Electronic Supplementary Information (ESI)

Hybrid Layer-by-Layer composites based on conducting polyelectrolyte and Fe_3O_4 nanostructures grafted on graphene for supercapacitors application

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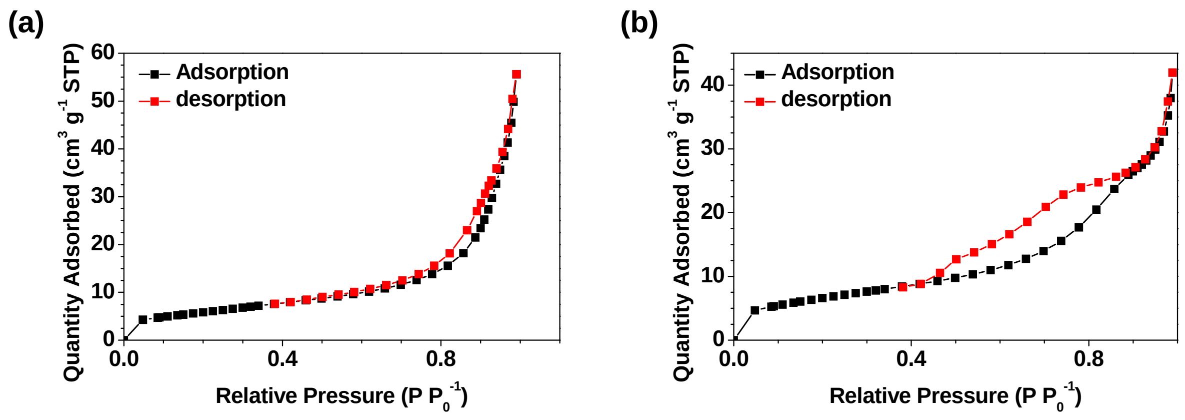

Fig. S1. N_2 adsorption-desorption isotherms of (a) Fe_3O_4 nanostructures and (b) Fe_3O_4@FLG composites.

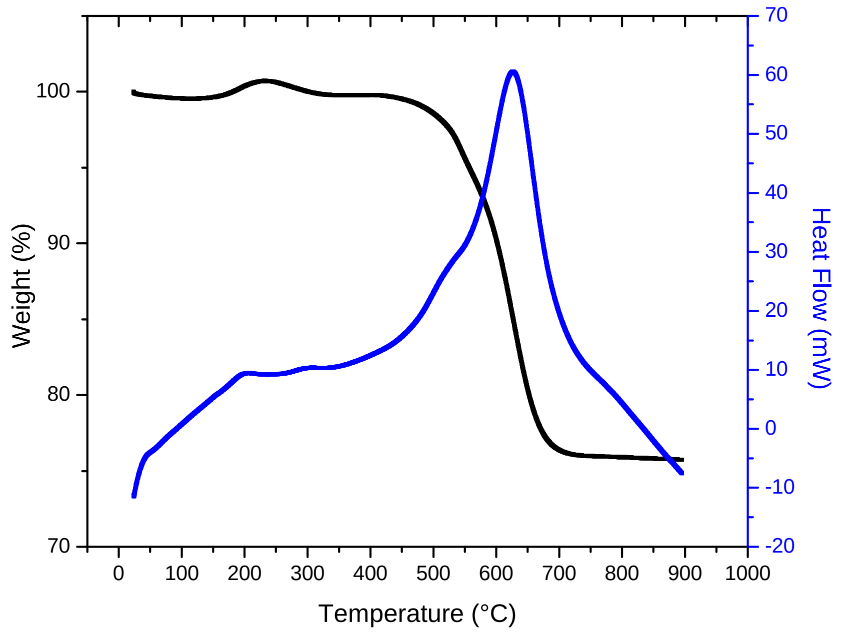

Fig. S2. Thermogram of iron oxide nanostructures on graphene (Fe_3O_4@FLG) carried out in air atmosphere.

