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Fig. S1. Schematic of the electrode surface modification. (A) 3 D schematic of the working electrode, (B) embedded VACNF tip, (C) formation of –COOH groups after  $HNO_3$  treatment, D) linker (EDC, Sulfo-NHS) binding and anti-CRP probe immobilization and E) CRP target binding with anti-CRP immobilized on VACNFs tips.



Fig. S2 2-D AFM (A,C,E,G) images and 2-D graphs (topographical profile) (B,D,F,H)obtained by drawing three lines (Blue, Red and Green) cross sections on 2-D images (A,C,E,G) of VACNF electrodes scanned after different durations of ECE performed in an aqueous solution of 1 M NaOH at 1.5 V. (A and B) 5.0 s, (C and D) 12.5 s, (E and F) 15.0 s and (G and H) 20.0 s respectively.





5 µm

## Table 1. List of Elements (Normalized)

								_					
Spectrum	In	с	0	Si	Cr	Total	Spectrum	In	с	0	Si	Cr	Total
	stats.							stats.					
							Spectrum 1	Yes		28.90	39.42	31.67	100.00
Spectrum 1	Yes	15.20	28.97	22.96	32.87	100.00	Spectrum 2	Yes		30.38	30.74	38.88	100.00
Spectrum 2	Yes	13.52	28.60	23.29	34.59	100.00	Spectrum 3	Yes		29.90	29.79	40.32	100.00
Spectrum 3	Yes	13.20	29.43	23.90	33.48	100.00	Spectrum 4	Yes	6.21	31.09	26.89	35.81	100.00
Spectrum 4	Yes	13.94	31.34	22.82	31.91	100.00	Spectrum 5	Yes		30.23	30.96	38.81	100.00
Spectrum 5	Yes		29.19	28.84	41.97	100.00	Spectrum 6	Yes	5.54	32.25	29.60	32.62	100.00
Spectrum 6	Yes		32.02	29.44	38.54	100.00	Spectrum 7	Yes		31.00	30.35	38.66	100.00
Max.		15.20	32.02	29.44	41.97		Spectrum 8	Yes		30.83	31.20	37.97	100.00
Min.		13.20	28.60	22.82	31.91		Spectrum 9	Yes	8.19	29.18	25.83	36.80	100.00
	-						Spectrum 10	Yes	7.33	30.07	26.27	36.33	100.00
							Spectrum 11	Yes	8.17	31.12	25.81	34.90	100.00
							Spectrum 12	Yes	6.81	30.27	27.03	35.90	100.00
							Spectrum 13	Yes	6.36	30.87	26.62	36.15	100.00
							Spectrum 14	Yes	5.01	29.92	28.05	37.02	100.00
							Spectrum 15	Yes	6.18	29.67	28.39	35.76	100.00
							Max.		8.19	32.25	39.42	40.32	
							Min.		5.01	28.90	25.81	31.67	

Fig. S3 SEM images with different regions marked as spectrum and tables for quantitatve %w values of consitutent material components from different spectrums. (A and B) SEM images of un-etched and etched in 1 M NaOH at 1.5 Volts for 17.5 s. (C) Table 1 and (D) Table 2 list of the %w of consitiuent components explored by EDS at different regions (spectrums) of SEM image (A and B).



Fig. S4 SEM images of excessively etched VACNF electrode in 1 M NaOH at 1.5 V for 22.0 s. (A) SEM image representing oxide etching region (Spectrum1) in a VACNF electrode cross section, (B) EDS spectrum for the region under study showing peaks for Si and onle as Cr and C are eteched away due to excessive etching. Table 3 lists the %w of consitiuent components explored by EDS for spectrum1.