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# Supporting information

Carbon allotropes grafted with poly(pyrrole) derivatives via living radical polymerizations. Electrochemical analysis of nano-composites for energy storage.

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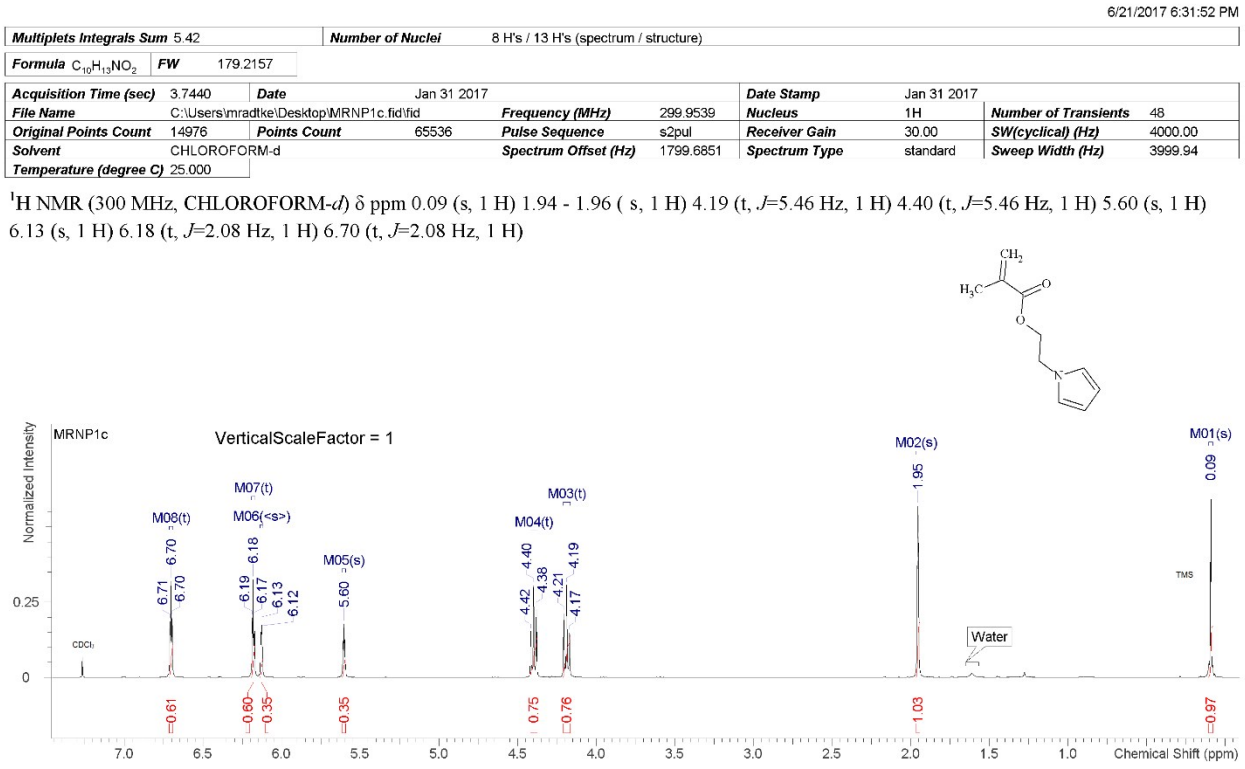


Fig. S1. $^1$H NMR data of 2-(1H-pyrrol-1-yl)ethyl methacrylate.

Table S1. Specific gravimetric capacitances obtained for pristine MWCNT, Graphene, SWCNH and PPy:

| | MWCNT | Graphene | SWCNH | Ppy |
|---|---|---|---|---|
| **C (F/g)[a,b]** | 20.07 | 11.64 | 15.92 | 17.40 |

[a] $E_1$(V)=0.8 V (vs Ag/AgCl 0.222 V), $E_2$(V)=-0.8 V (vs Ag/AgCl 0.222 V), m=8.5 $10^{-5}$g, ν=0.1 V/s

[b] Calculated according to: $$C(F/g) = \frac{\int_{E1}^{E2} I(E)dE}{2mv(E_2 - E_1)}$$ , 0.196 $cm^2$ RRDE working electrode, Ag/AgCl reference electrode, m=8.5 $10^{-5}$g Platinum wire counter-electrode.

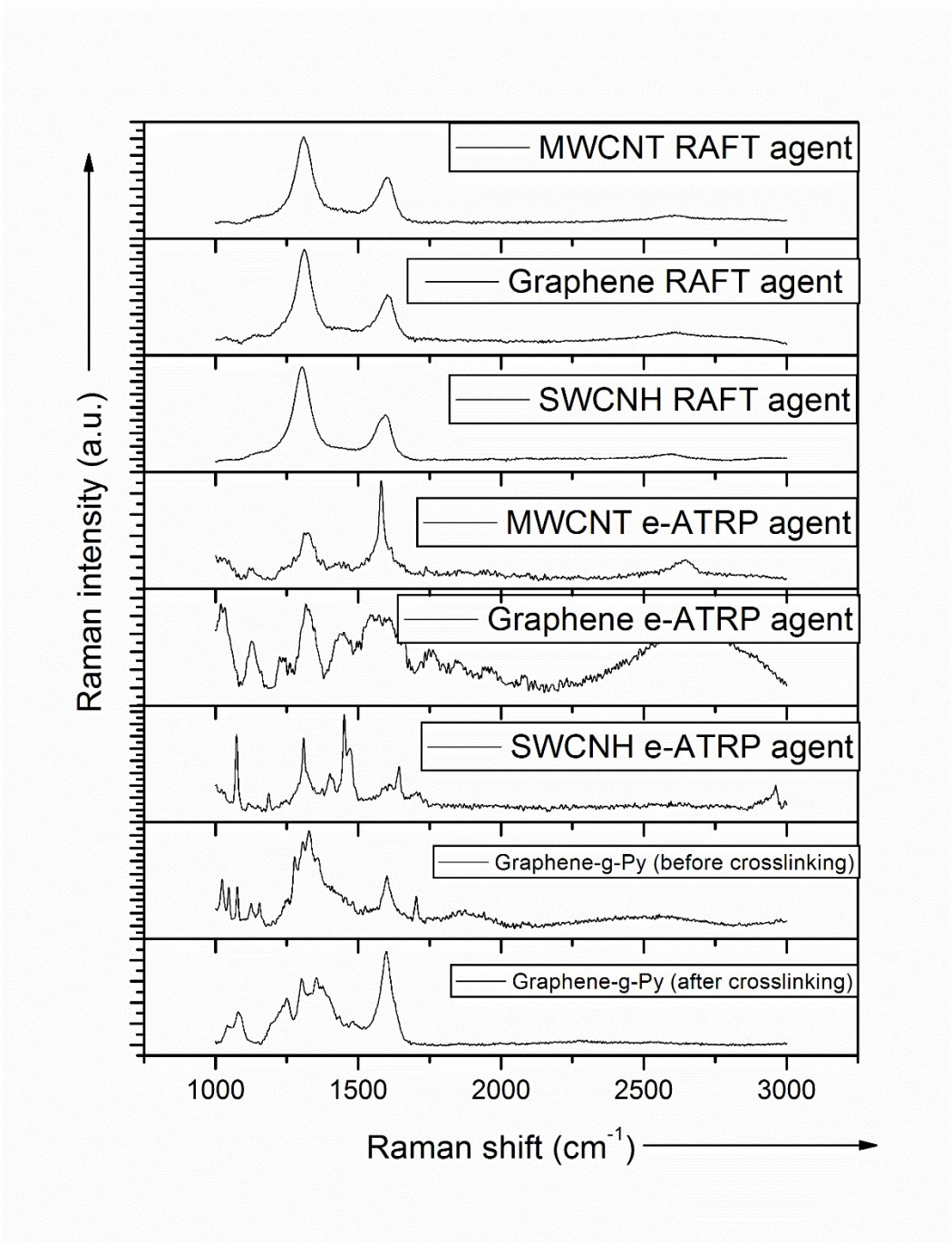


Fig. S2. Raman spectra for the MWCNT, Graphene RAFT and e-ATRP initiators. MRSP21c stands for the Raman spectrum of MWCNT before the crosslinking of pyrrole on the methacrylic backbone and MRSP21d after the crosslinking.

