

## Supplementary Information

### **Layer-by-Layer Assembly of Inorganic-Organic Molybdovanadogermanic (GeMoV)-Polyluminol Composite Electrodes for Capacitive Charge Storage**

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**Table S 1:** Comparison of the volumetric capacitance of CNT modified with P, Ge, and Si containing Keggin type polyoxometalate composite electrodes.

Materials	Capacitance	Cycling Stability	Voltage window ( $\Delta V$ ) $\pm$	Ref
PMo-PDDA-CNT	84 F/cm <sup>3</sup> at 50 mV/s	-	0.58	1
PMoV <sub>2</sub> -PDDA-CNT	88 F/cm <sup>3</sup> at 50 mV/s	-	0.65	1
PMo-PDDA-CNT	0.4 F/cm <sup>2</sup> at 5 mV/s	-	0.55	2
PMo-CNT	-	-	0.55	3
PMo-AC	-	91 % (8000 cycles)	0.65	4
GeMo-PPDA-CNT	109 F/cm <sup>3</sup> at 50 mV/s 41.9 mF/cm <sup>2</sup> at 1V/s	93.7 % (5000 cycles)	0.55	5
SiMo-PDDA-CNT	111.2 F/cm <sup>3</sup> at 50 mV/s	-	0.5	5
PMo-p-EVIM-Br <sup>+</sup> -CNT	102.1 F/cm <sup>3</sup> at 100 mV/s	-	0.45	6
GeMoV-PDDA-CNT	72.4 F/cm <sup>3</sup> at 100 mV/s (35.6 mF/cm <sup>2</sup> at 1V/s)	77% (4000 cycles)	0.77	This work
GeMoV-CpLum-CNT	66.3 F/cm <sup>3</sup> at 100 mV/s (32.05mF/cm <sup>2</sup> at 1V/s)	87 % (4000 cycles)	0.9	
GeMoV-PDDA-CpLum-CNT	80.7 F/cm <sup>3</sup> at 100 mV/s (83.6 mF/cm <sup>2</sup> at 1V/s)	83 % (4000 cycles)	0.9	
*1-ethyl-3-vinylimidazolium bromide (p-EVIM-Br) $\pm$ Windows of redox activity measured from literature data				

**Table S 2:** The peak position for CNT coated with GeMoV-PDDA , CpLum, GeMoV-CpLum, and GeMoV-PDDA-CpLum .

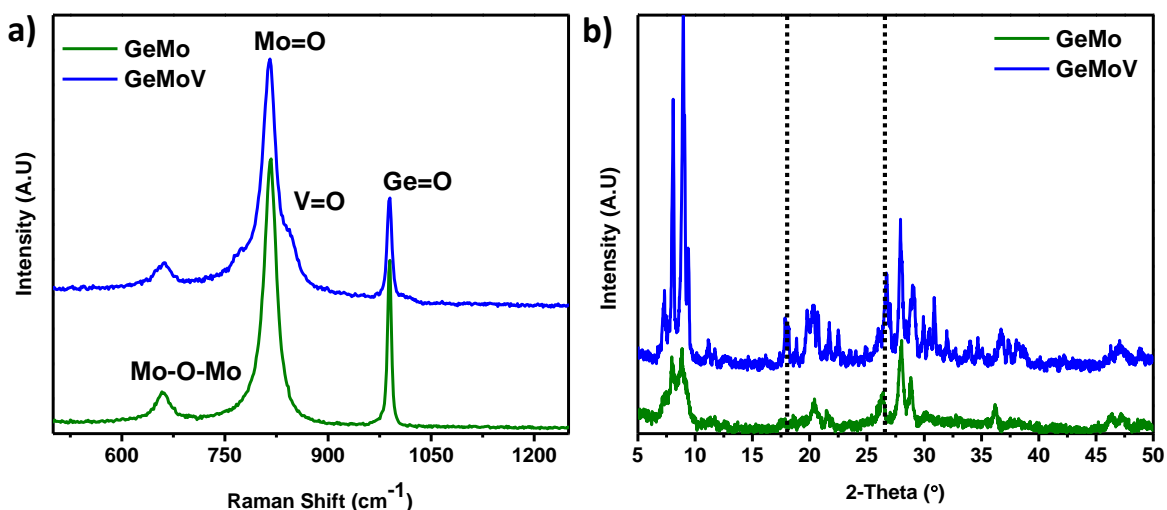
	E <sub>ox</sub> Position (V)						CpLum
	Peak I	Peak II	Peak III	Peak IV	Peak Va	Peak Vb	
GeMoV-PDDA	-0.08	0.08	0.22	0.29	0.38	0.59	
CpLum							0.36, 0.46, 0.64
GeMoV-CpLum	-0.07	0.08	0.23	0.29	0.40	-	0.62
GeMoV-PDDA-CpLum	-0.07	0.09	Sh	0.29	0.39	-	0.62

