Comparative Studies of Electrochemical Performance and Characterization of TiO_2 /Graphene Nanocomposites as Anode Materials for Li-Secondary Batteries

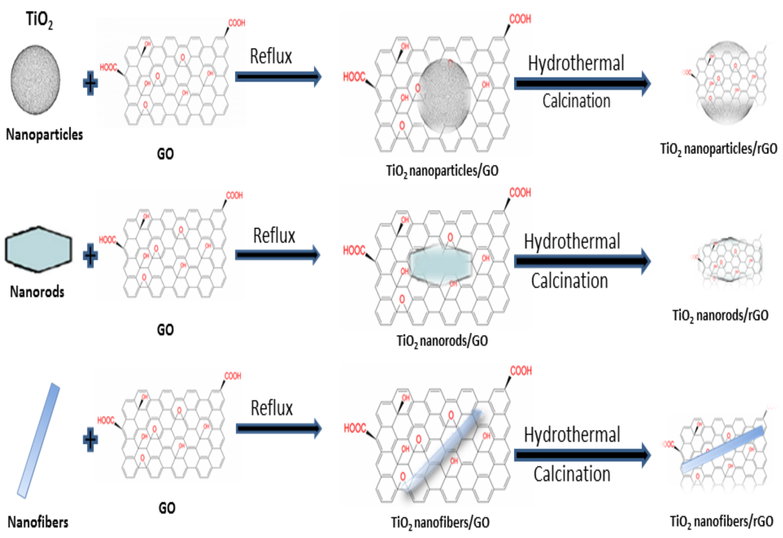
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Abstract

Using graphene oxide (GO) and titanium dioxide (TiO_2), various types of composites comprised of graphene-bonded and grafted anatase TiO_2 were synthesized without employing a cross-linking reagent in this study. Graphene sheets were uniformly dispersed among the TiO_2 particles, to enhance the cyclability and electronic conductivity of the TiO_2 anode for lithium ion batteries. A composite of GO prepared with three types of TiO_2 (nanoparticles, nanorods, nanofibers) were synthesized by hydrothermal followed by calcination treatment. The reduction of GO increased simultaneously after calcination under argon atmosphere at 400 °C for 4 h. To achieve overall better electrochemical performance we used the anatase type of TiO_2. TiO_2 nanoparticles composite with graphene delivered rate capability of 155 mAh g^{-1} at 0.5 C and restored the rate capacity of 109 mAh g^{-1} after 20 C, with a capacity loss of 30 %. TiO_2 nanorods composite with graphene benefited from its unique morphology exhibited rate capability of 124 mAh g^{-1} at 0.5 C and regain the rate capability of 97 mAh g^{-1}, with a capacity loss of 22 %. In addition, TiO_2 nanofibers graphene composite with low surface area 19 m^2g^{-1} and pore volume of 0.086 cm^3g^{-1} transported rate capability of 68 mAh g^{-1} at 0.5 C and recover the rate capacity of 64 mAh g^{-1} after 20 C owing to its higher value of lithium-ion diffusion coefficient.

Experimental Methods



XRD

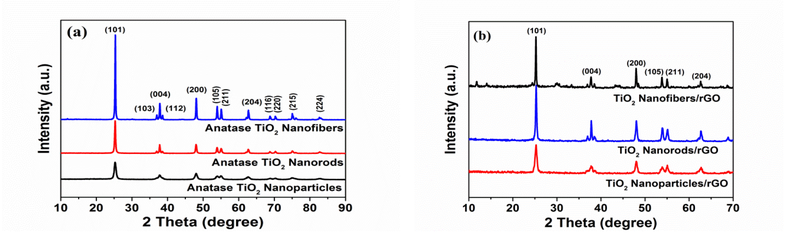


Fig 1. XRD patterns of anatase TiO_2 (a) nanoparticles, nanorods, nanofibers (b) nanoparticles/rGO, nanorods/rGO, nanofibers/rGO.

Raman & FTIR spectra

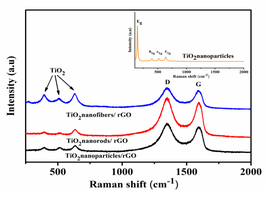


Fig 2. Raman spectra of anatase TiO_2 nanoparticles/rGO, nanorods/rGO, nanofibers/rGO.

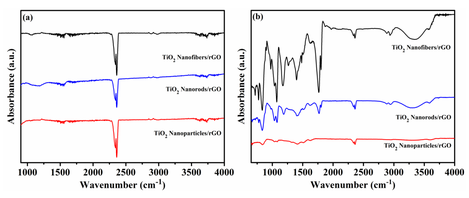


Fig 3. FT-IR spectra of TiO_2/rGO nanocomposites (a) before cyclibility of 100 cycles at 10 C (b) after cyclability of 100 cycles at 10 C for TiO_2 nanoparticles/rGO, TiO_2 nanorods/rGO and TiO_2 nanofibers/rGO..

