carbon nanocone shells have been produced directly on titanium foils via a simple one-step thermal reaction under acetone vapor at 850 °C. The nanowire cores are single-crystalline rutile TiO<sub>2</sub> with diameters of 15–20 nm and the conical carbon shells are amorphous with gradually decreasing thicknesses from 200–300 nm at the bases to 5–10 nm at the tips. Disparity of precipitation and etching of carbon shell give rise to the conical shape. Such TiO<sub>2</sub>/C nanocone arrays on a conducting substrate are a new member of the conical nanostructures and promising field electron emitters. © 2008 American Institute of Physics. [DOI: 10.1063/1.2955519]

One-dimensional nanostructures such as nanotubes, nanowires, and nanocones have the proper electron field emission (FE) geometries because of their sharp tips and high aspect ratio, that is, high field enhancement factor ( $\beta$ ).<sup>1,2</sup> Different from nanowires or nanotubes with uniform diameters, nanocones constitute a new class of nanomaterials which have gradually decreasing diameters from the base to the tip.<sup>3–6</sup> The unique morphology makes nanocones better suited for applications in scanning probes and field emitters due to their radial rigidity which can enhance the signal-to-noise ratio that can otherwise be affected by mechanical and/or thermal vibration.<sup>3,4</sup> Furthermore, conical field emitters exhibit a smaller screening effect because the distances between adjacent nanotips are large as a result of the submicrometer scale bases.<sup>7,8</sup> Thus, nanocones are more suitable as cathode field emitters on account of the stability and high  $\beta$  offered by the conical structure. Recently, modification of nanocones or nanowires by coating with other materials to form core-shell nanostructures has been shown to significantly improve their chemical and physical properties including FE performances.<sup>9–17</sup> In general, the shell materials are introduced after formation of the nanocones or nanowires via complex multistep processes.<sup>15–17</sup> It will be technologically simpler and more economical if coating of the nanocones or nanowires can be implemented *in situ* during growth of the core-shell structures.

In this work, quiasaligned TiO<sub>2</sub> nanowire/carbon nanocone core-shell nanostructure arrays (TiO<sub>2</sub>/C nanocone arrays) were fabricated directly on a conducting Ti substrate via a simple one-step thermal reaction under acetone vapor at 850 °C. Different from the conventional core-shell nanocone arrays such as Si/C nanocones<sup>12</sup> possessing a nanoconical core and carbon coating, these TiO<sub>2</sub>/C nanocone arrays have a uniform TiO<sub>2</sub> nanowire core and a conical carbon shell,

thus embodying a conical shape. Since the Ti foil serves as both the Ti source and substrate, synthesis and assembly of the TiO<sub>2</sub>/C nanocone arrays on a conducting Ti substrate are accomplished in a single step. The conducting Ti substrate provides a direct path for electron transport from the cathode to the nanocones. This configuration bodes well for FE as confirmed by this study. The TiO<sub>2</sub>/C nanocone arrays reported here not only constitute a new member of the conical nanostructures, but also are excellent field electron emitters.

Titanium foils (99.6% purity, 10 × 10 × 1 mm<sup>3</sup>) were degreased ultrasonically in acetone, isopropanol, and ethanol sequentially, followed by polishing in a solution containing H<sub>2</sub>O, HF, and HNO<sub>3</sub> with a volume ratio of 5:1:4 for 5 min to remove the surface native oxide layer. After rinsing with de-ionized water and drying under flowing nitrogen, the Ti foil was loaded onto a ceramic substrate placed in the center of an alumina tube inside a horizontal tube furnace. The reactor was purged with argon several times to remove residual oxygen and/or moisture before being heated to 850 °C under Ar. Acetone was subsequently introduced into the chamber by argon at a flow rate of 150 SCCM (SCCM denotes standard cubic centimeter per minute at STP). The reaction proceeded for 1.5 h and then the sample was cooled to room temperature under Ar. The black homogeneous products were characterized by x-ray diffraction (XRD) (Philips X' Pert Pro), FE scanning electron microscopy (FE-SEM) (JSM 6335F), transmission electron microscopy (TEM) (Philips CM20), high-resolution TEM (HR-TEM) (JEM-2010F), selected-area electron diffraction (SAED), and energy-dispersive x-ray spectroscopy (EDS) (Oxford INCA 200). Micro-Raman spectra were acquired at room temperature on a Renishaw 2000 Raman spectrometer equipped with a 514.5 nm Ar<sup>+</sup> laser as the excitation source. The FE measurements were conducted on a parallel-plate diode configuration in a test chamber maintained at a pressure of 9.0 × 10<sup>-5</sup> Pa.