**Table S 3:** Peak to peak separation for GeMoV-PDDA, GeMoV-CpLum , and GeMoV-PDDA-CpLum at 100 mV/s.

	Peak Separation (mV)					Peak VI (CpLum)
	Peak II	Peak III	Peak IV	Peak Va	Peak Vb	
CpLum	-	-	-	-	-	100
GeMoV-PDDA	46	38	-	47	14	-
GeMoV-CpLum	26	22	10	31	-	56
GeMoV-PDDA-CpLum	48	49	*Sh	45	-	56

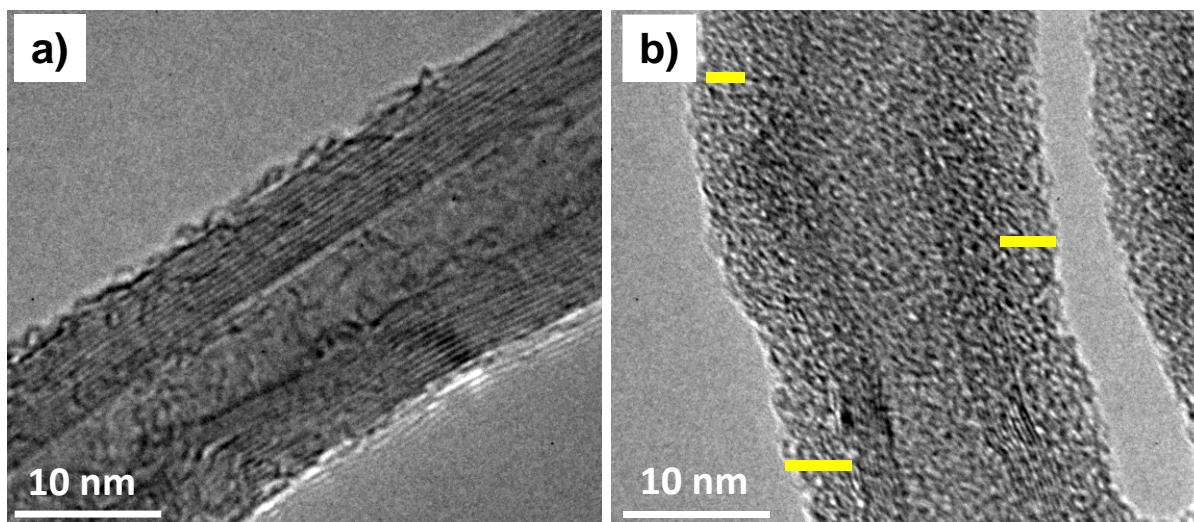
### Supplementary figure 1

The X-ray powder diffraction was conducted on GeMoV to confirm the Keggin structure of the synthesized materials. The XRD pattern of GeMoV is compared to that of GeMo in **Figure S1a**. Typical features of the Keggin structure were observed for both materials at  $2\theta$  between  $7.3^\circ$  and  $9^\circ$  and  $26.7^\circ$ <sup>1, 7, 8</sup>, indicating the successful synthesis of GeMoV crystals. The Raman spectrum of GeMoV was also recorded and compared to GeMo as seen in **Figure S1b**). Both spectra had bands at  $281.17\text{-}331.69\text{ cm}^{-1}$  (Mo-o),  $661.5\text{ cm}^{-1}$  (Mo-O-Mo),  $815.4\text{ cm}^{-1}$  (Mo=O), and  $990\text{ cm}^{-1}$  (GeMo). However, the GeMoV had an additional Raman shoulder at  $843\text{ cm}^{-1}$  that may be attributed to the V=O signal.