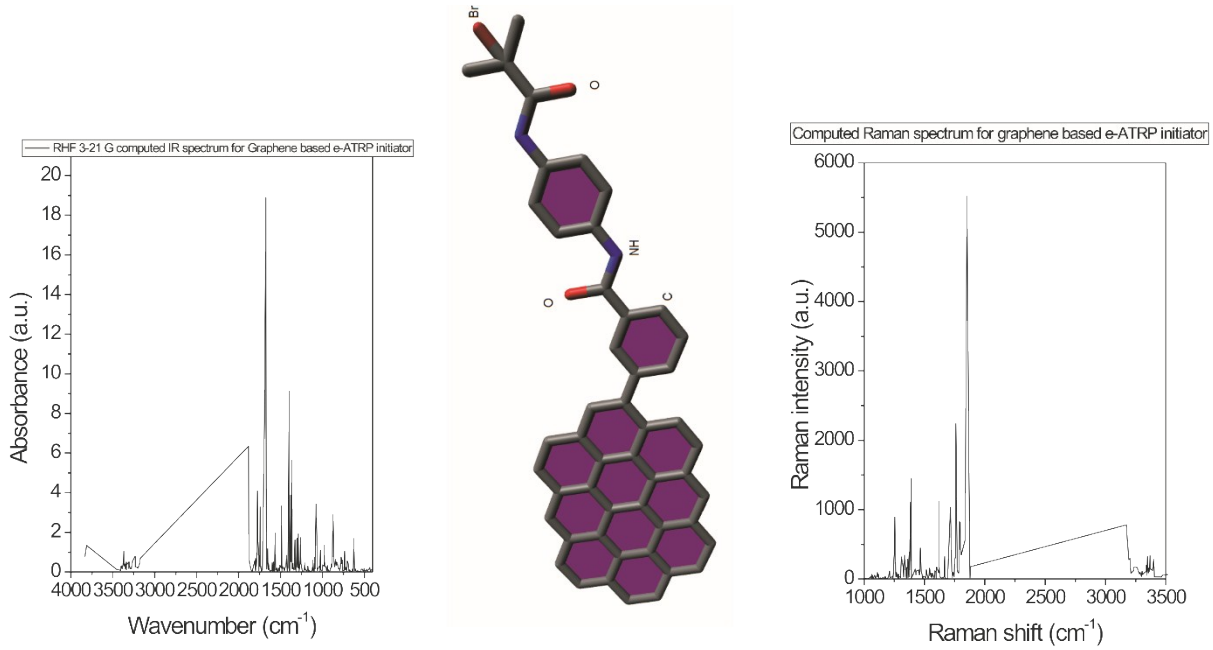


Fig. S3. HF 3-21G computed FTIR and Raman spectra of simplified graphene based e-ATRP initiator.

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| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| ***Multiplets Integrals Sum*** | 0.00 | | ***Number of Nuclei*** | 0 H's / 10 H's (spectrum / structure) | | | | | |
| ***Formula*** | $C_5H_{10}ClMgS_2^-$ | | ***FW*** | 194.0214+? (88.8191+105.2023+?) | | | | | |
| ***Acquisition Time (sec)*** | 3.7440 | ***Date*** | Mar 14 2016 | | | ***Date Stamp*** | Mar 14 2016 | | |
| ***File Name*** | C:\Users\mradtke\Desktop\M3.fid\fid | | | ***Frequency (MHz)*** | 299.9539 | ***Nucleus*** | 1H | ***Number of Transients*** | 8 |
| ***Original Points Count*** | 14976 | ***Points Count*** | 65536 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 18.00 | ***SW(cyclical) (Hz)*** | 4000.00 |
| ***Solvent*** | CHLOROFORM-d | | | ***Spectrum Offset (Hz)*** | 1799.6851 | ***Spectrum Type*** | standard | ***Sweep Width (Hz)*** | 3999.94 |
| ***Temperature (degree C)*** | 25.000 | | | | | | | | |

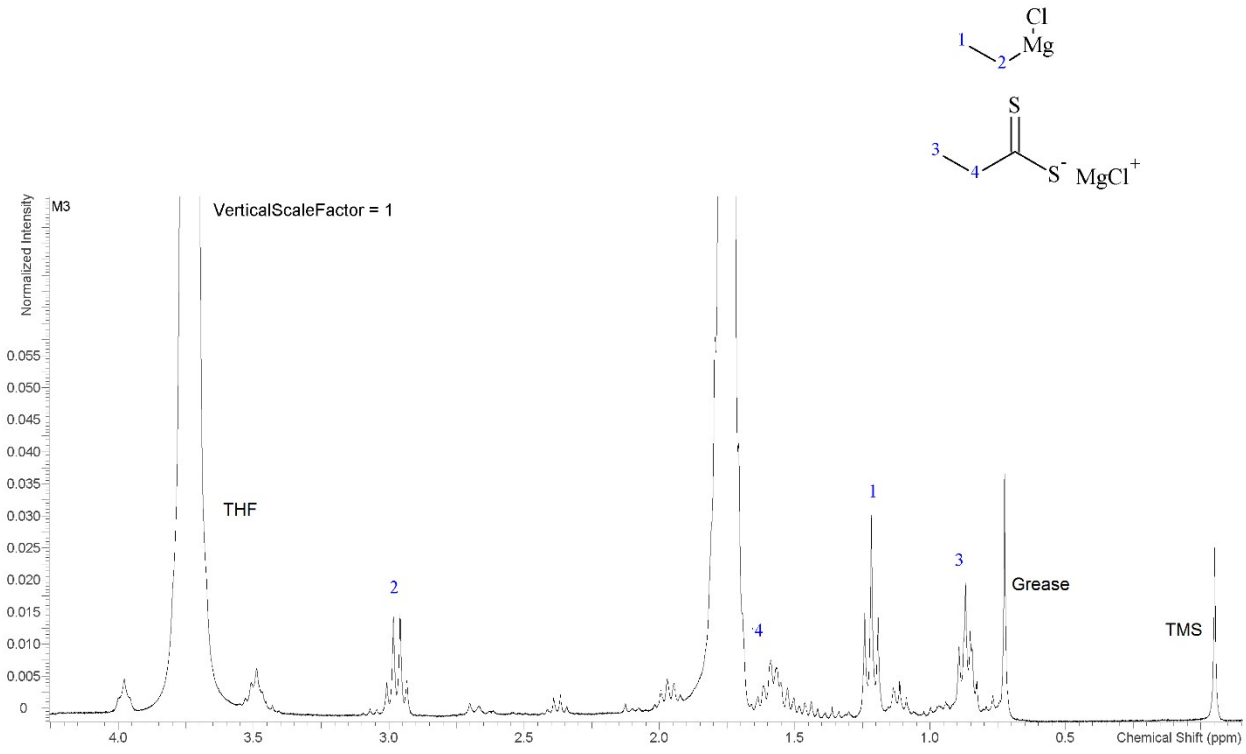



Fig. S4. $^1$H NMR spectrum obtained after 20 minutes for the dithiopropanoic magnesium chloride salt preparation reaction.