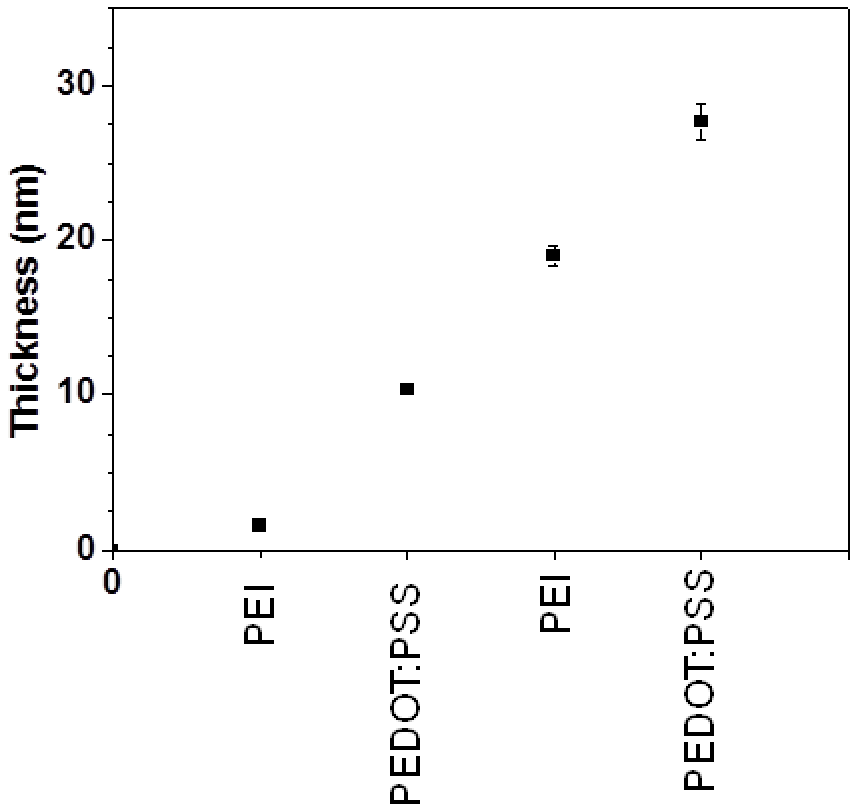

Fig. S3. Evolution of the thickness of (PEI/PEDOT:PSS)$_2$, measured by ellipsometry, as a function of the last deposited layer.

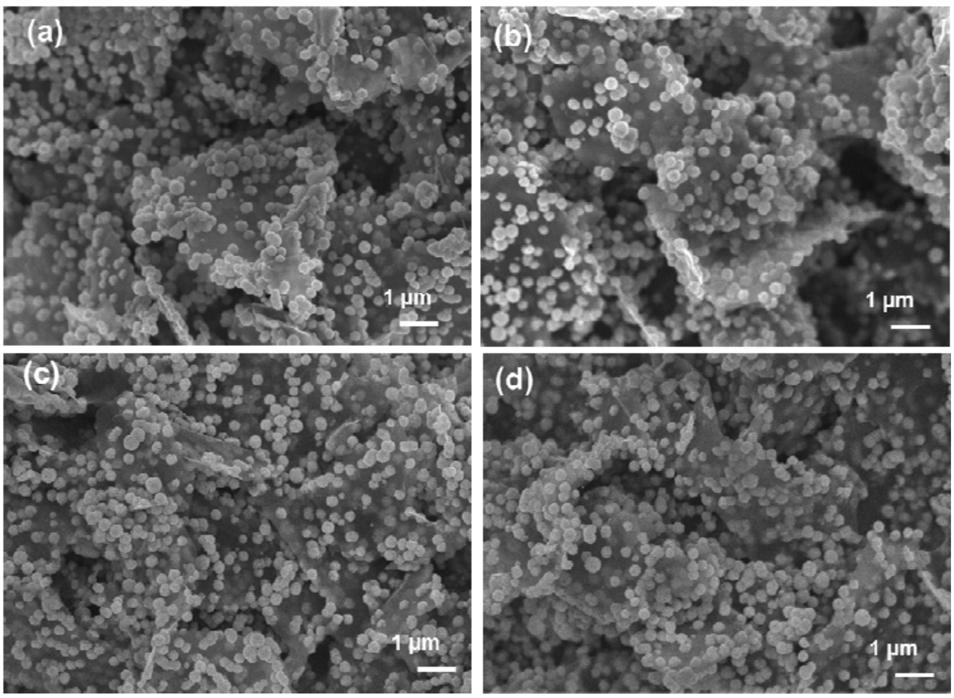

Fig. S4. Typical SEM images of the top view of (Fe_3O_4@FLG/PEDOT:PSS$_2$)$_n$ hybrid architecture for (a) n = 15 bilayers, (b) n = 20 bilayers, (c) n = 30 bilayers and (d) n = 120 bilayers.