Figures 1(a) and 1(b) depict the representative low- and high-magnification FE-SEM images of the product and reveal uniform growth of quiasaligned nanocone arrays on the Ti substrate. These nanocones have a smooth surface and

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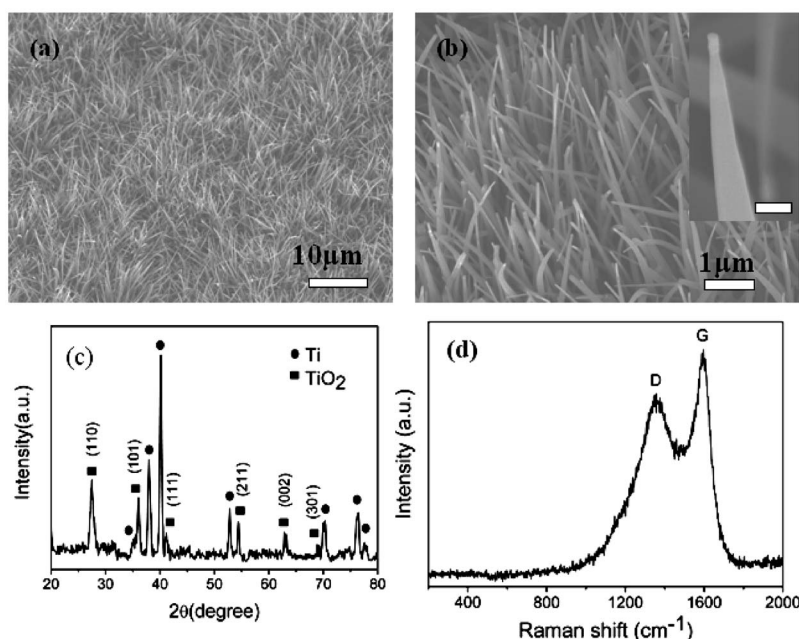


FIG. 1. (a) Low-magnification SEM image, (b) high-magnification SEM image, (c) XRD pattern, and (d) Raman spectroscopy of the synthesized product. The inset in (b) shows the tip of a nanocone. The scale bar is 100 nm.

have lengths of several micrometers. Their diameters decrease along the growth direction ending with sharp tips of about 20–30 nm [inset in Fig. 1(b)]. The corresponding XRD pattern of the products is displayed in Fig. 1(c). The main diffraction peaks can be indexed to tetragonal rutile  $\text{TiO}_2$  (Ref. 18) in addition to those from the Ti substrate.<sup>19</sup> The Raman spectrum [Fig. 1(d)] of the products shows two strong peaks located at 1356 and 1596  $\text{cm}^{-1}$ , which correspond to the D and G bands of amorphous carbon, respectively.<sup>20</sup> A shift of the G peak from its normal value of 1580–1596  $\text{cm}^{-1}$  is an indication of nanocrystalline graphite or  $sp^2$  clusters<sup>20,21</sup> suggesting that the conical carbon shell contains nanocrystalline graphite or  $sp^2$  clusters. Such a structure favors FE because the high content  $sp^2$  provides better electron conduction.<sup>20</sup>