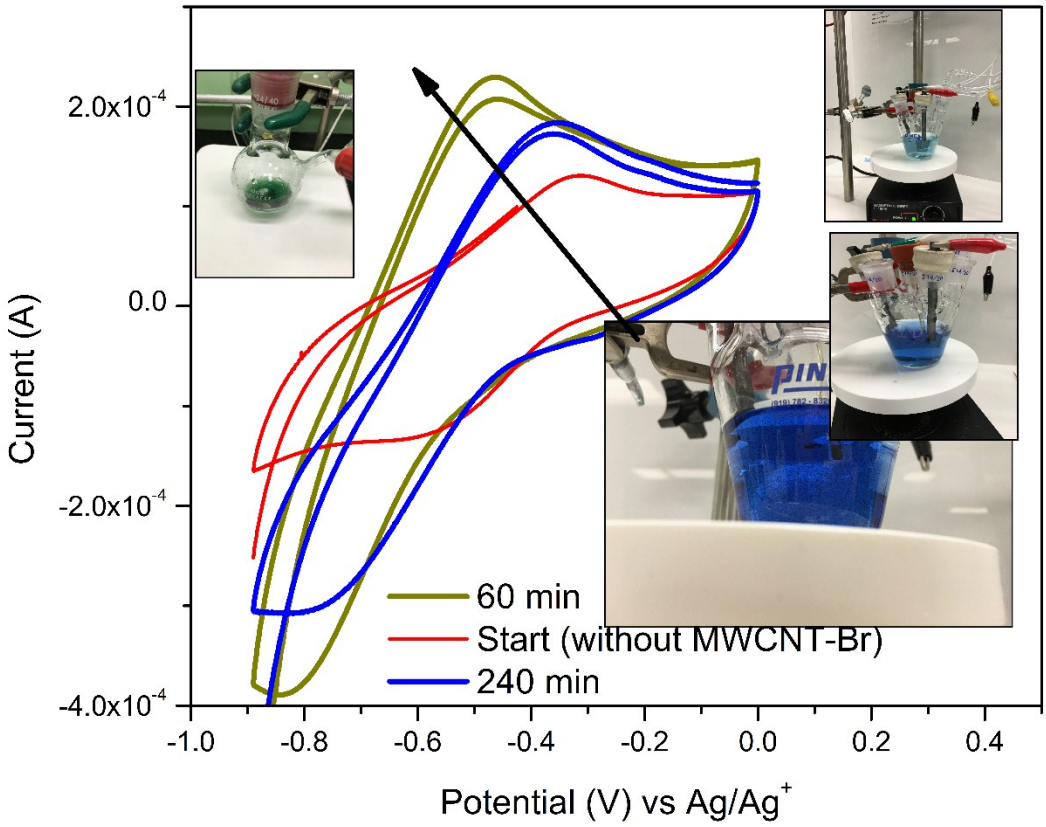



Fig. S5. e-ATRP process with MWCNT-based initiator.

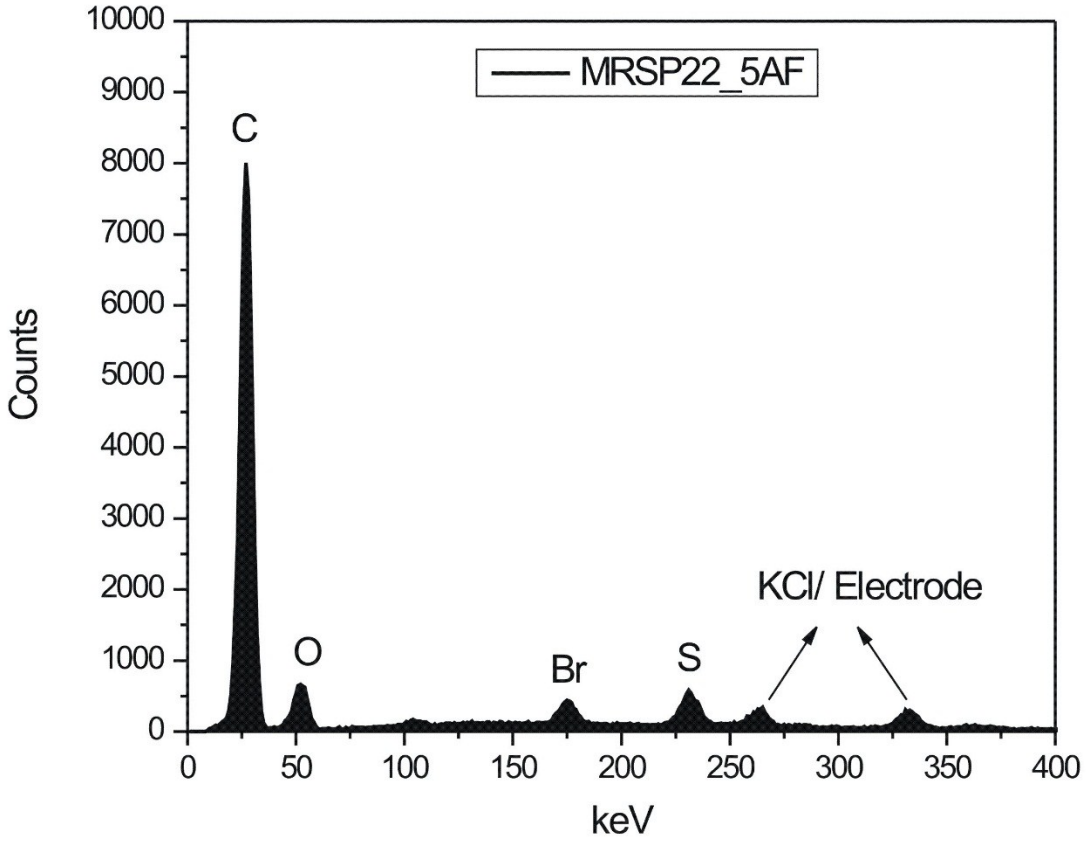



Fig. S6. EDX spectrum of graphene-g-PPy prepared by e-ATRP polymerization.