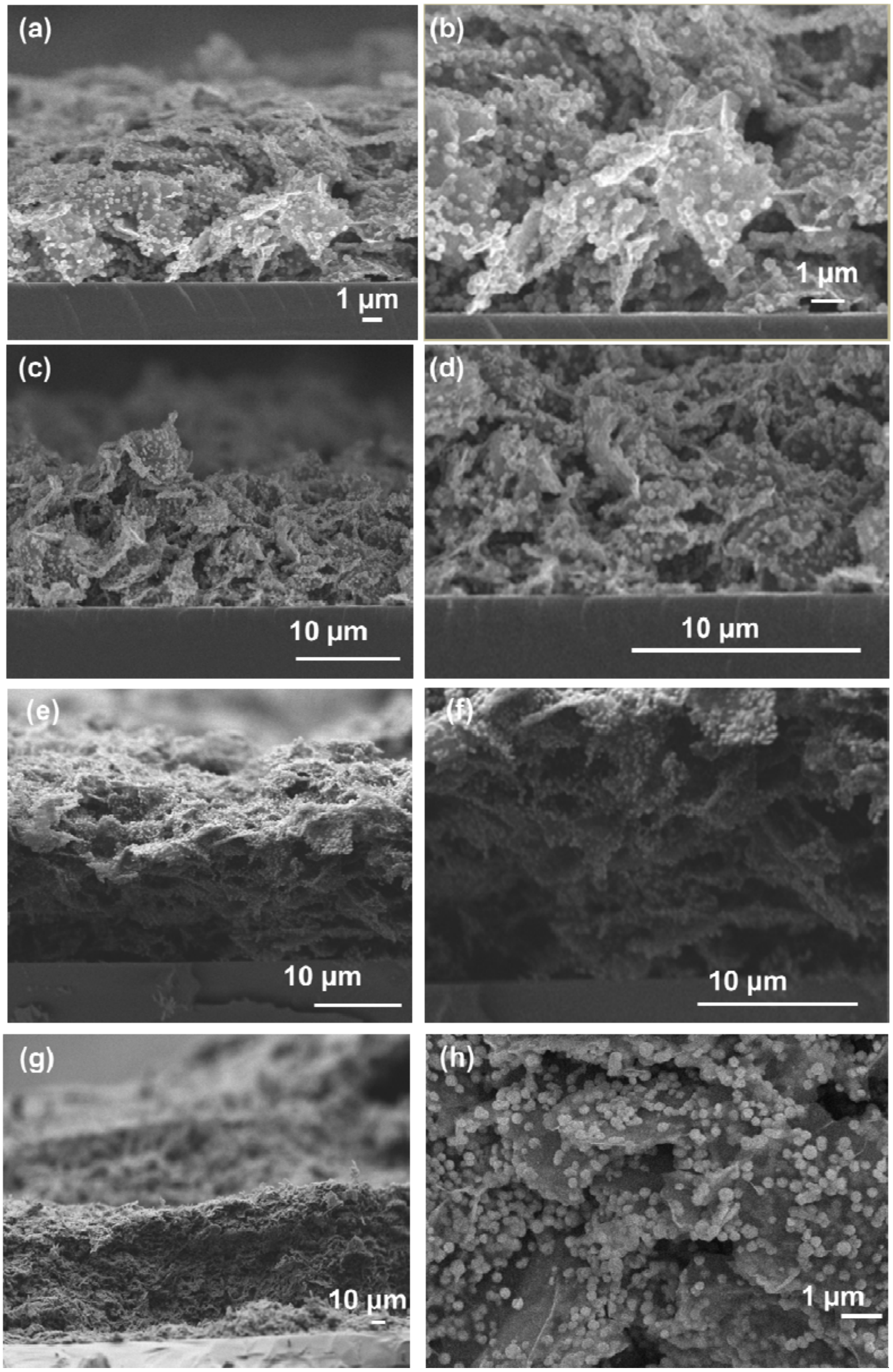

Fig. S5. Typical SEM images of the cross-sectional view of $(Fe_3O_4@FLG/PEDOT{:}PSS_2)_n$ hybrid architectures for (a, b) *n* = 15 bilayers (thickness estimated at 9 μm), (c, d) *n* = 20 bilayers (thickness estimated at 12 μm), (e, f) *n* = 30 bilayers (thickness estimated at 17 μm) and (g, h) *n* = 120 bilayers (thickness estimated at 72 μm).

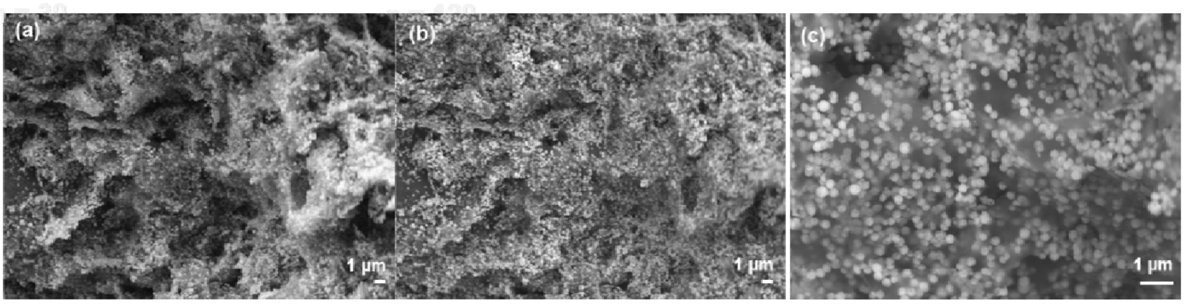

Fig. S6. Typical SEM images of the cross-sectional view of $(Fe_3O_4$@FLG/PEDOT:$PSS_2)_{120}$ hybrid architecture obtained in different mode (a) include secondary electrons (SEI mode) and (b, c) same image and zoom in compo mode where iron oxide nanostructures are clearly in contrast than the other materials present.

