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Enhanced field emission properties of tilted graphene nanoribbons on aggregated TiO_2 nanotube arrays

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ABSTRACT

Graphene nanoribbons (GNRs) slanted on aggregate TiO_2 nanotube arrays (A-TNTs) with various compositions as field-emitters are reported. The morphology, crystalline structure, and composition of the as-obtained specimens were characterized by field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and Raman spectrometry. The dependence of the turn-on electric field and the field enhancement factor β on substrate morphology was studied. An increase of GNRs reduces the specimens' turn-on electric field to 2.8 V/μm and the field enhancement factor increased rapidly to about 1964 with the addition of GNRs. Results show a strong dependence of the field emission on GNR composition aligned with the gradient on the top of the A-TNT substrate. Enhanced FE properties of the modified TNTs can be mainly attributed to their improved electrical properties and rougher surface morphology.

1. Introduction

In electron field emissions (FE), 1-D nanoscale field emission electron sources, such as nanowires, nanofibers and nanotubes, have been extensively investigated because of their high aspect ratio and small radii of curvature [1–4]. TiO_2 nanotube arrays (TNTs) are a natural oxide with a wide band gap (3.1–3.2 eV) and work function (~4.4 eV) [5,6], and have been used as FE emitters [7–9] due to their unique advantages including high aspect ratio, stable mechanical structures, and good thermal and chemical stability in various special environments. TNTs have recently been successfully fabricated by chemical bath deposition [10,11], hydrothermal techniques [12], seed growth method [13] electro deposition [14,15], and electrochemical anodic oxidation. Electrochemical anodization growth is simpler, cheaper, and more easily controlled by adjusting technical parameters to fabricate a high degree of TNT uniformity. However, TNTs in the anatase phase are wide band-gap semiconductors with high resistance which will depress the transmission of electrons in FE applications. Therefore, some studies have tried to dope selective elements into TNTs to enhance FE properties because doping creates additional energy levels within the band-gap, thus reducing the work function and increasing conductivity. For example, Wang et al. doped very small amounts of iron atoms into TiO_2 to prepare Fe-doped TNTs, thus obtaining a lower turn-on electric field of 12 V/μm [16]. Liu et al. found that nitrogen implanted by thermal treatment resulted in a lower turn-on electric field of 11.2 V/μm [6]. Moreover, Wang et al. treated TiO_2 nanotubes at 550 °C under a mixed flux of argon and acetylene to form carbon-doped TNTs which can reduce the turn-on electric field to 5.0 V/μm [17]. TNTs modified with carbon or carbon nanotubes could induce localized occupied states in the band-gap, resulting in an enhanced emission effect [18–20]. Recently, graphene nanoribbons (GNRs) have been shown to be excellent field emitters due to their high aspect ratio, large number of edges, and excellent conductivity [21]. GNRs could be easily implanted into TNTs without thermal treatment, and can even be deposited easily onto plastic or glass substrates at room temperature. However, field emissions using GNRs remain a challenge, because they lay widthways on the substrate surface which will depress the field emission efficiency. In this research, TNTs are transformed into aggregated TNTs (A-TNTs) with different geometrical structures after H_2O_2 post-treatment for 1 h at room temperature. Various quantities of GNRs are deposited on top of A-TNTs (GNRs/A-TNTs) with different morphologies to make the GNRs lay on a slant with respect to the substrate surface, leading to

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improved field emission performance. The influence of the field emission property and the composition of GNRs/A-TNTs on the field emission performance are discussed and compared.

2. Experiment

High purity Ti foils (99.6% purity, 0.2 mm thickness) with dimensions of $2 \times 2\ cm^2$ were dislodged ultrasonically in acetone and ethanol for 30 min each, followed by rinsing with deionized water for 30 min and dried in air at room temperature. The cleaned Ti foils were immersed in an anodizing electrolyte solution mixed with 0.3 wt% of ammonium fluoride (NH_4F), 2 wt% Deionized water (Deionized water, H_2O), and glycol (Ethylene glycol, EG) as an anode with a distance of 20 mm to the platinum cathode. TNTs were grown by anodization of the electropolished Ti sheets in a two-electrode system at a constant applied voltage of 20–50 V for 1 h with magnetic agitation at room temperature. The cleaned TNTs in an amorphous state were then air-dried and crystallized in