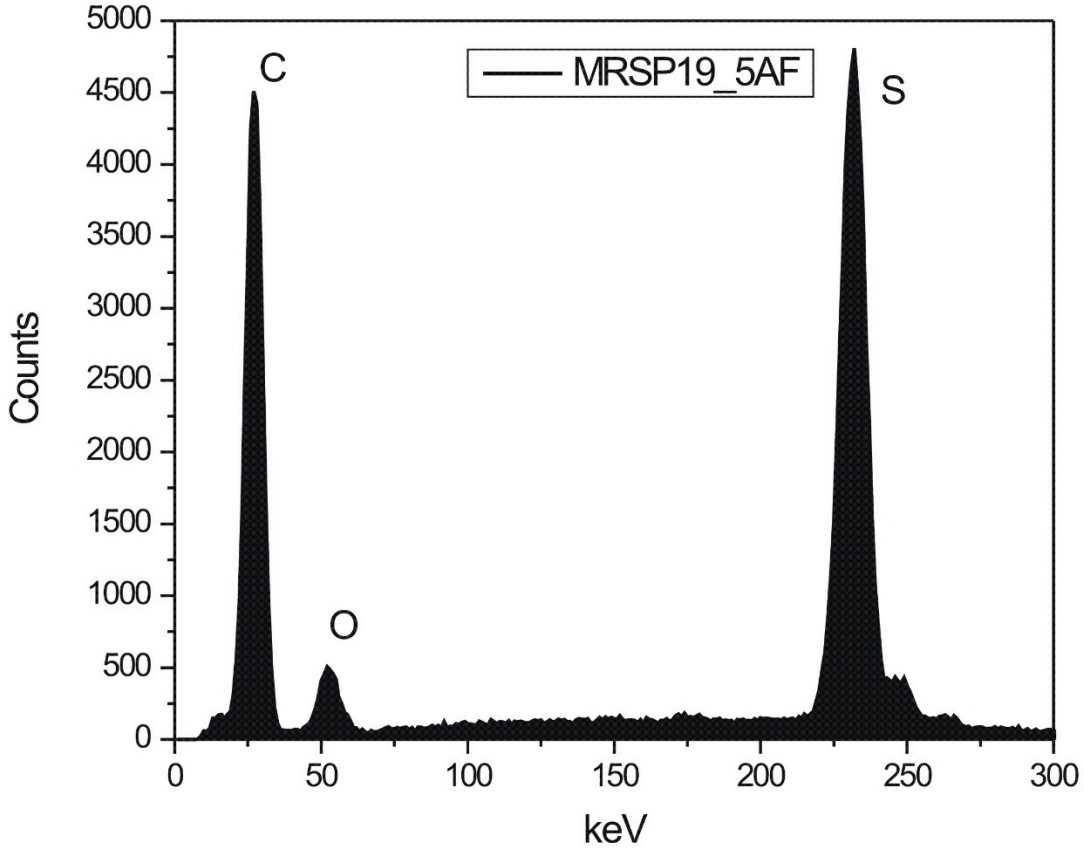



Fig. S7. EDX spectrum of graphene-g-PPy prepared by RAFT polymerization.

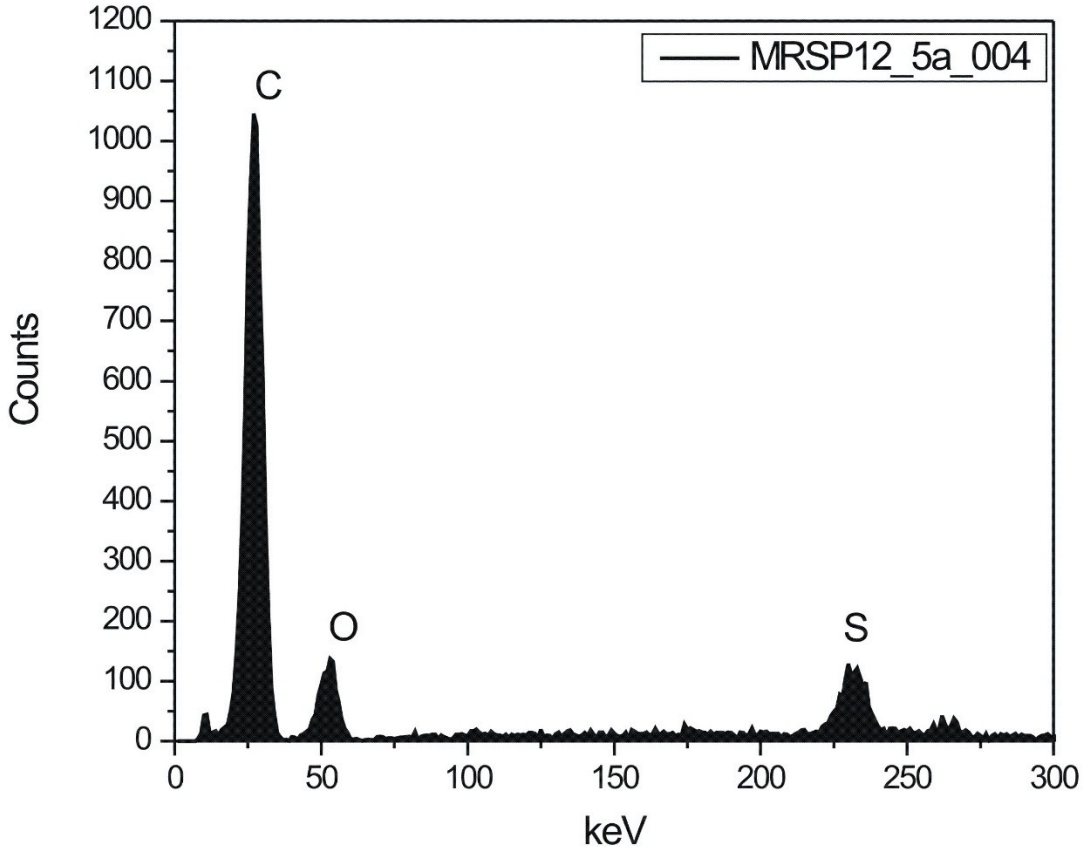



Fig. S8. EDX spectrum of MWCNT-g-PPy prepared by RAFT polymerization.