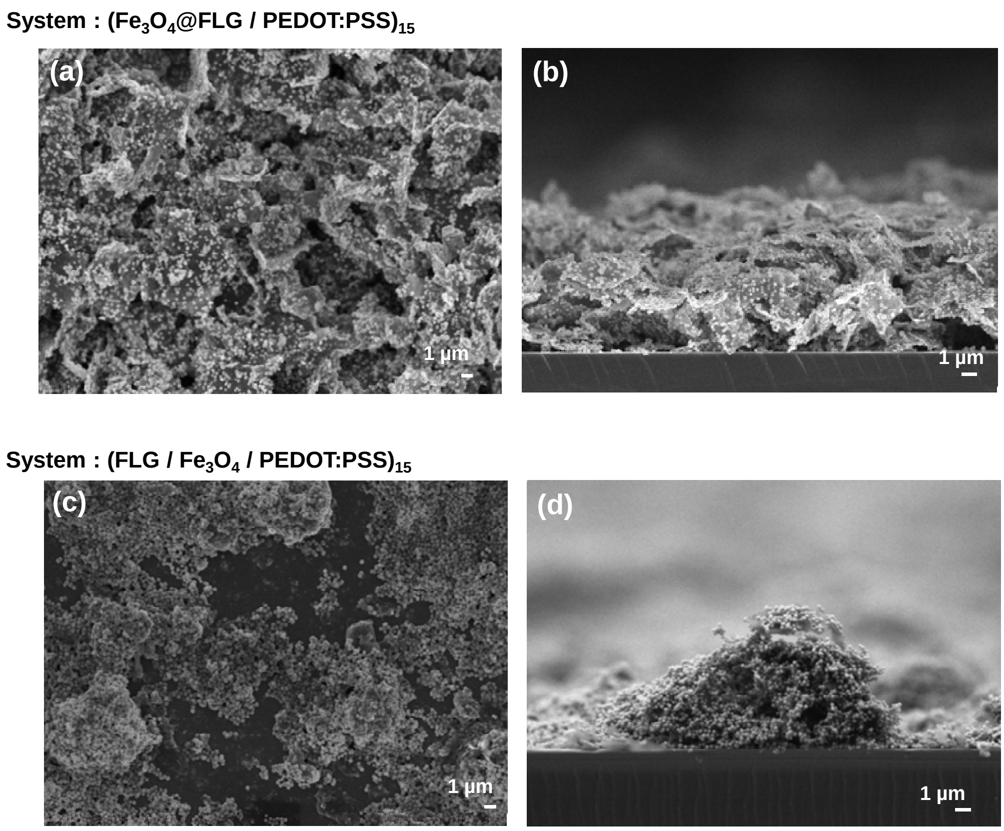

Fig. S7. Typical SEM images of the top and the cross-sectional view of the (a, b) grafted $(Fe_3O_4$@FLG /PEDOT:PSS$)_{15}$ and (c, d) ungrafted (FLG/Fe_3O_4/PEDOT:PSS$)_{15}$ hybrid architectures.

