

Supplementary Information

Synthesis of positively-charged amino-functionalized MWNTs: Amino-functionalized MWNTs were employed herein for the layer-by-layer assembling with GT_x -Pd. Firstly, the raw MWNTs were refluxed in a concentrated H_2SO_4/HNO_3 mixture (3/1, v/v) at $70^\circ C$ to prepare carboxylic acid functionalized MWNTs (COOH-MWNTs), followed by washing several times with distilled water and drying under vacuum. Then, 0.3 g of the dried COOH-MWNTs was chlorinated by refluxing with 30 ml $SOCl_2$ under a dry air atmosphere at $70^\circ C$ for 12 h. Surplus $SOCl_2$ was removed from the system by vacuum distillation. Amine functionalized MWNTs (NH_2 -MWNTs) were then obtained by reaction with $NH_2(CH_2)_2NH_2$ in dehydrated toluene (Aldrich) for 24 h at $70^\circ C$. After washing with ethanol and distilled water several times, the as-obtained powder was dried under vacuum at $50^\circ C$ for 24 h.

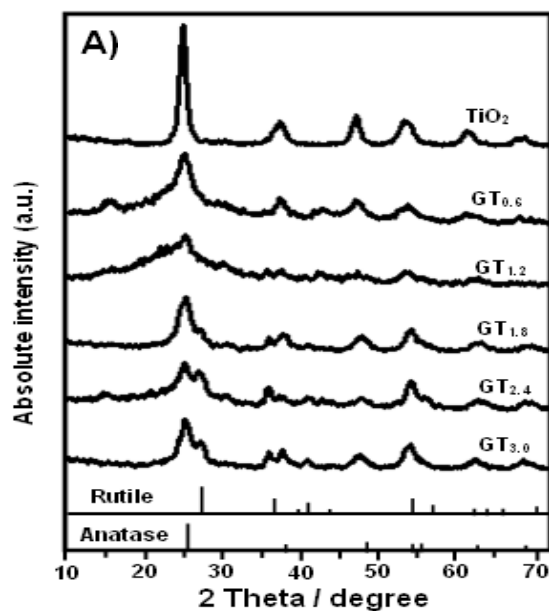


Figure S1. Typical XRD patterns of pure TiO_2 and the five anatase and rutile GT_x nanocomposites. Standard diffraction peaks of anatase (JCPDS No. 21-1272) and rutile TiO_2 (JCPDS No.21-1276) are shown as vertical bars.

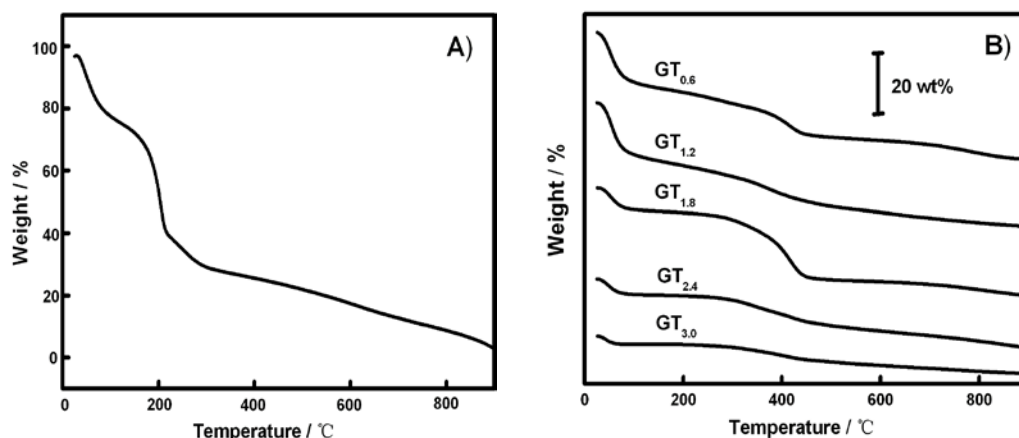


Figure S2. TGA curves of A) pure GO and B) the five GT_x nanocomposites under nitrogen atmosphere from room temperature to 900 at 10 °C min⁻¹.