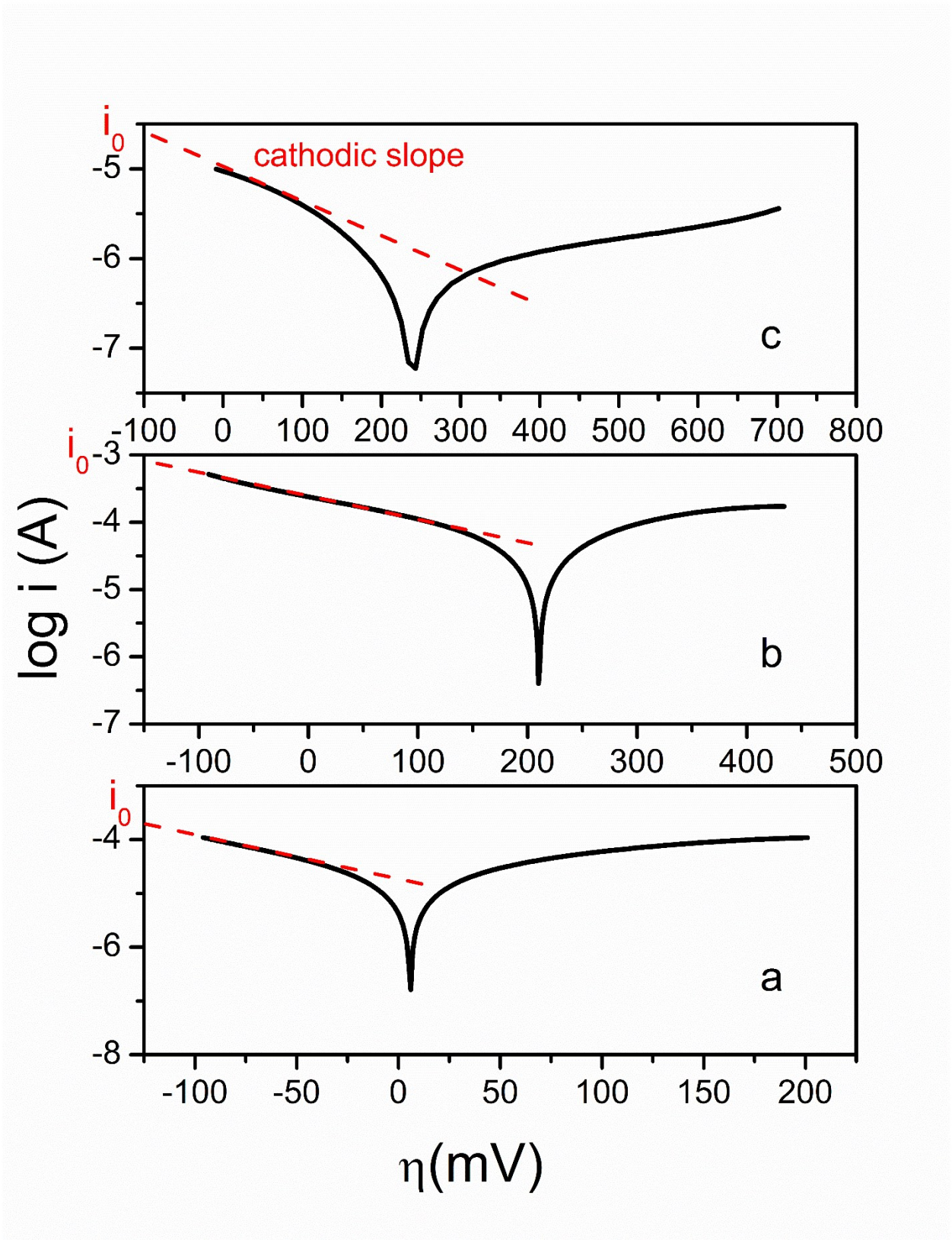



Figure S9. Tafel plots for MWCNT- (a), Graphene- (b) and SWCNH-based e-ATRP initiators.

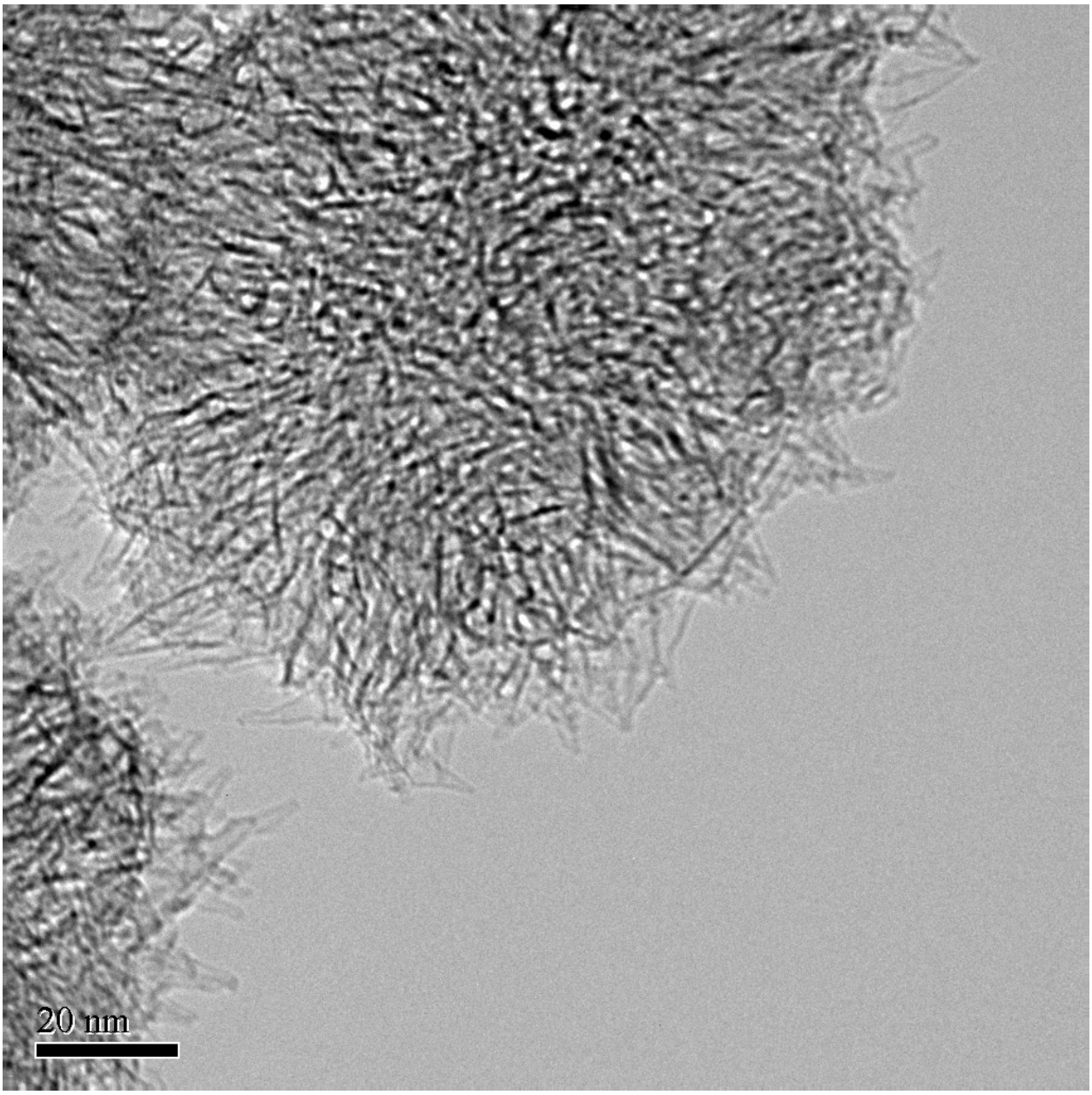



Fig. S10. Pristine Single-Walled Carbon Nanohorns.