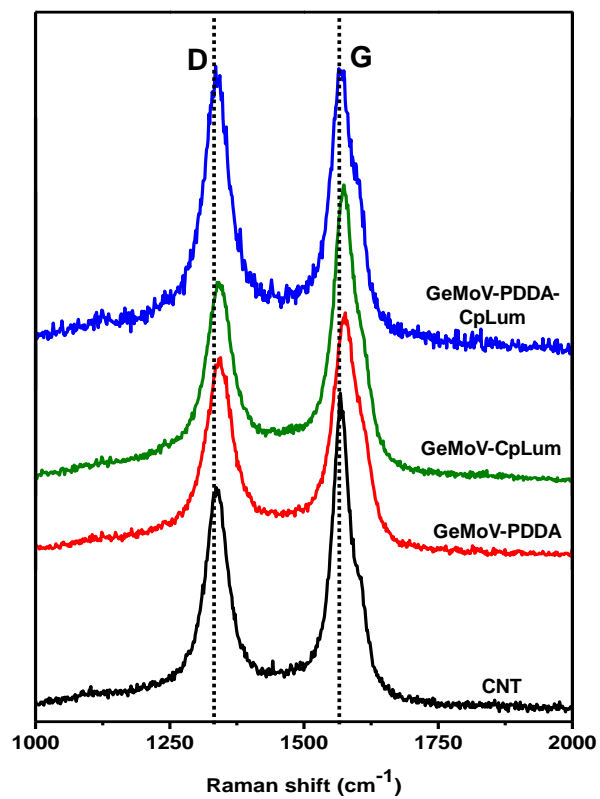
**Figure S 1:** Comparison of a) Raman spectra and b) XRD pattern of GeMoV vs GeMo

