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Few-layer graphene improves silicon performance in Li-ion battery anodes

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In table 1 we report the main figures of merit (FoM) of the as lithium-ion battery (LIBs) anodes based on silicon nanoparticles (SiNPS) mixed with few-layer graphene flakes (FLG), reduced graphene oxide (RGO) and carbon black (CB) and the comparison with state of the art values reported currently in literature.

Specific capacity (mAh g _{tot} -1)	Fading (% per cycle)	Cycling CE	SiNPs Size	Graphene- based material anode	CB+binder before assembly	electrolyte Additives	Ref.
3500	1.7	98	700		v	FEC	1
3000	1.3	98	<500		v	VC	2
1940	1.3	-	80	CB+rGO	v	-	3
3500	1.0	98	50		v	FEC	1
3500	0.6	99	<500		v	FEC	2
1500	0.6	98.5	50-100	CB +rGO	v	FEC	4
1930	0.6	98	50		v	FEC	5
1470	0.5	98.5	4-10	СВ	v	all PC	6
2094	0.4	98.5	80	CB +rGO	v	_	7
1250	-	99.5	<10	С	-	-	8
750	0.25	98.5	50	rGO	-	-	9
620	0.25	99	7	CB+rGO	-	FEC	this work
1400	0.22	98.5	100	CB+SnNPs	-	FEC	10
594	0.21	99.3	7	СВ	-	FEC	this work
1400	0.2	99.2	5	СВ	v	_	11
1160	0.2	98.5	50	CB +rGO	v	VC	12
710	0.2	99.5	50 100	С	v	_	13
2250	0.17	99	50	TiN synth	v	FEC	14
1300	0.14	98	50 100	rGO	v	-	15
620	0.09	99.8	100	СВ	v	_	16
2500	0.08	-	3	rGO+rSiOx	-	_	17
1400	0.08	99.5	5	СВ	v	FEC	11
1000	0.06	99	50-100	CB +EG	v	_	18
675	0.04	99.5	7	CB +LPEgraphene	-	FEC	this work
1142	0.02	99	80	CB +rGO	v	_	7
1000	0.018	99.4	150 200	CB +rGO	v	FEC	19
663	0.005	99.7	50-100	CB +rGO	v	FEC	4
900	0.004	99	3	rGO	v	-	20

Table S1: Main figures of merit of the as-produced anodes SiNPs-FLGs; SiNPs-RGO and SiNPs-CB and the comparison with literature values.

CE= Coloumbic efficiency; SiNPs= silicon nanoparticles; CB=carbon black; EG= expanded graphite; FEC= fluoroethylene carbonate; VC= vinylene carbonate.

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Figure S1 reports the X-ray powder diffraction and the Raman spectra of amorphous silicon nanoparticles (a-SiNPs). In Figure S1a the Gaussian peaks centred at ~28° (blue curve) and 50° (red curve) correspond to the broad peaks characteristic of the silicon amorphous phase. In figure S1b the two broad Gaussian components centred at ~380 cm⁻¹ and ~480 cm⁻¹ correspond to the longitudinal optical –LO- (blue curve) and transversal optical –TO- (red curve) Si-Si vibration modes of a-SiNPs. ^[21]



The atomic force microscopy (AFM) analysis gives us information about the thickness of the exfoliated graphitic flakes (Fig. S2a). The statistical analysis ((Fig. S2a) shows that the flakes thickness is in the 1-15nm range with the maximum population peaked at ~2 nm. The thickness distribution mostly corresponds to a combination of single- (SLG) and few-layer (FLG) graphene flakes (i.e., <8 layers), with the presence of multi-layer graphene (MLG), i.e., >8 layers. In particular, flakes thicker than 5 nm account for ~25% of the total dispersed flakes.



Figure S2. a) AFM image of the LPE produced graphene-based flakes. The main population of flakes in the sample is peaked at \sim 2nm, corresponding to few-layer (FLG) graphene flakes (i.e., <8 layers). The AFM image shows also the presence of thick unexfoliated graphitic flakes.



Figure S3: a) Raman spectra at a 532 nm excitation wavelength for representative flakes in the ethanol dispersion (red curve) and pristine graphite flakes (black curve). Distribution of b) Pos(2D), c) FWHM(2D) and d) I(D)/I(G) as a function of FWHM(G), for the ethanol dispersion.