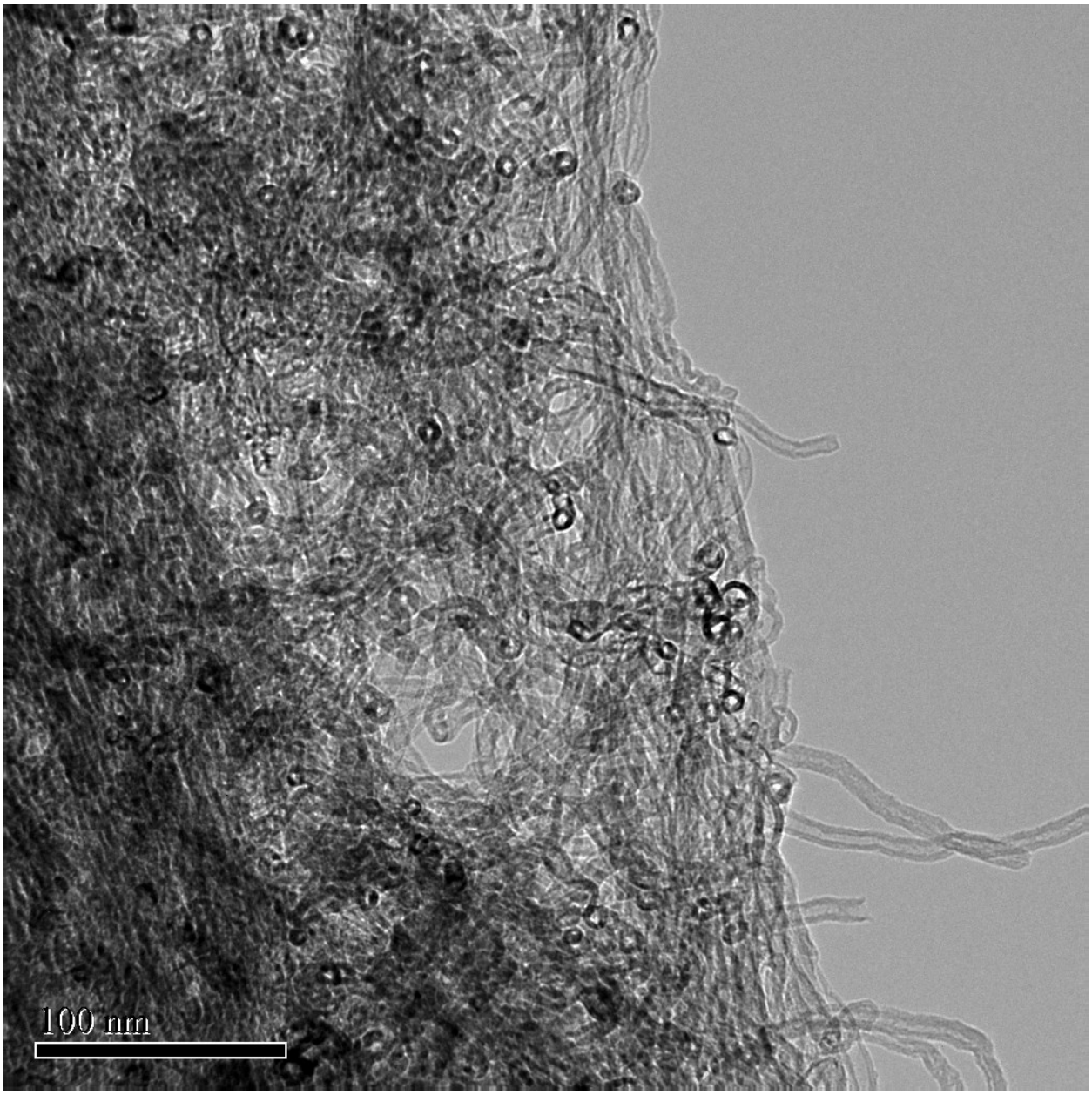



Fig. S11. Pristine Multi-Walled Carbon Nanohorns.

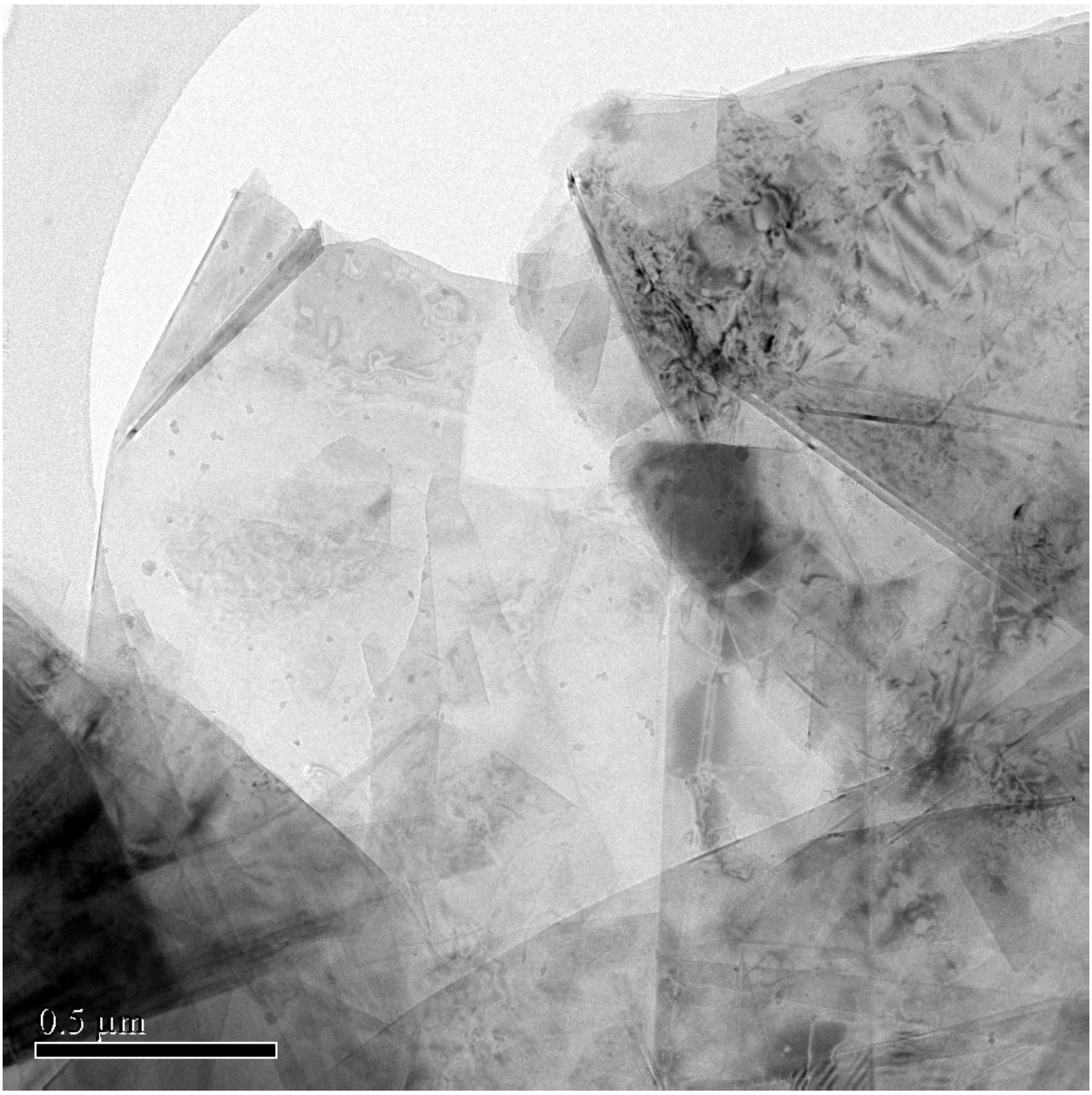



Fig. S12. Pristine Graphene flakes.

