

Supplementary Materials

Functionalized graphene-polyoxometalate nanodots assembly as “organic-inorganic” hybrid supercapacitors and insights into electrode/electrolyte interfacial processes

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Materials and Methods

Structural characterization

Samples for transmission electron microscopy (TEM) and energy dispersive x-ray spectra (EDX) were prepared by placing two drops of individual component and of composite hybrids on commercial lacey carbon coated Cu grids (Ted Pella Inc. CA) and allow to air dry giving several regions and particles for imaging. They were taken using a JEOL instruments (Model 1400 Plus, OR) operating in cryo-EM modes at 120 kV and 1 nA with a Be specimen holder, a Gresham SiLi detector with Moxtek AP3.3 window. For EDX spectral signals providing elemental distribution, we used 0.10 μm aperture producing a small spot size and spread the beam to increase the electron coherence length at the samples. TEM measurements provided nanoscale microstructure and determines interplanar spacing.

For understanding of the interactions between graphene and polyoxometalates, we measured optical spectroscopy including UV-Vis absorption and fluorescence spectroscopy using BioTek spectrometer (Model Synergy H1 Multi-mode plate Reader, Winooski, VT) equipped with a xenon lamp as broadband excitation source. UV-Vis the absorption is measured between 210 nm and 450 nm in interval of 1 nm and for fluorescence measurements, the excitation wavelength used was $\lambda_{\text{ex}} = 270$ nm in interval of 0.5 nm in the range 300-370 nm at room temperature ~ 298 °K. Micro-Raman spectroscopy is used to determine the crystallinity and localized lattice vibrational structure. The Raman spectra were recorded at various points on the hybrids using a Raman spectrometer (Model InVia Renishaw *plc*, UK) equipped with laser excitation wavelength 633 nm ($E_L = 1.92$ eV) and ~ 500 μW power incident at the sample, with edge filters cutting at ~ 100 cm^{-1} and an objective lens of 50x used to provide spot size of ~ 1 -2 μm . The scattered light from the sample is collected in backscattering geometry, transmitted by a beam splitter and detected by CCD camera. Extreme care was taken to avoid sample damage caused by laser-induced thermal degradation. Raman shift ranged from 120 cm^{-1} to 3400 cm^{-1} for POM and POW containing hybrids with spectral resolution of 1 cm^{-1} . Allowing more details of the interaction between graphene and polyoxometalates nanodots, we measured room temperature electrical (I-V) properties. We made electrical contacts with colloidal silver paste and attached a Cu wire for connection and the data was acquired with Keithley 2400 source meter (Keithley, OH). We measured two point contact resistance and determined room temperature dc electrical conductivity (σ_{dc}) of the samples studied. The electrical conductivity for all of these hybrid films ranged between 1–50 S/cm.