EDS

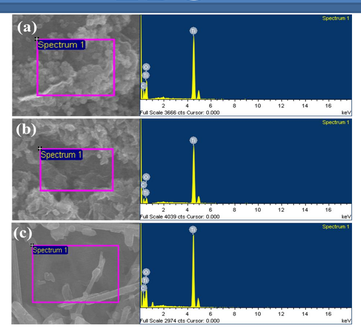


Fig 4. EDX pattern of (a) TiO_2 nanoparticles/rGO. (b) TiO_2 nanorods/rGO. (c) TiO_2 nanofibers/rGO.

SEM

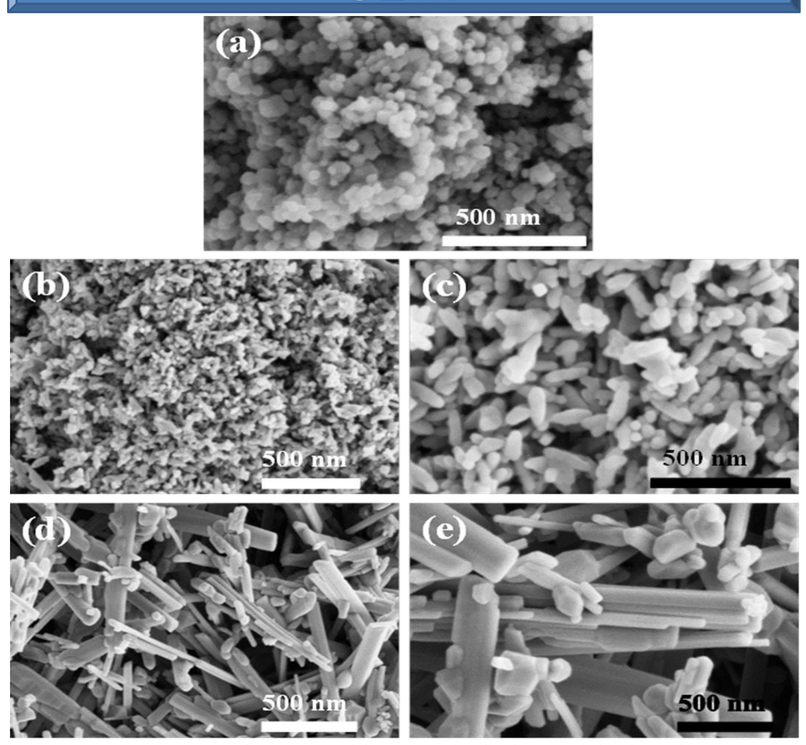


Fig 5. FE-SEM images of anatase TiO_2 (a) nanoparticles (b, c) nanorods (d, e) nanofibers.

TEM

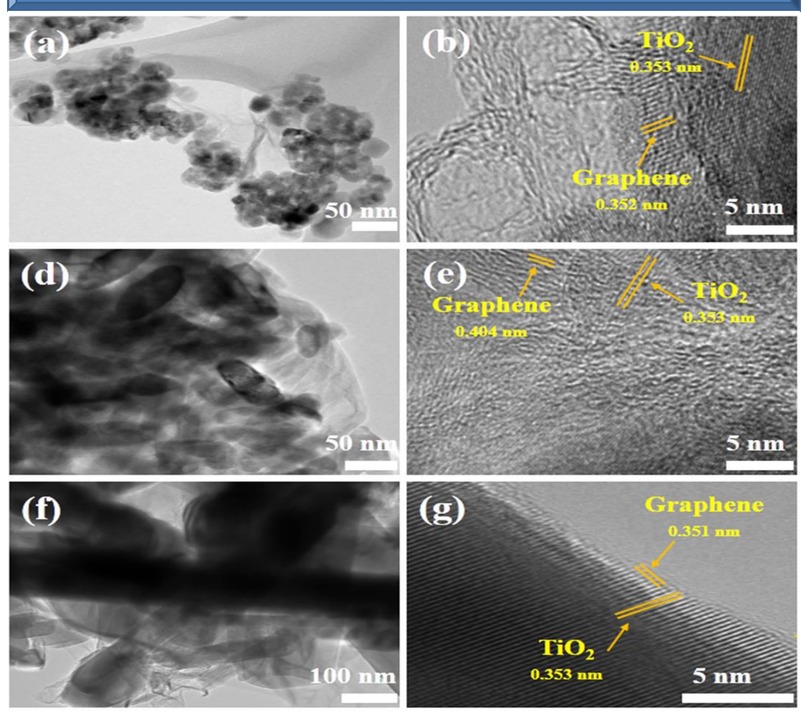


Fig 6. HR-TEM images of well dispersed TiO_2/rGO. (a, b) Nanoparticles. (c, d) Nanorods. (e, f) Nanofibers.