The TEM micrographs in Figs. 2(a) and 2(b) show that the nanocones have a core-shell structure with a uniform nanowire core and conical shell. The nanowire core has a uniform diameter of about 15–20 nm. However, the shells have diminishing thicknesses varying from 200–300 nm at the base to 5–10 nm at the tip, thus providing a conical shape. The HR-TEM images indicate that the nanowire core is single crystal and the conical shell is amorphous. The SAED pattern in the inset of Fig. 2(b) suggests that the nanowire core has a tetragonal rutile  $\text{TiO}_2$  structure with growth along the [101] direction. Figure 2(c) is a typical HR-TEM image of the tip of a core-shell nanocone. The disordered lattice planes of carbon around the  $\text{TiO}_2$  core have a thickness of 6 nm. The lattice spacing between adjacent lattice planes of the nanowire core is approximately 0.25 nm, corresponding to the distance between the two (101) planes of rutile  $\text{TiO}_2$ . The chemical composition of the center core and conical shell of the nanocones are further determined by EDS. As shown in Fig. 2(d), the nanowire core is mainly composed of Ti and O whereas the outer conical shell is mostly carbon.

At 850 °C, acetone first decomposes thermally into carbon-containing and oxygen-containing species such as  $\cdot\text{CH}_3$  radicals and CO.<sup>22</sup> The CO gas preferentially adsorbs on the Ti surface and reacts with Ti to form  $\text{TiO}_2$  and C.<sup>23</sup> The Ti atoms in the Ti foil diffuse upwards through the

formed  $\text{TiO}_2$  and react continuously with CO to form more  $\text{TiO}_2$  species, which precipitate or deposit on the freshly formed  $\text{TiO}_2$  particles epitaxially. Finally,  $\text{TiO}_2$  nanowires are formed. At the same time, carbon atoms produced by the reaction  $\text{Ti} + 2\text{CO} = \text{TiO}_2 + 2\text{C}$  and decomposition of  $\cdot\text{CH}_3$  radicals precipitate *in situ* on the surface of the  $\text{TiO}_2$  to form the carbon shell. On the substrate surface,  $\cdot\text{CH}_3$  is more

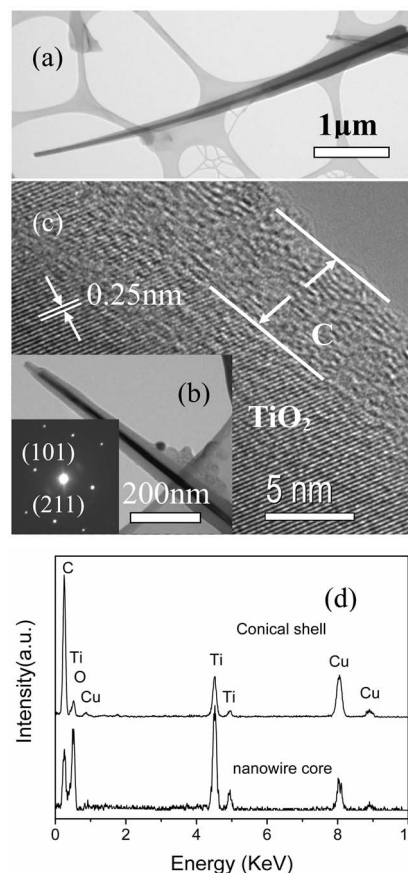


FIG. 2. TEM image of (a) nanocone and (b) its tip part. The inset in (b) is the corresponding SAED pattern. (c) Lattice-resolution HRTEM image. (d) EDS spectrum of a core-shell nanocone revealing that the core is single crystalline rutile  $\text{TiO}_2$  and the conical shell is amorphous carbon.

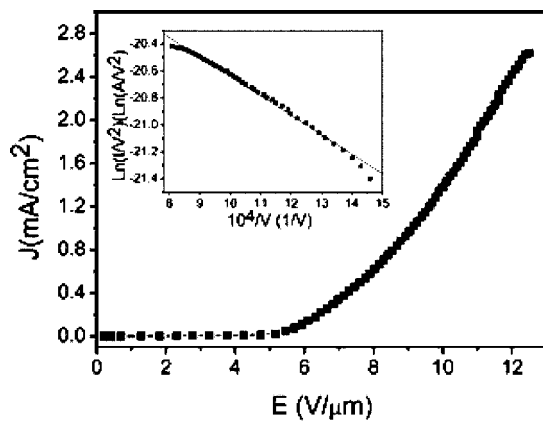


FIG. 3. FE current density ( $J$ ) of the  $\text{TiO}_2/\text{C}$  core-shell nanocone arrays as a function of the applied electric field ( $E$ ). The inset is the corresponding FN plot of  $\ln(I/V^2)$  vs  $1/V$ .