Raman characterization: Raman spectroscopy was also carried out to further characterize the structural change of the GT_x nanocomposites before and after reduction of GO, as shown in Figure S3. According to Choi et al. [1], in carbonaceous material, D- and G-band in the Raman spectrum correspond to sp² and sp³ carbon stretching modes and their intensity ratio (I_D/I_G) is a measure of the amount of disorder present within the material [2]. As shown in Figure S3A, the Raman spectrum of GO exhibits Raman shifts at ~ 1594 and ~ 1363 cm⁻¹, corresponding to the G- (the E_{2g} mode of sp² carbon atoms) and D-bands (the symmetry A_{1g} mode), respectively (curve a) [3]. Upon reduction with 2.4 mL TiCl₃, the frequencies of D and G bands of GT_{2.4} nanocomposite do not change evidently compared with that of pure GO, yet a marked increase in the D/G intensity ratio is observed, indicating a decrease in the average size of the sp² domains upon reduction of the exfoliated GO and the reduction of GO to graphene did take place (curve b). Figure S3B displays the overall Raman spectroscopy comparison among the five GT_x nanocomposites. No discrepancy can be found with respect to the observed characteristic bands at 1594 and 1363 cm⁻¹ among them. However, the I_D/I_G value rises step by step with the increase of TiCl₃ amount, especially when the amount is increased from 0.6 to 1.2 mL and 2.4 to 3.0 mL. The difference is comparatively small as compared among GT_{1.2}, GT_{1.8} and GT_{2.4}.

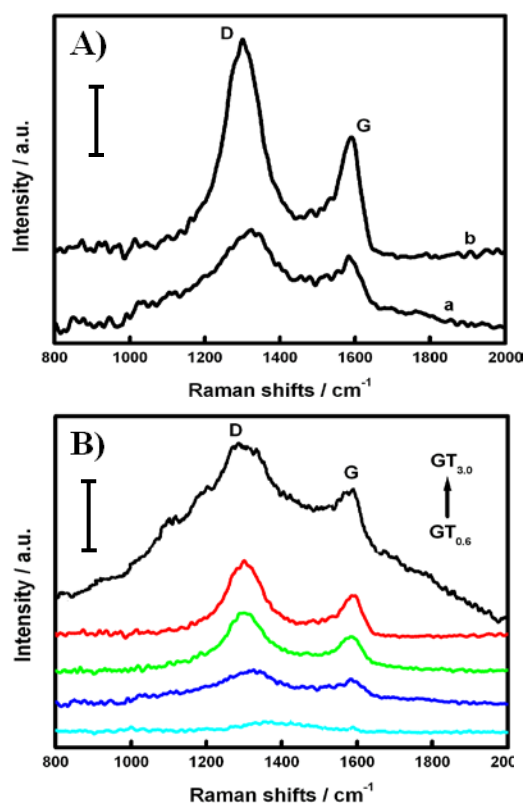


Figure S3. (A) Representative Raman spectra of GO (a) and the obtained $GT_{2.4}$ nanocomposite (b). (B) Raman spectra comparison among the five GT_x nanocomposites.