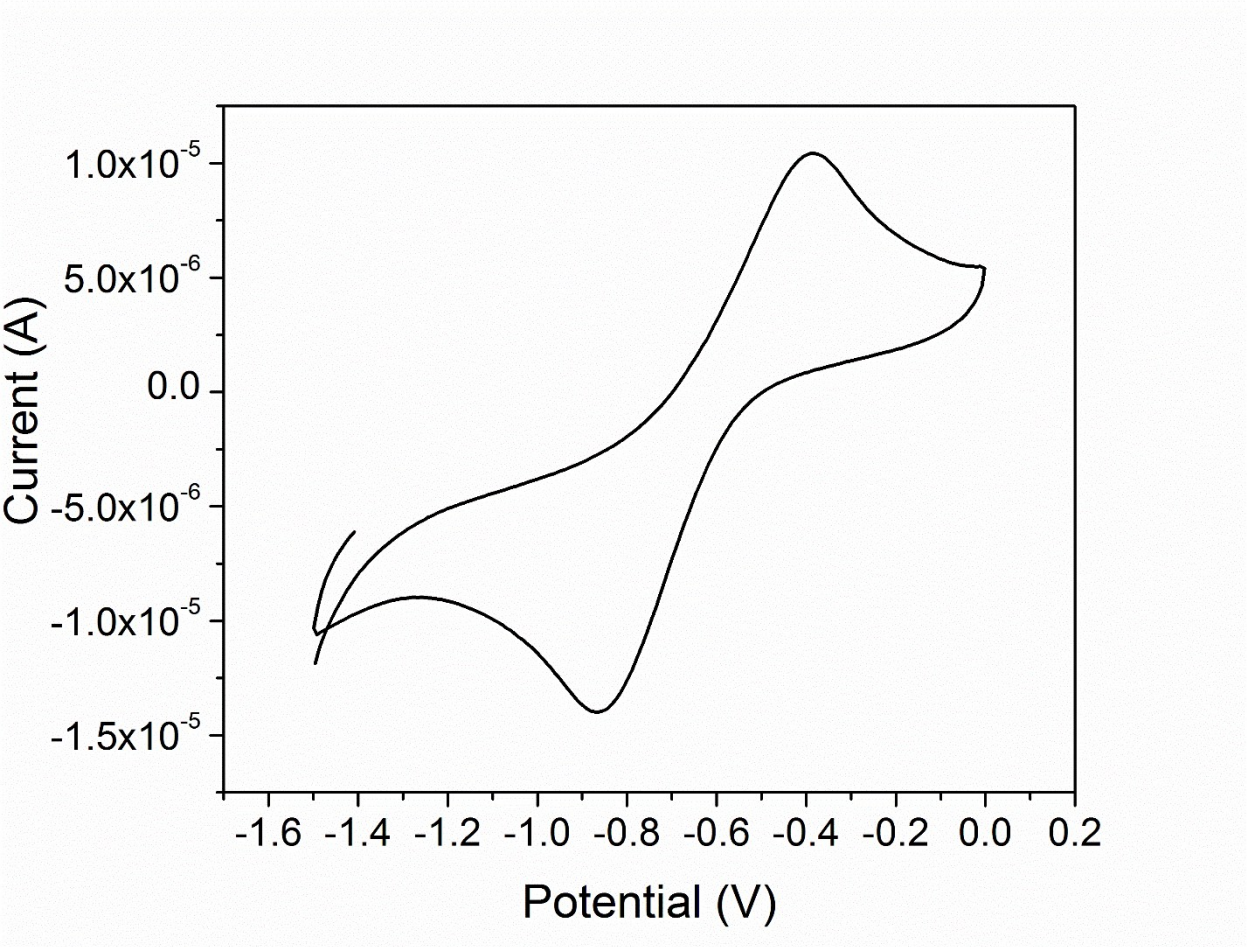



Fig. S13. Electrochemical response of Cu(I)Br(PMDETA) in e-ATRP polymerization with Graphene as initiator.

$$k_f = k_0 \exp\left[\left(-\frac{\alpha n F}{RT}(E - E_0)\right)\right] (Eq.\ F1)$$

Where Tafel slope for the cathodic process (activation: $slope = \frac{(1-\alpha)F}{2.3RT}$) and $k^0 = \frac{i_o}{FAC}$), where C=1.1 mM=1.1E-03 mol/cm$^3$, F=96485.3329 sA/mol and $i_o$=5.38E-06 (read and recalculated from the common logarithm with the base of 10); $k_f$= 2.61E-01 L/mol s= $k_{act}$

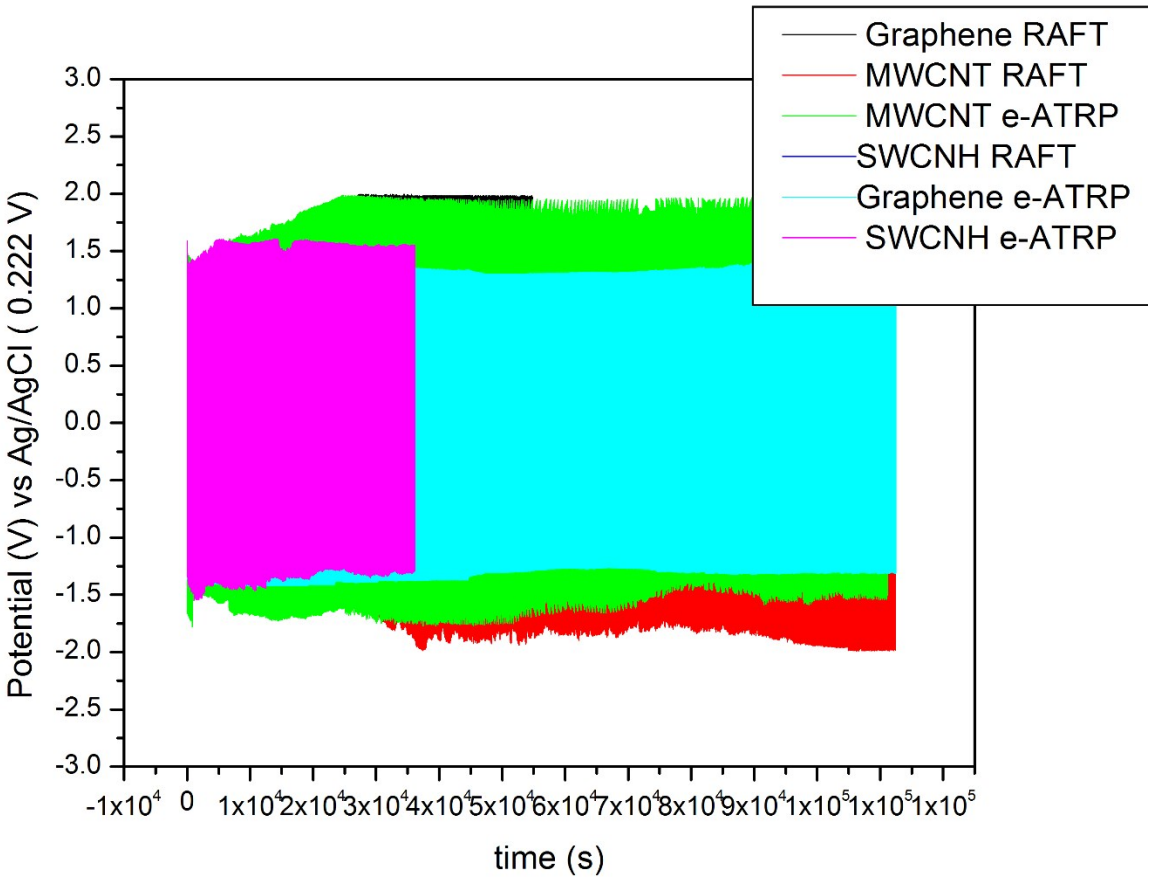



Fig. S14. Stability data for different carbon allotrope-g-PPy products.