BET & BJH Table

BET and BJH data extracted from nitrogen desorption isotherms of pristine TiO_2 and its composites.

Samples	BET surface area (m^2g^{-1})	BJH pore diameter (nm)	Cumulative pore volume (cm^3g^{-1})
TiO_2 nanoparticles	69.0	10.3	0.2113
TiO_2 nanorods	22.76	43.47	0.3010
TiO_2 nanofibers	10.9	11.68	0.0215
TiO_2 nanoparticles/rGo	97.709	3.761	0.307
TiO_2 nanorods/rGO	69.385	3.739	0.350
TiO_2 nanofibers/rGO	19.358	3.695	0.086

XPS

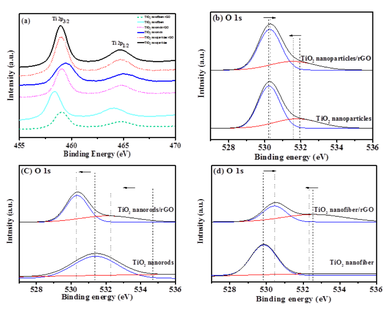


Fig 7. HR-XPS spectra of (a) Ti 2p and (b-d) O 1s for TiO_2 nanoparticles/rGO, TiO_2 nanorods/rGO and TiO_2 nanofibers/rGO with respective pristine TiO_2.

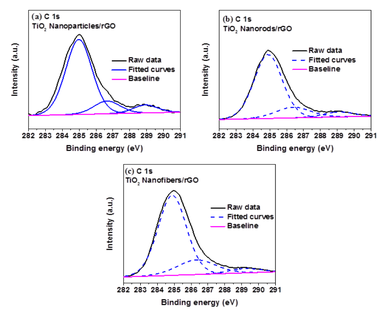


Fig 8. HR-XPS spectra of C 1s for (a) TiO_2 nanoparticles/rGO. (b) TiO_2 nanorods/rGO and (c) TiO_2 nanofibers/rGO.

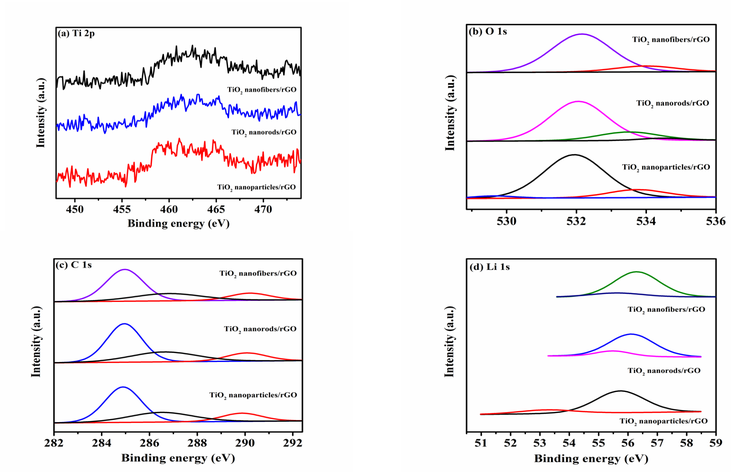


Fig 9. HR-XPS spectra of (a) Ti 2p, (b) O 1s, (c) C 1s, (d) Li 1s for TiO_2 nanoparticles/rGO, TiO_2 nanorods/rGO and TiO_2 nanofibers/rGO after cyclibility of 100 cycles at 10 C.

Electrochemical Performance

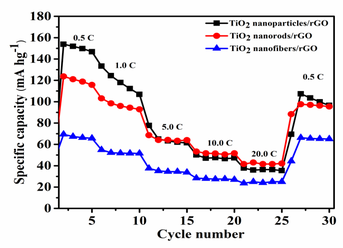


Fig 10. Rate dependent cyclic performances of anatase TiO_2 nanoparticles/rGO, nanorods/rGO and nanofibers/rGO at different C rates.

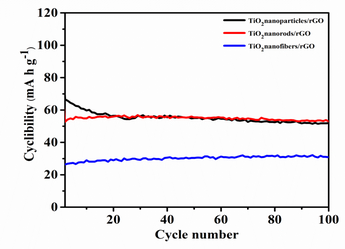


Fig 11. Cycling performances of TiO_2 nanoparticles/rGO, nanorods/rGO and nanofibers/rGO at current rate of 10 C for 100 cycles.