## Supplementary figure 2



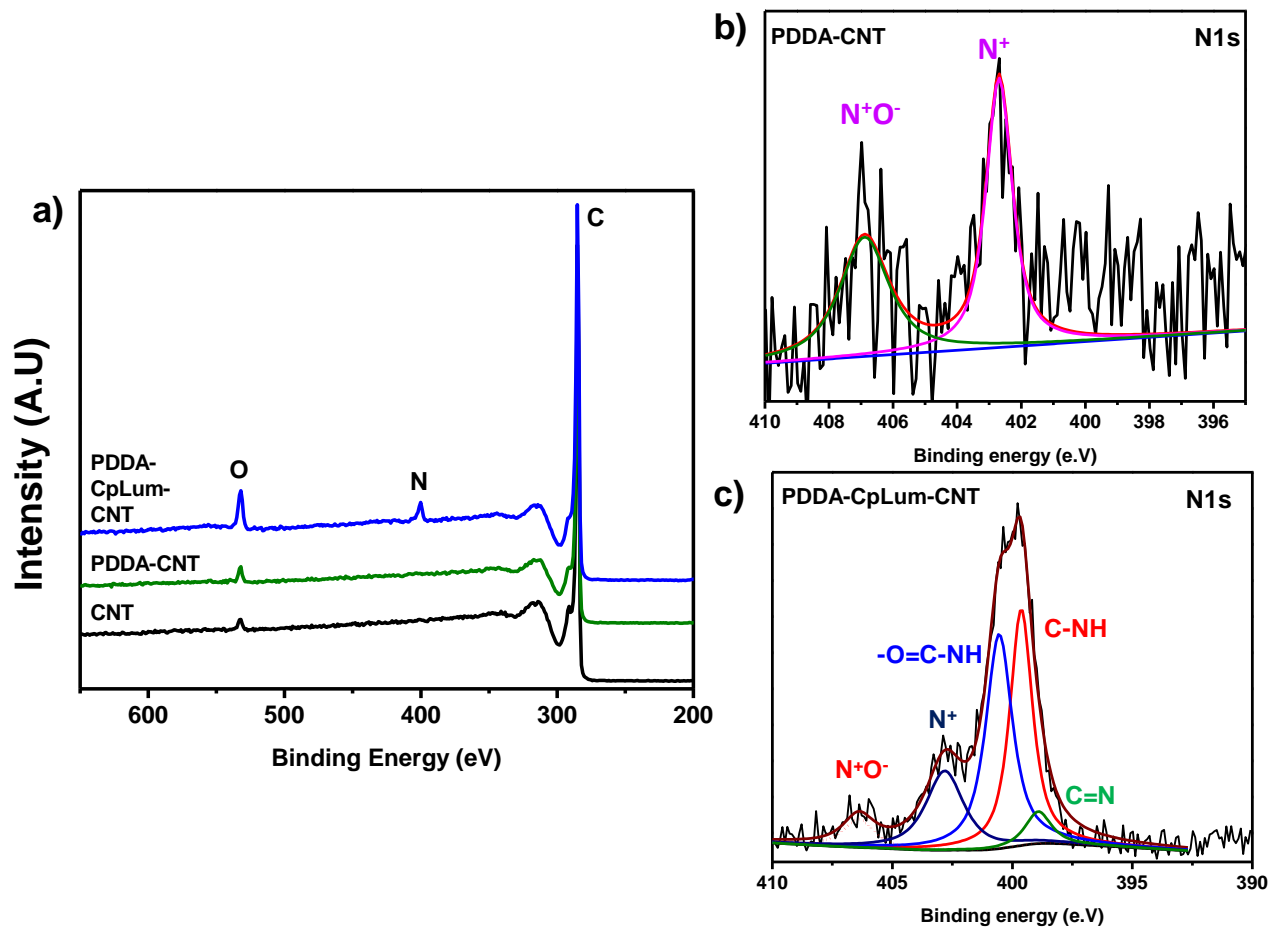
**Figure S 2:** HRTEM images of a) unmodified CNT and b) GeMo-PDDA-CpLum-CNT composite.

## Supplementary figure 3



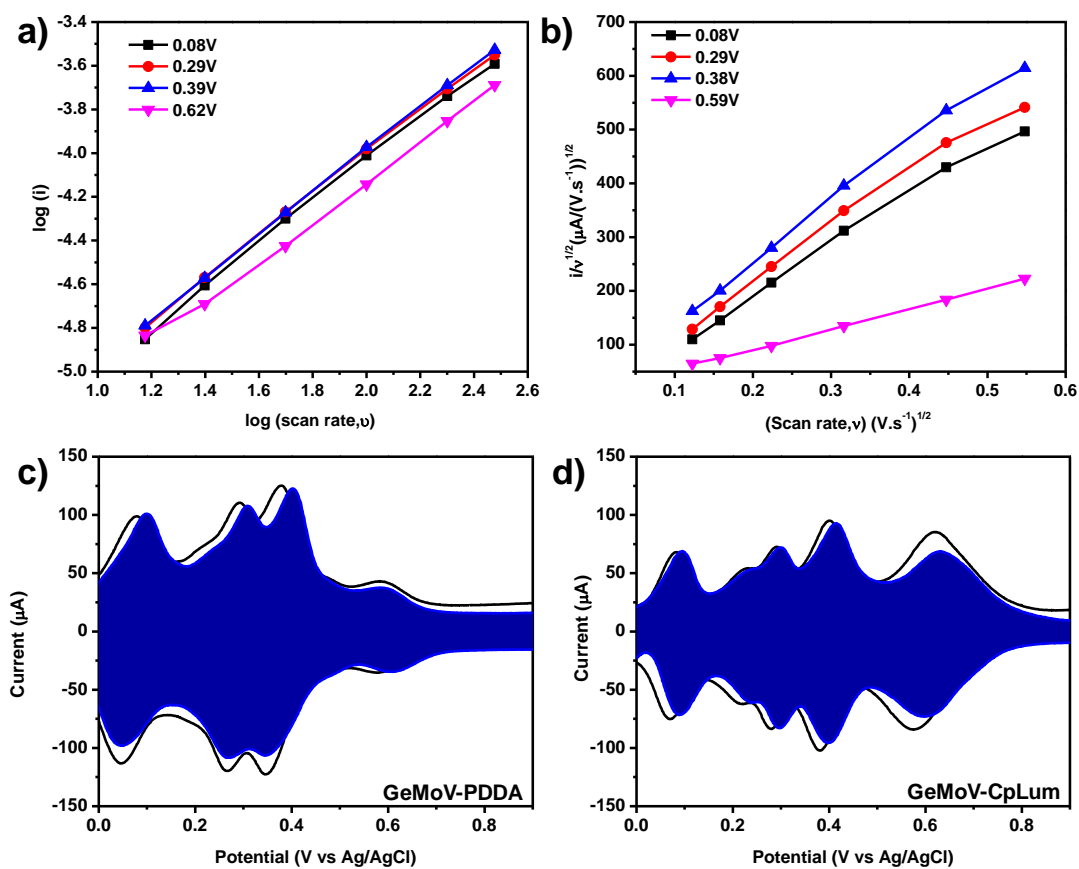
**Figure S 3:** Raman spectra of bare CNT and CNT modified with: GeMoV-PDDA, GeMoV-CpLum, and GeMoV-PDDA-CpLum.