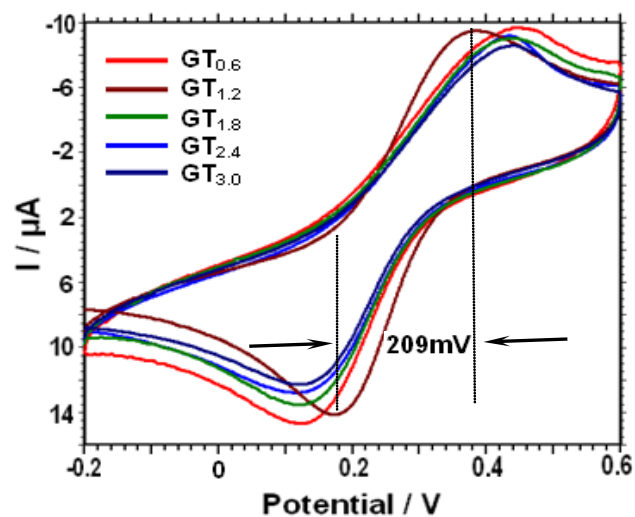


Figure S4. Cyclic voltammograms obtained at five GT_x -Pd hybrid nanocomposite-based electrodes in 0.1M KCl solution containing 1mM $K_3Fe(CN)_6$.

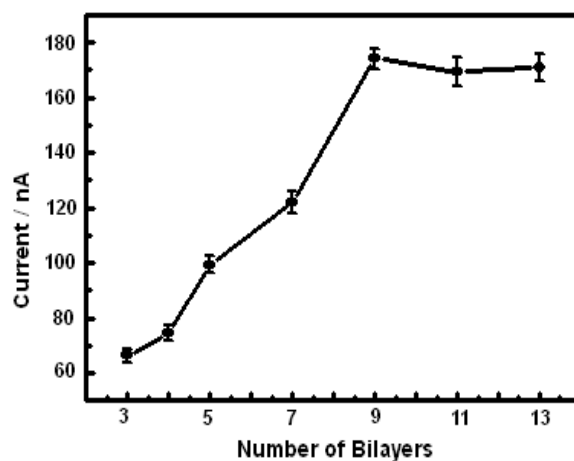


Figure S5. Current responses of $(\text{NH}_2\text{-MWNTs/GT}_{1.2}\text{-Pd})_n\text{-GOx-Nafion}$ based electrode toward 1.0 mM glucose with different numbers of bilayer.

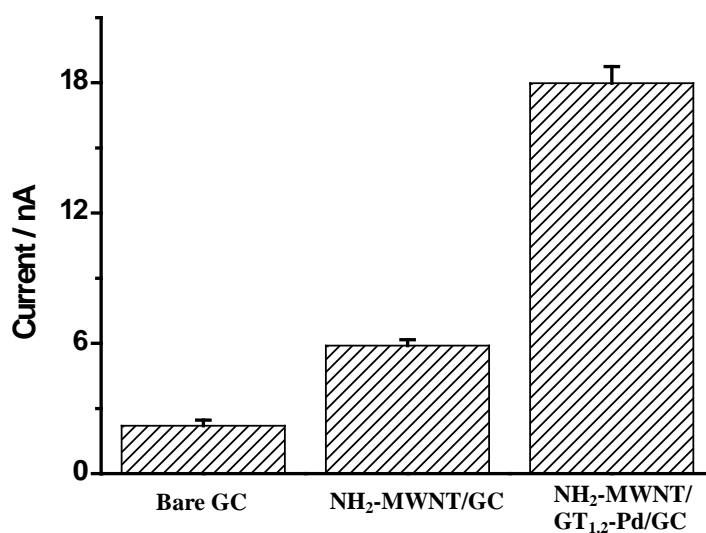


Figure S6. Comparison of the electrocatalytic response between bare GC, NH₂-MWNT and NH₂-MWNT/GT_{1.2}-Pd based glucose biosensor toward 0.1 mM glucose in PBS.

References

1. W. S. Choi, S. H. Choi, B. Hong, D. G. Lim, K. J. Yang, J. H. Lee, *Mater. Sci. Eng. C*. 2006, **26**, 1211-1214.
2. A. Subbiah, E. Arzum, L. Chang, Z. L. Chen, *J. Phys. Chem. C*. 2009, **113**, 8853-8857.
3. K. N. Kudin, B. Ozbas, H. C. Schniepp, R. K. Prud'homme, I. A. Aksay, R. Car, *Nano Lett.* 2008, **8** (1), 36-41.