EIS

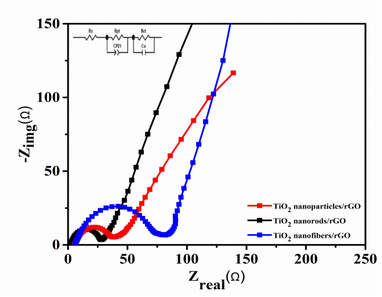


Fig 12. EIS spectra of anatase TiO_2 nanoparticles/rGO, nanorods/rGO, nanofibers/rGO after 100 cycles at 10 C. (inset: corresponding equivalent circuit).

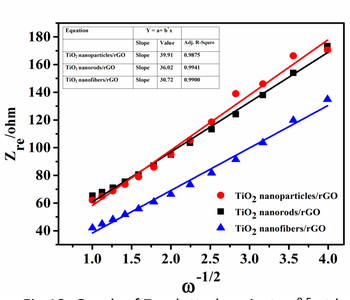


Fig 13. Graph of Z_{re} plotted against $\omega^{-0.5}$ at low frequency region for the anatase TiO_2 nanoparticles/rGO, nanorods/rGO and nanofibers/rGO (inset: corresponding slope value).

The values of Rs and Rct calculated from EIS spectra

Samples	R_s (Ω)	R_{ct} (Ω)
TiO_2 nanoparticles/rGO	5.11	33.17
TiO_2 nanorods/rGO	1.38	26.67
TiO_2 nanofibers/rGO	5.35	74.84

HR-TEM

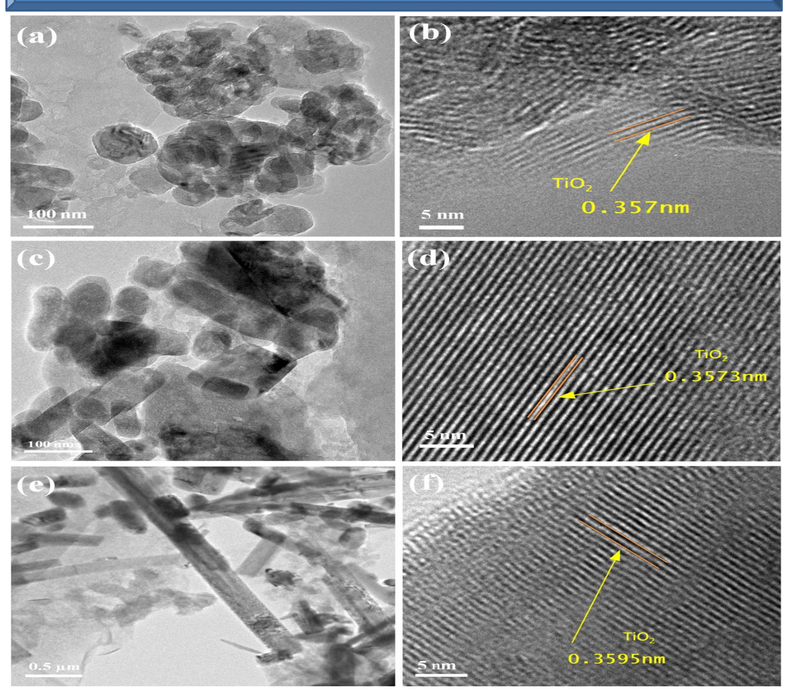


Fig 14. HR-TEM of (a,b) TiO_2 nanoparticles/rGO, (c,d) TiO_2 nanorods/rGO and (e,f) TiO_2 nanofibers/rGO electrode after cyclibility of 100 cycles at 10 C.

Conclusions

- We have successfully fabricated graphene bonded and grafted anatase TiO_2 (nanoparticles, nanorods, and nanofibers) composites without using any crosslinking reagents.
- TiO_2 nanoparticles/rGO possesses a high surface area of 97 m^2g^{-1} and pore volume. It demonstrates rate capability of 155 mAh g^{-1} at 0.5 C and restored the rate capacity of 109 mAh g^{-1} after 20 C, with a high capacity loss of 30 % as compared to TiO_2 nanorods/rGO of 22 %.
- TiO_2 nanorods/rGO delivers cyclibility of 53 mAh g^{-1} at 10 C for 100 cycles with ~100 % retention capacity at high current density, demonstrates the strong bond between TiO_2 nanorods and graphene.
- TiO_2 nanofibers/rGO with low surface area of 19 m^2g^{-1} and pore volume of 0.086 cm^3g^{-1} transports rate capability of 68 mAh g^{-1} at 0.5 C and recover the rate capacity of 64 mAh g^{-1} after 20 C due to its higher value of lithium-ion diffusion coefficient.

Acknowledgements

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