prone to decomposing thermally due to the relatively high temperature and hence, more carbon atoms precipitate onto the base of the  $\text{TiO}_2$  nanowires. However, at the tip, the precipitation rate of C from  $\cdot\text{CH}_3$  decomposition is smaller due to the lower temperature, thus resulting in the conical shape. On the other hand, hydrogen produced by pyrolytic decomposition of  $\cdot\text{CH}_3$  can also etch the deposited carbon atoms to generate hydrocarbons.<sup>24</sup> Owing to the light mass, H atoms from  $\cdot\text{CH}_3$  decomposition will move upwards and so there is more H at the top (tip) than on the bottom (base). That is to say, etching of the carbon shell is faster at the tip. It is considered that the different deposition and etching rates of C atoms at different sites along the nanowire core growth direction are responsible for the final conical shape.

FE measurements of  $\text{TiO}_2/\text{C}$  nanocone arrays are similar to those reported in our previous study.<sup>25</sup> The synthesized products serve as the FE cathode and another plate-shaped stainless steel electrode is used as the anode. Figure 3 shows the measured FE current density ( $J$ ) as a function of the applied electric field ( $E$ ) at a sample-cathode distance ( $d$ ) of  $100\ \mu\text{m}$ . The turn-on field ( $E_{\text{to}}$ ), which is usually defined as the electric field that produces a current density of  $10\ \mu\text{A}/\text{cm}^2$ , is found to be  $3.1\ \text{V}/\mu\text{m}$ . When the applied electric field is raised to  $12.5\ \text{V}/\mu\text{m}$ , a current density as high as  $2.7\ \text{mA}/\text{cm}^2$  is obtained. The  $E_{\text{to}}$  of the  $\text{TiO}_2/\text{C}$  nanocone arrays is comparable to that of carbon nanotubes<sup>26</sup> and lower than that of SiC nanorods,<sup>27</sup> ZnO nanowires,<sup>28</sup> ZnO nanopencils,<sup>29</sup>  $\text{TiO}_2$  nanowires,<sup>30</sup> AlN nanocones,<sup>4</sup> and core-shell  $\text{Ga}_2\text{O}_3/\text{C}$  nanowires,<sup>10</sup> SiC/C nanowires,<sup>14</sup> SiC/BN nanowires.<sup>31</sup>

The FE current-voltage characteristics are further analyzed by the Fowler–Nordheim (FN) equation,<sup>1,25</sup>

$$I = \alpha(A\beta^2 V^2 / \varphi d^2) \exp(-B\varphi^{3/2} d / \beta V),$$

where  $I$  is the emission current,  $V$  is the applied voltage,  $\varphi$  is the work function of the emitting materials,  $\alpha$  is emission area,  $\beta$  is field enhancement factor, and  $A$  and  $B$  are constants with values of  $1.56 \times 10^{-10}\ \text{A eV V}^{-2}$  and  $6.83 \times 10^3\ \text{V eV}^{-3/2}\ \mu\text{m}^{-1}$ , respectively. The FN plots of  $\ln(I/V^2)$  versus  $1/V$  (inset in Fig. 3) show good linearity within the measurement range suggesting that electron emission from the  $\text{TiO}_2/\text{C}$  nanocone arrays follows the FN behavior. As-

suming the work function of C to be  $5\ \text{eV}$ ,<sup>2,26</sup> the  $\beta$  value is estimated to be about 5304. The high  $\beta$  value of the quialigned  $\text{TiO}_2/\text{C}$  nanocone arrays is believed to stem from the sharp tips, high aspect ratio, low screening effect, and good electrical contact between the  $\text{TiO}_2/\text{C}$  nanocones and conducting Ti substrate. The emission current stability is also examined. A current density fluctuation within 8% at an average current of  $1.05\ \text{mA}/\text{cm}^2$  over 4 h indicates rather stable emission.

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