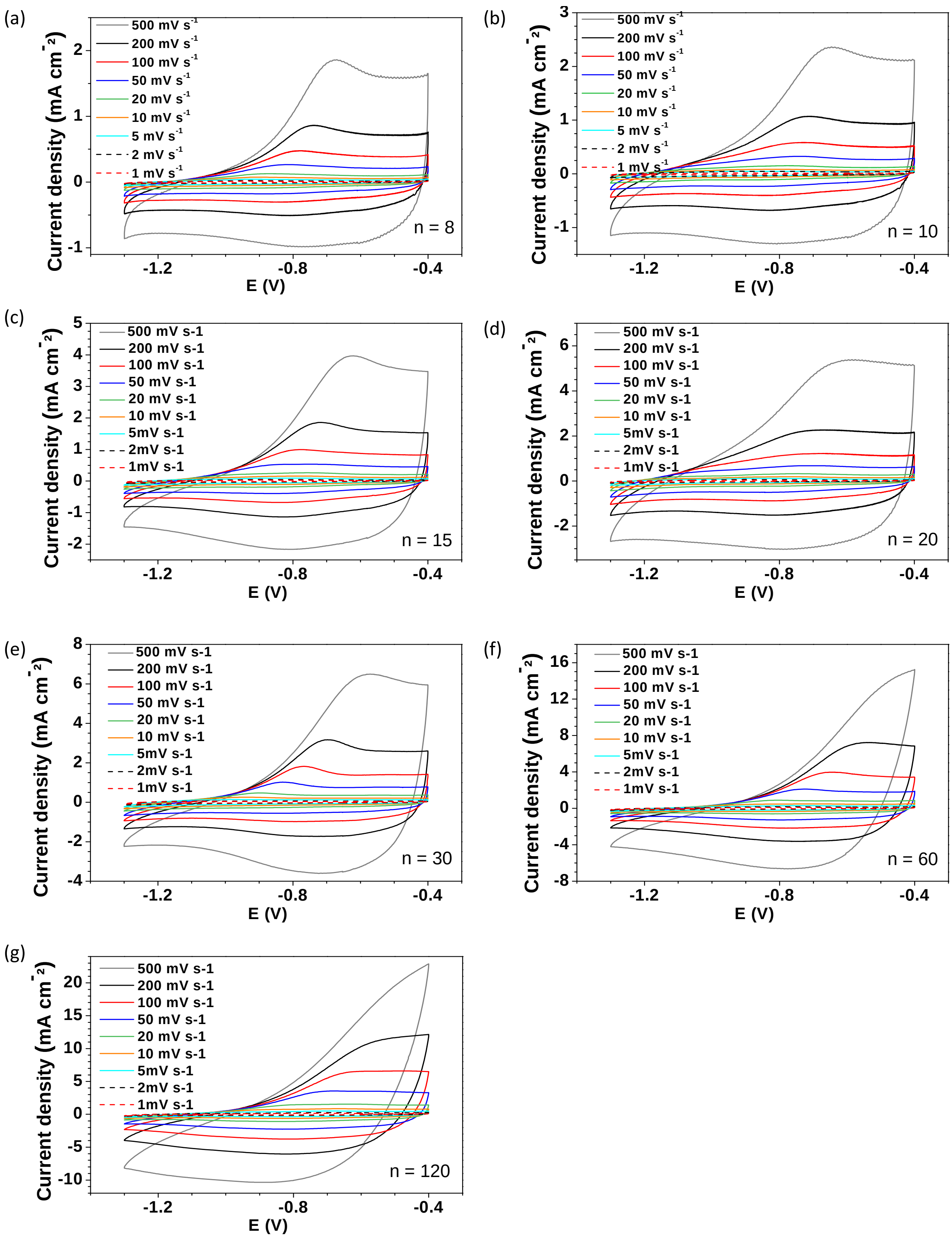

Fig. S8. Voltamogramms of (Fe_3O_4@FLG /PEDOT:PSS)$_n$ hybrid architecture recorded at different scan rates from 1 to 500 mV s^{-1} for (a) n = 8 bilayers, (b) n = 10 bilayers, (c) n = 15 bilayers, (d) n = 20 bilayers, (e) n = 30 bilayers, (f) n = 60 bilayers and (g) n = 120 bilayers.