Results and Discussion

Surface morphology, microstructure and elemental composition

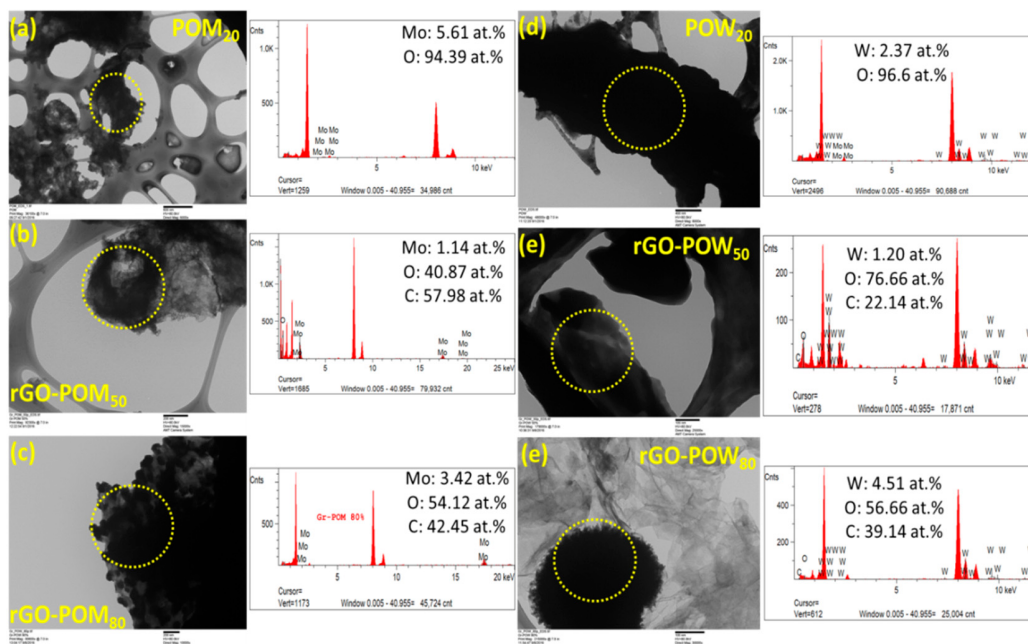


Figure S1. Representative TEM images and EDX spectra of (a-c) rGO-POM_x and (d-f) rGO-POW_x graphene-based hybrid series ($x = 0, 50$ and 80 wt.%) revealing the nanoscale morphology and elemental (Mo, W, O and C) peaks. (Scale bars are shown at the bottom of the images).

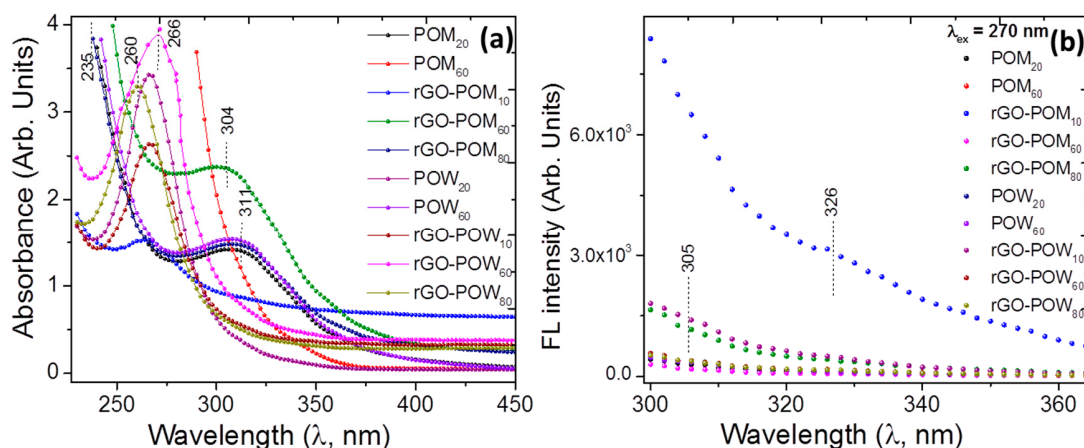


Figure S2. UV-Visible optical absorption and fluorescence spectra excited at $\lambda_{ex} = 270$ nm of (a) POM₂₀, POM₆₀, rGO-POM_x and (b) POW₂₀, POW₆₀, rGO-POW_x graphene-based hybrid series ($x = 5, 10, 20, 40, 50, 60$ and 80 wt.%) revealing the prominent bands associated with graphene and polyoxometalates.

Methanol was chosen as a solvent because of its low UV cutoff value of 200 nm and its compatibility and stability for several days with both HPAs and rGO support. They have been shown to spontaneously form POM-shells, which contain up to a 100s of individual POMs and can grow up to a few tens of nanometers in solution. For hetero-polyoxomolybdates (and tungstates), this type of bands is usually

observed between 200 and 400 nm with main band centered at 310 nm for Mo^{6+} (W^{6+}) and V^{5+} in octahedral coordination in good agreement with published reports

[1,2] Methanolic solutions of $\text{POM}_{20,60}$ and $\text{POW}_{20,60}$ show a strong LMCT absorption band at ~ 311 nm. To this aim, the intersection of straight-lines (not shown) through the low energy region of the LMCT band following Tauc's relation $(h\nu\alpha)^{1/n} = A(h\nu - E_g)$ adapted for Kubelka-Munk function for $n = 1/2$ (direct transition) and 2 (indirect transition) versus wave energy (photon energy) gives the bandgap energy values in the range of 2.5-4.2 eV. This band is shifted to higher energies (higher band gap and lower wavelength) as the stability of the resulting complex becomes higher and with increase of degree of condensation [3]. The second intense band around 250 nm is assigned to the transition $d\pi \rightarrow p\pi$ of electrons from $\text{M}=\text{O}_d$ bond. Interestingly, the same phenomenon was noticed at the increase of clusters size in the case of some rGO supported hybrids. However, the interpretation of the absorption spectra require more processing because of the additional contributions to UV-Vis spectrum from the rGO support which has less feature due to reduced state of graphene. It is worth noting that at lower loading the band edge energy is lower. Likewise, the fluorescence emission spectra excited at 270 nm are shown in Fig. 4b. They show somewhat apparent *albeit* weaker emission at ~ 326 nm hinted at 305 nm, which may be associated with the graphene platelets. These studies are particularly useful and indicative of the hierarchical structure that may influence the accessibility of HPA clusters (diffusion of reactants or electrolyte) and the location of protons, both of which can impact HPAs performance in heterogeneous catalysis and energy storage via modification of electronic structure [4].