## Supplementary figure 4



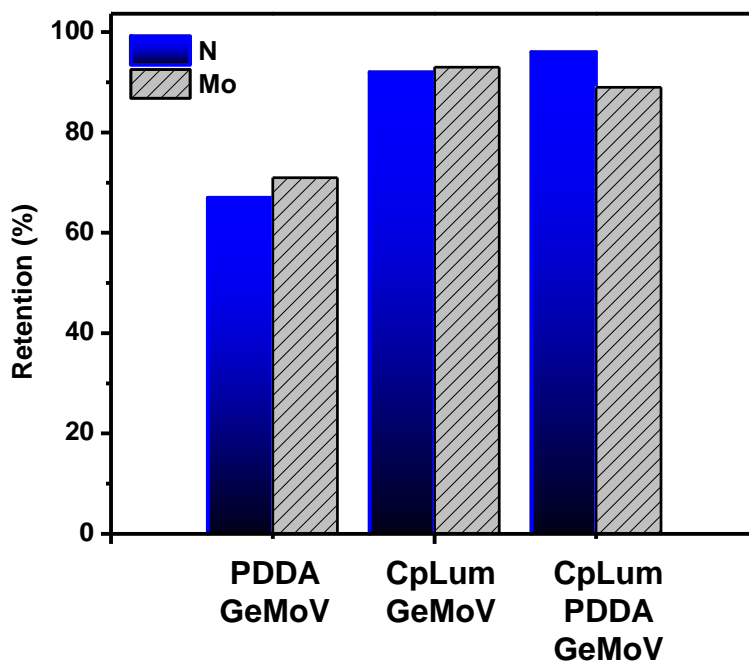
**Figure S 4:** a) and XPS survey spectra, b and c) High resolution N1s XPS spectra for PDDA-CNT and PDDA-CpLum-CNT, and d) high resolution O1s spectra for CNT modified with PDDA, PDDA-CpLum, GeMoV-PDDA , GeMoV-CpLum and GeMoV-PDDA-CpLum.

## Supplementary figure 5



**Figure S 5:** Example of extrapolated curve for GeMoV-PDDA-CpLum-CNT with a)  $\log(i)$  vs  $\log(\text{scan rate})$ , b) Current vs square root of scan rates from equation 2, and c and d) CV curve for capacitive contribution for CNT: GeMoV-PDDA and GeMoV-CpLum at 100 mV/s.

## Supplementary figure 6



**Figure S 6:** Mo and N retention after 4000 cycles for CNT modified with GeMoV-PDDA , GeMoV-CpLum and GeMoV-PDDA-CpLum.

### References:

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