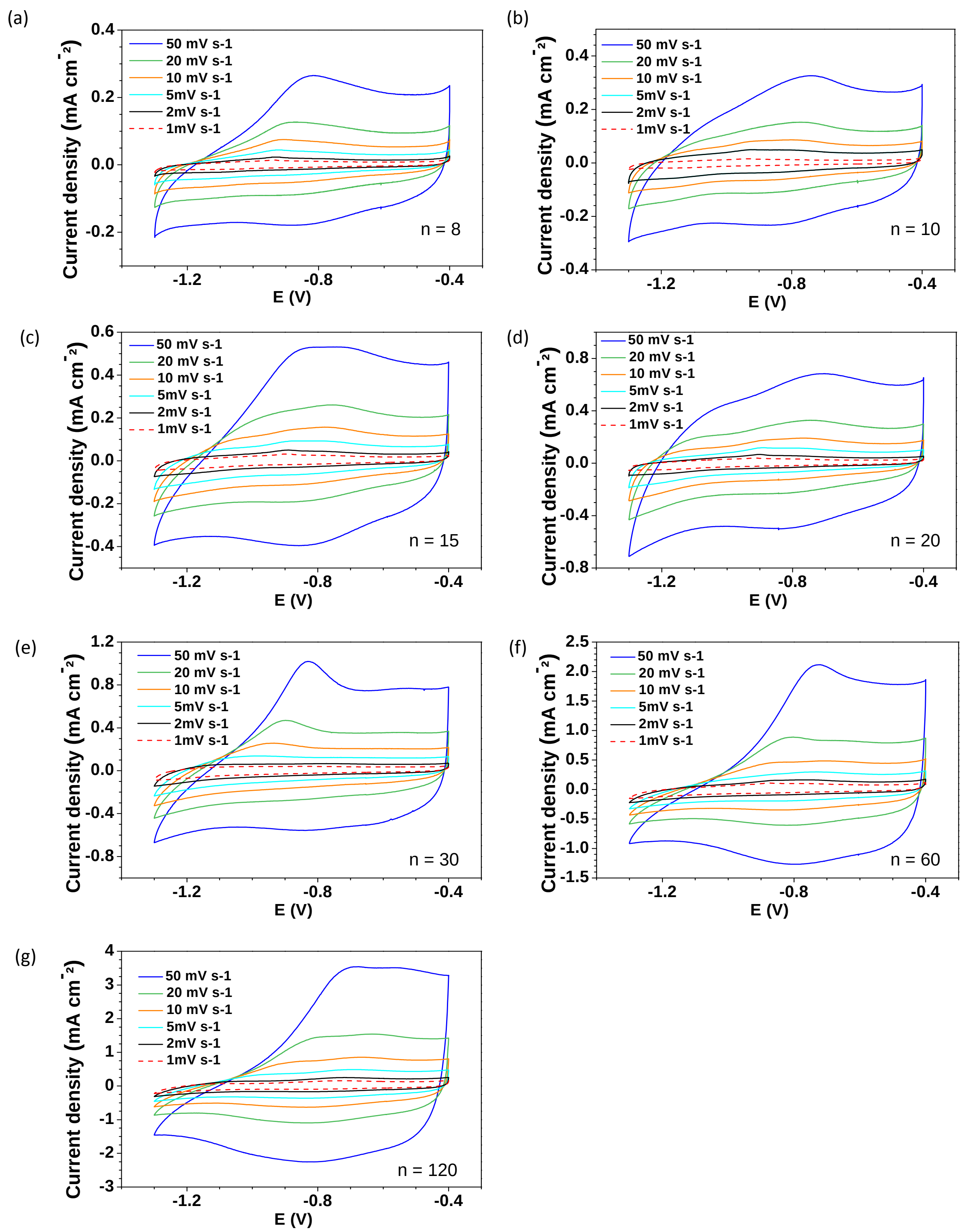

Fig. S9. Voltamogramms of (Fe_3O_4@FLG /PEDOT:PSS)$_n$ hybrid architecture recorded at different scan rates from 1 to 50 mV s^{-1} for (a) n = 8 bilayers, (b) n = 10 bilayers, (c) n = 15 bilayers, (d) n = 20 bilayers, (e) n = 30 bilayers, (f) n = 60 bilayers and (g) n = 120 bilayers.