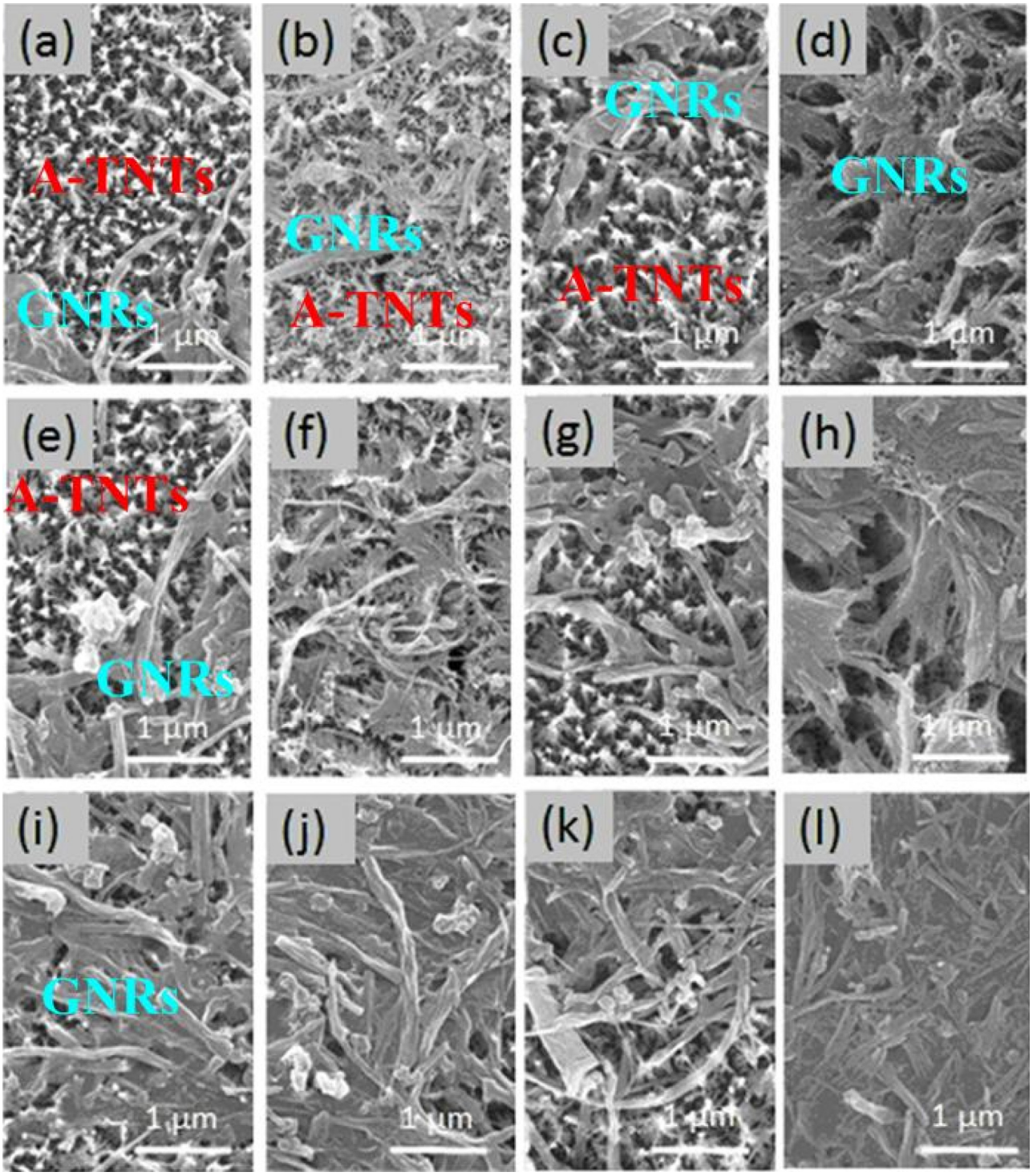

Fig. 1. FE-SEM images of the surface morphology of 0.3 ml GNRs/A-TNTs fabricated with applied voltages of (a) 20 V, (b) 30 V, (c) 40 V, and (d) 50 V; 0.6 ml GNRs/A-TNTs fabricated with applied voltages of (e) 20 V, (f) 30 V, (g) 40 V, and (h) 50 V; 0.9 ml GNRs/A-TNTs fabricated with applied voltages of (i) 20 V, (j) 30 V, (k) 40 V, and (l) 50 V.