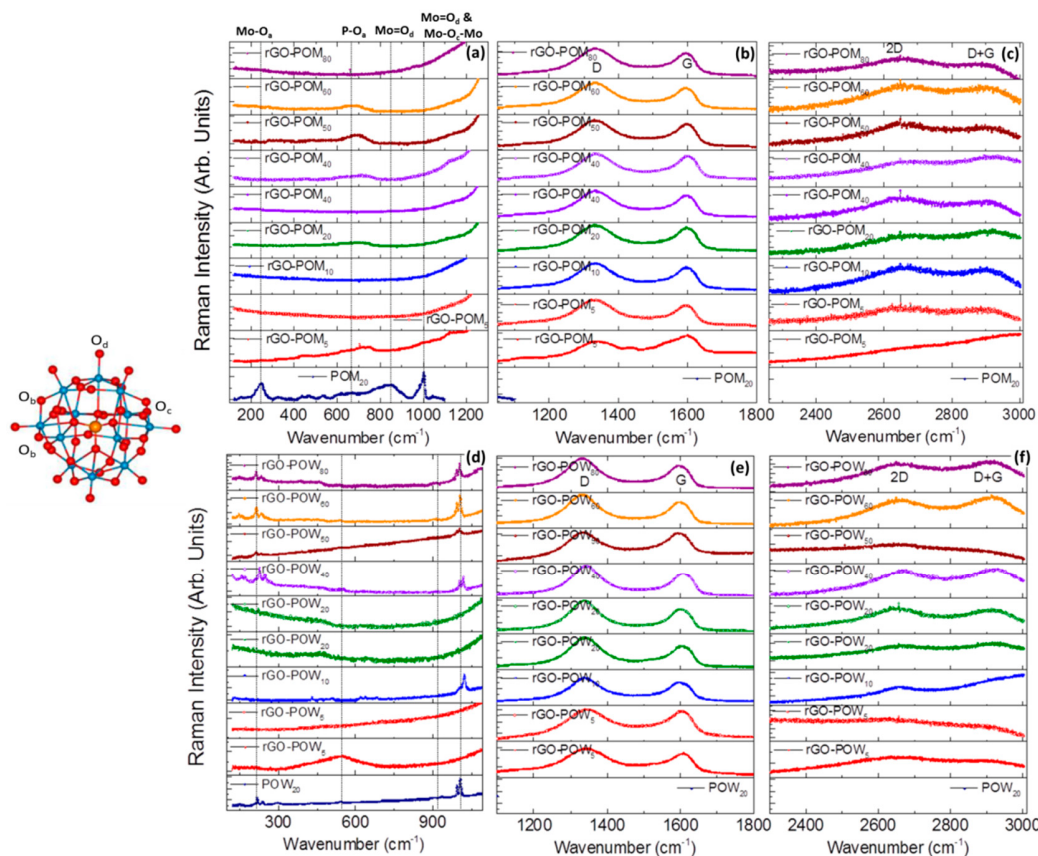


Figure S3. Micro-Raman spectra excited at $\lambda_{\text{exc}}=633$ nm of (a-c) rGO-POM_x and (d-f) rGO-POW_x graphene-based hybrid series ($x = 5, 10, 20, 40, 50, 60, 80$ and 100 wt.%) revealing the prominent Raman spectral bands associated with graphene nanosheets (D, G, 2D and D+G) and polyoxometalates along with a schematic of a polyhedral representation of the Keggin-type molecular superstructure of polyoxometalate.