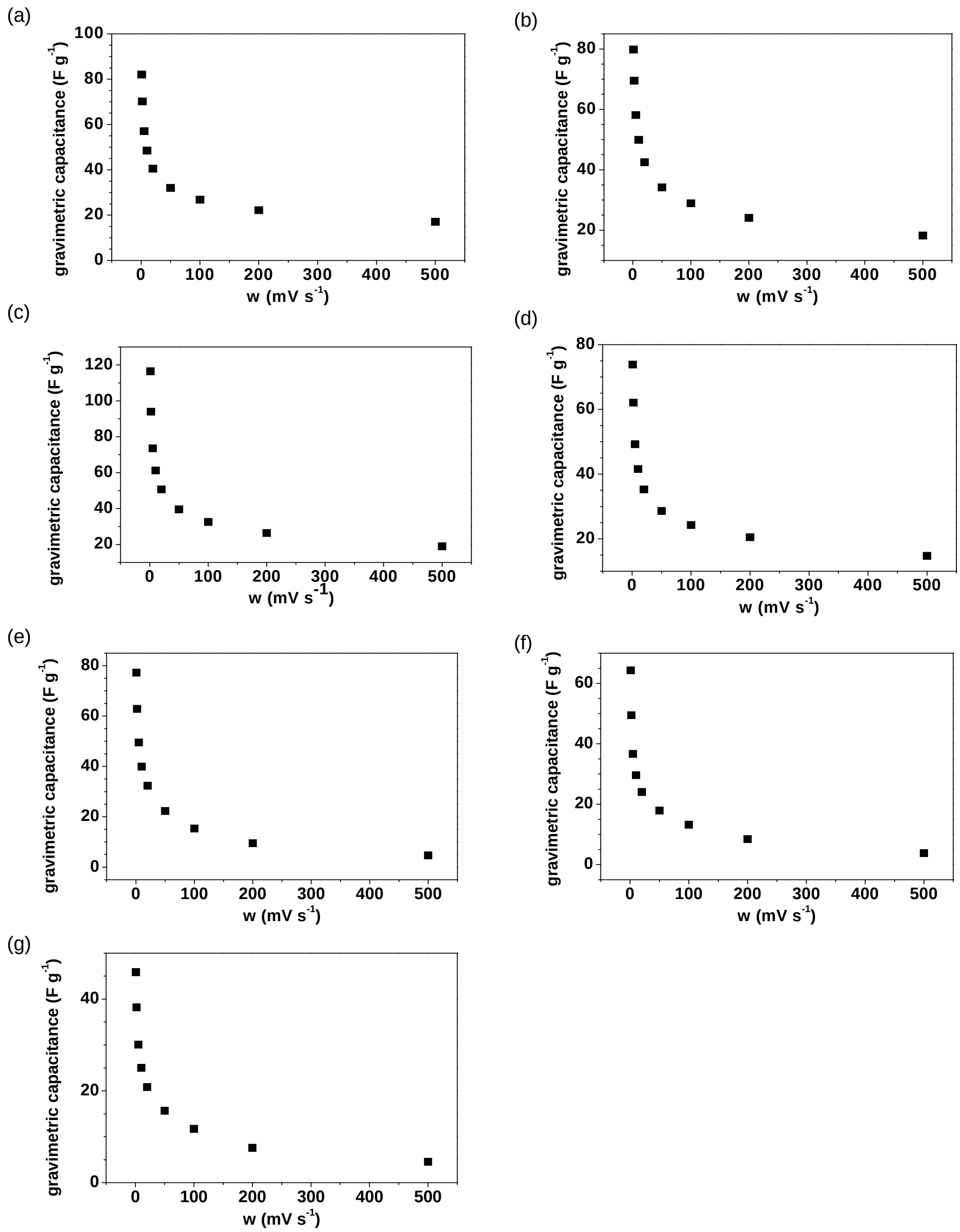

Fig. S10. Gravimetric capacitance of (Fe_3O_4@FLG /PEDOT:PSS)$_n$ hybrid architecture as a function of scan rate recorded with a potential range between -1.3 and -0.4 V for (a) *n* = 8 bilayers, (b) *n* = 10 bilayers, (c) *n* = 15 bilayers, (d) *n* = 20 bilayers, (e) *n* = 30 bilayers, (f) *n* = 60 bilayers and (g) *n* = 120 bilayers.

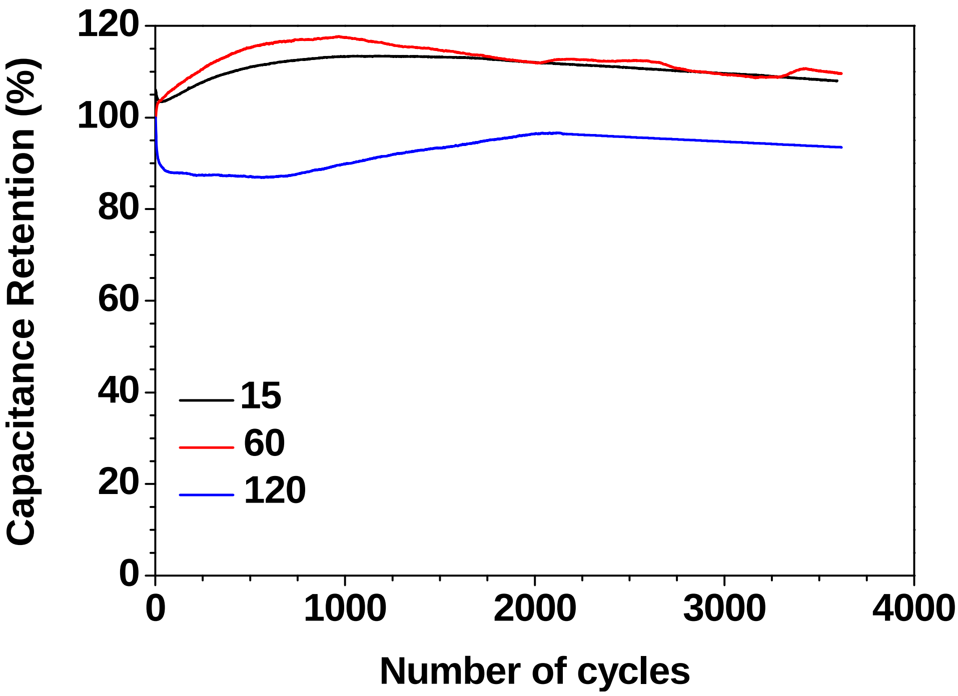

Fig. S11. Capacitance retention (%) as a function of number of cycles of (Fe_3O_4@FLG /PEDOT:PSS)$_n$ hybrid architecture for different number of bilayers (*n*).