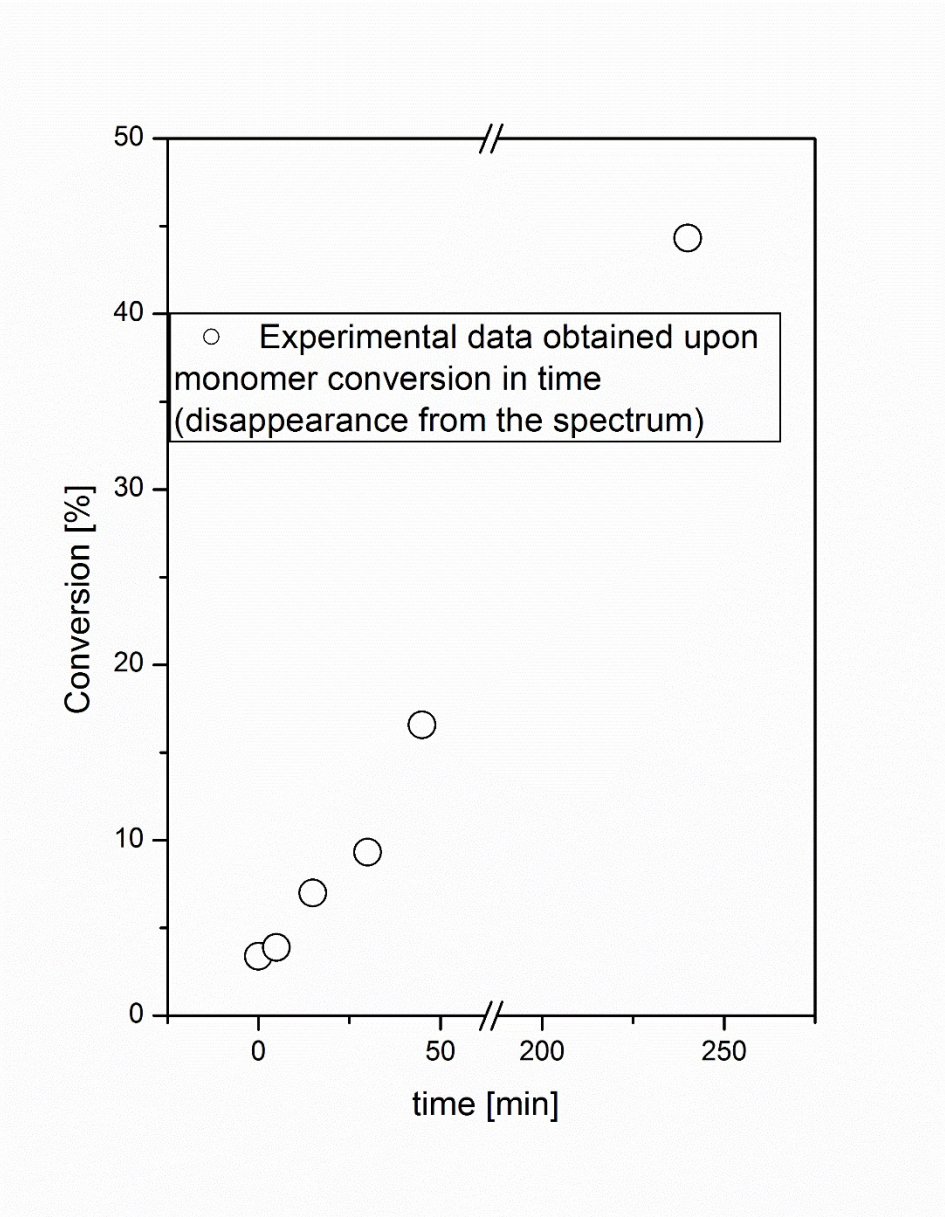
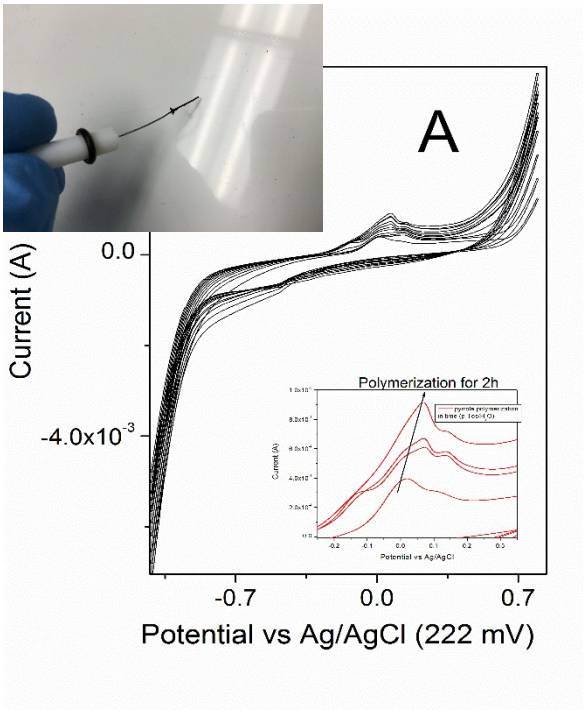



Fig. S15. Conversion chart obtained by the consecutive disappearance of the monomer from the $^{1}$H NMR spectrum. Once the polymer was attached to the carbon core, the product was insoluble, making obtaining of NMR spectrum impossible.


A
Current (A)
0.0
-4.0x10-3
-0.7
0.0
0.7
Potential vs Ag/AgCl (222 mV)
Polymerization for 2h

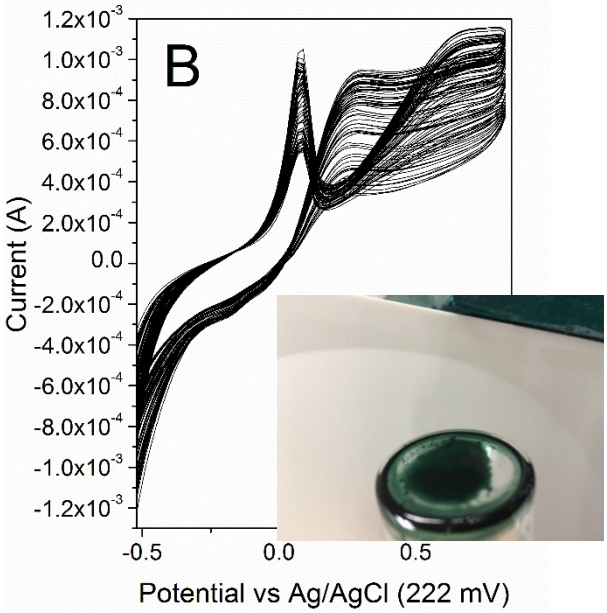

B
Current (A)
1.2x10-3
1.0x10-3
8.0x10-4
6.0x10-4
4.0x10-4
2.0x10-4
0.0
-2.0x10-4
-4.0x10-4
-6.0x10-4
-8.0x10-4
-1.0x10-3
-1.2x10-3
-0.5
0.0
0.5
Potential vs Ag/AgCl (222 mV)

Fig. S16. An alternative electropolymerization approach of MWCNT attached to methacrylate backbone bearing pyrrole in the structure. (A) CV spectrum in p-toluene sulfonic acid with an insert demonstrating the increase in redox signals related to the growth of the polymer and the photo of product generated on the Pt working electrode. (B) CV scans of the product synthesized using electropolymerization approach with signals related to redox activity of Cu (insert photo also show the color of the product that is dark green due to Cu contaminations that becomes problematic in this method of polypyrrole synthesis).