The Raman spectrum of graphene-based flakes produced by LPE mainly consists of three main peaks. The G peak, at 1580 cm⁻¹, corresponding to the E_{2g} phonon at the Brillouin zone centre,^[22] the D peak, located at 1350 cm⁻¹, associated with the breathing modes of the sp² carbon rings, requiring a defect for its activation,^[22,23] and the 2D peak at ~2700 cm⁻¹, which is the second order of the D peak.^[22,24] This peak has a single Lorentzian component in single layer graphene (SLG), upshifting in position and splitting up for the case of few-layer (FLG) and multi-layer (MLG) graphene flakes.^[25] An estimation of the number of graphene layers composing a flake can be carried out from a statistical Raman analysis of the peak position (Pos(2D)) and lineshape, i.e., the full width at half maximum (FWHM(2D)), of the 2D peak.^[25] The Raman spectrum of graphene-based dispersion shows I(2D)/I(G) ratio of ~0.6, the position of the 2D peak (Pos(2D)) (Fig. S2b) at ~2700 cm⁻¹, the FWHM(2D) peaked at ~68 cm⁻¹ (Fig. S2c). These data indicate that the sample is mostly composed by a combination of SLG and FLG flakes,^[22,26] in agreement with the AFM data reported in Figure S2. The Raman spectrum of graphene-based dispersion shows also significant D peak intensity (Fig. S2a). However, the high I(D)/I(G) ratio is attributable to the edges of the sub-micrometre flakes (see Fig. 2c,d of the main text), rather than to the presence of in-plane defects. In fact, in the latter case the D peak would

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be much broader, and G and D' are merged in a single band.^[22,23] In our case, the lack of a clear correlation between I(D)/I(G) and FWHM(G) (Fig. S2d) supports the absence of structural defects onto the flakes basal plane.

The black curve in Figure S4 shows the thermo gravimetric analysis (TGA) of a composite silicon-carbon anode (containing Super P) during the annealing process in nitrogen. The measurement highlights a weight loss of ~25% when the temperature reaches 600 °C. The blue curve depicts the corresponding differential thermal gravimetric analysis (DTG). Two distinct features can be observed as a result of the thermal decomposition of poly acrylic acid (PAA). The first one, at ~200 °C, corresponds to water effusion, residual monomers, hydrocarbons and CO₂, while the second one, at ~400 °C, is related to the release of acrylic acid moieties.^[27]



Figure S4. The black curve shows the thermo gravimetric analysis (TGA) of a hybrid silicon-carbon anode (containing Super P) during the annealing process in nitrogen. The blue curve depicts the corresponding differential thermal gravimetric analysis (DTG).

Fourier Transform InfraRed Spectroscopy (FTIR) analysis is carried out both on the as-deposited (pristine) and annealed anodes. The FTIR spectrum of the as-deposited anode (figure S5a, blue line) reveals the presence of two prominent peaks at ~1050 cm⁻¹ and ~1709 cm⁻¹. The first one is associated to the Si-O-Si asymmetric stretching model,^[28] which thus confirms the possible SiNPs surface oxidation upon extraction from the synthesis reactor, while the latter is associated to the PAA C=O stretching mode.^[29] After the high temperature annealing step, the peak at ~1709 cm⁻¹ becomes negligible as a consequence of the polymer thermal decomposition. The appearance of Si-C and Si-CH₂ modes in figure S5a (pink curve) reveals the

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bonding between the SiNPs and the carbon matrix, beneficial for the mechanical stability of the assembled anodes.^[30] The individual materials (*i.e.*, SiNPs, PAA, and Super P) used for the slurry preparation are also analyzed and the corresponding FTIR peaks showing the known spectral features widely reported in literature,^[31-33] are shown in figure S4b.



Figure S5 a) FTIR spectra of dried and annealed hybrid silicon-carbon anodes. b)FTIR spectra of the three compounds comprising the slurry: SiNPS, PAA and Super P.

The structural properties of the fabricated anodes are investigated via energy-dispersive X-ray (EDX) spectroscopy to better understand the effect of the annealing process on the composite material. The EDX analysis performed on a 100 μ m × 100 μ m area shows the formation of islands with mixed Si and C elemental composition over the Cu current collector substrate. The EDX maps reveal, on one hand, that silicon is confined in the aforementioned islands (see Fig. S6 d and Figure 3 in the main text), while, on the other hand, carbon uniformly covers the entire electrode surface (Fig. S6 f). This is beneficial for the electrical contact both with the copper substrate and amongst the components of the anode.

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Figure S6. High resolution scanning electron microscopy (HR-SEM) top view analysis of a hybrid anode material containing Super P (a) before and (b) after thermal annealing. Figures c-f show the EDX elemental analysis of the electrode surface: SEM micrograph of the (c) investigated surface, (d) copper and (e) carbon signals respectively. A carbon coating is observed over the whole electrode surface, hence promoting improved electrical contact with the copper substrate and among the components encompassing the anode material.^[34]

A more in depth analysis via high resolution-EDX line scans over a 100 µm region reveals a partial segregation between silicon and carbon and an oxidation of the SiNPs, possibly due to unintentional ambient air exposure in between the different fabrication steps (especially after extraction from the SiNPs synthesis reactor). Oxidation of silicon can be inferred by the matching of the signal shapes between the Si (red) and O (blue) signals, while silicon-carbon segregation at these length scales can be deduced by the opposite occurrence of peaks and valleys in the C (black) and Si (red) signals.



Figure S7. EDX line scan. a) SEM micrograph showing the direction of EDX line scan (yellow dotted line). b) carbon, silicon and oxygen EDX signals along the line scan. Data are shown for the anode material containing Super P.

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