Table S1 Phase shift constants of CPE of equivalent circuit used for the modelling of EIS spectra of (Fe_3O_4@FLG /PEDOT:PSS)$_n$ hybrid architecture with n = 15 bilayers and n = 120 bilayers. The values of constant phase shift a have been determined from the impedance of CPE: $Z_{CPE}=((jw)^a Q_0)^{-1}$, where w is the frequency and Q_0 is a capacity of CPE. The value of Z_{CPE} was calculated from fitting the parameters of equivalent circuit to experimental impedance spectra.

	a_1		a_2	
	Before 1000 cycles	After 1000 cycles	Before 1000 cycles	After 1000 cycles
n = 15	0.79	0.78	0.90	0.88
n = 120	0.67	0.66	0.83	0.78

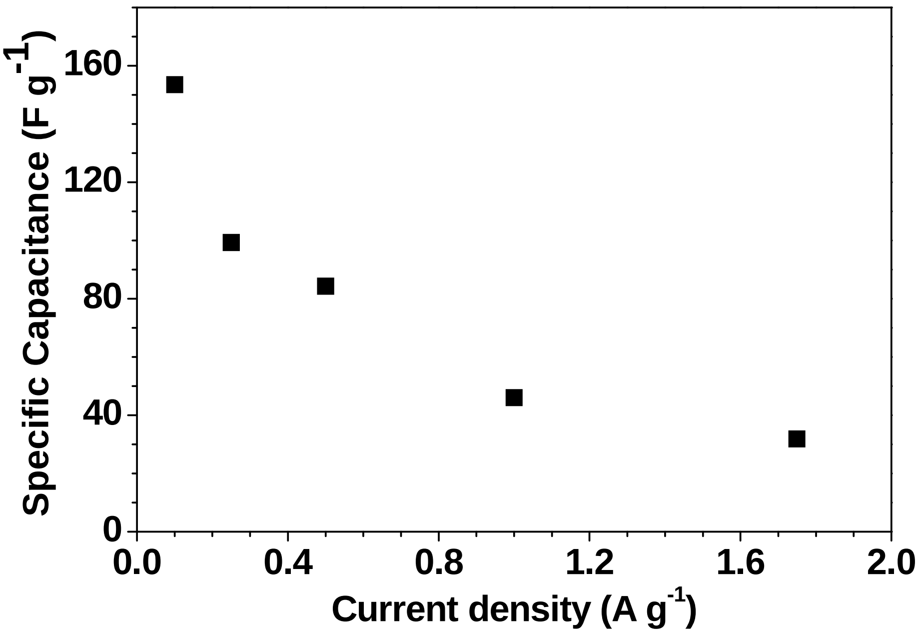

Fig. S12. Specific capacitance of (Fe_3O_4@FLG /PEDOT:PSS)$_{15}$ hybrid architecture at various discharge current densities.

Table S-2: Comparison of different studies dealing with carbon and Fe_3O_4 based materials for supercapacitor applications. CNT: carbon nanotubes; RGO: reduced graphene oxide; LbL: layer-by-layer.

Sample	Developed working electrode	Electrochemical measurement	Specific capacitance	References
CNT/Fe_3O_4	Nickel foam coated with CNT/Fe_3O_4 obtained by hydrothermal reaction, acetylene black and polytetrafluoroethylene (weight ratio 80:15:5) and dispersed in ethanol.	Three-electrode cell 6M KOH electrolyte	117.2 F g^{-1} at 0.01 A cm^{-2}	Guan *et al.* *Mater. Sci. Eng.*, 2013, **178,** 736.
Fe_3O_4/rGO	LbL assembly alternating Fe_3O_4 and GO layers on ITO electrode. Multilayers film were further reduced using hydrazine	Three-electrode cell 1M NaCl electrolyte	151 F g^{-1} at 0.9 A g^{-1}	Khoh *et al.* *Colloids Surf. A*, 2013, **436**, 104
Fe_3O_4@FLG	LbL assembly alternating Fe_3O_4 grafted on graphene and PEDOT:PSS on a gold electrode.	Three-electrode cell 0.5 M Na_2SO_3 electrolyte	153 F g^{-1} at 0.1 A g^{-1}	Our study
co-Fe_3O_4/rGO	co-Fe_3O_4 obtained by coprecipitation and mixed with rGO (weight ratio 9:1), acetylene black and polytetrafluoroethylene (weight ratio 80:10:10) pressed onto Ni-mesh.	Three-electrode cell LiOH electrolyte	154 F g^{-1} at 0.5 A g^{-1}	Qu *et al.* *Adv Mater*, 2011, **23**, 5574.
Fe_3O_4/carbon nanosheets	Self-Assembly of iron precursor $FeCl_3$ and ethylene glycol in presence of NH_3HCO_3. After calcination treatment Fe_3O_4/carbon nanosheets were obtained as working electrode.	Three-electrode cell 1 M Na_2SO_3 electrolyte	164.3 F g^{-1} at 0.9 A g^{-1}	Liu *et al.* *J. Mater. Chem. A*, 2013, **1**, 1952.
Fe_3O_4/rGO	Nickel foam coated with Fe_3O_4/rGO obtained by hydrothermal reaction, acetylene black and polyvinylidiendifluoride (weight ratio 80:10:10)	Three-electrode cell 1 M KOH electrolyte	220 F g^{-1} at 0.5 A g^{-1}	Wang *et al.* *J. Power Sources*, 2014, **245**, 101.