The I_D/I_G ratio of both the hybrid samples show systematic increase from 0.84 to 1.23 (and systematic decrease from 1.12 to 0.81) indicative of more (and less) disordered structure with increasing POM (and POW) mass ratio, respectively. Alternatively, a converse relationship is observed if these two hybrids are compared with increasing heteropolyatomic acids mass ratio. On the other hand, the band at 1000 (or 990) cm^{-1} , consisting of $\nu_{\text{as}}(\text{Mo or W=O}_d)$ and $\nu_s(\text{P-O}_a)$ stretching vibrations loses its shape and upshifts by a few wavenumbers 5 cm^{-1} and these changes are indicative of dehydration process of the acids due to laser heating. Qualitatively, there is a change in intensity ratio of prominent bands at 1010 and 990 cm^{-1} with increasing mass ratio for hybrids. It is noteworthy that the Keggin structure is preserved since the bands at 101 and 990 cm^{-1} are present. The marginal change in G position from 1602 to 1598 cm^{-1} is indicative of good reduction of graphene oxide to reduced graphene oxide due to the POM and POW successful incorporation. Changes in band position is also due to the interactions between POMs and POWs and rGO support reflective of weaker doping or charge transfer to rGO. The rGO interacts with POM and POW keggian anion via the external oxygen atoms thereby cause weaker doping for the HOPG surface where there is no charge transfer possibly due to lack of functional groups. The prominent peaks of HPAs are slightly shifted (up or down) in polyoxoanion complexes while interacting with rGO support and that is partly because of the structural stability. It is known that Keggin anions in HPAs are stabilized mostly by dioxonium ions, but also by oxonium ions and protonated water [5]. External oxygens interact with the support through oxonium ions (H_3O^+) and/or dioxonium ions (H_5O_2^+) of POM and POW, causing prolongation and weakening of Mo-O or W-O bonds and a downshift of the Mo=O_d band in the spectra [6]. The Keggin anions creates interaction with rGO and causes weak doping or charge transfer to rGO surface, findings are provided in Tables 1 and 2. These interactions cause slight distortion of POMs and POWs anions and a downshifting of the $\nu_s(\text{Mo or W=O}_d)$ band for POM/rGO and POW/rGO. Hence the downshifts and decrease in intensity ratio of $\nu_s(\text{Mo=O}_d \text{ or W=O}_d)$ and a mixture of the $\nu_{\text{as}}(\text{Mo or W=O}_d)$ and $\nu_s(\text{P-O}_a)$ vibrations indicate that the Keggin structure was preserved but slightly distorted during anion-anion interactions in aggregated clusters. While the basal plane of HOPG devoid of surface oxygen atoms has very low electroactivity, the edge sites of HOPG or the surface functional moieties on rGO support promotes electrochemical activity borne out of interactions with POMs and POWs, such as hydrogen bonding and/or charge transfer useful for electrochemical energy storage, electrocatalysis, biomedicine and water treatment [7].

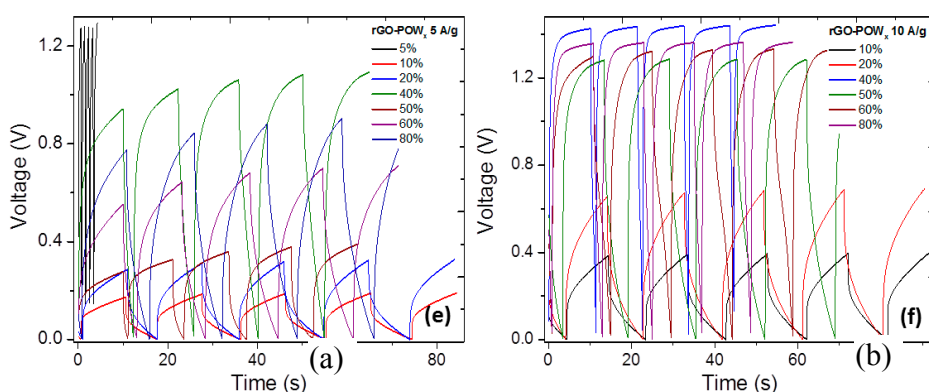


Figure S4. Galvanostatic charge-discharge (V-t) profiles for rGO-POW_x series at (a) 5 and (b) 10 A/g specific current densities.

Table S1. Summary of Raman spectral positions (in cm^{-1}) of POM, D, G and 2D bands and I_D/I_G and I_{2D}/I_G ratio for pristine rGO and hybrids.

Electrode Material	ν_s (Mo-O _a)	ν_s (P-O _a)	ν_s (Mo=O _d)	ν_{as} (Mo=O _d) and (Mo-O _b -Mo)	D band (cm^{-1})	G band (cm^{-1})	2D band (cm^{-1})	I_D/I_G	I_{2D}/I_G
POM	248.5	850.3	981 (1001.3)	1050.8 (1127.2)	-	-	-	-	-
rGO	-	-	-	-	1331.5	1600.1	2674.1	0.84	0.04
rGO-POM ₅	243.1	-	985.5	1110.4	1331.8	1601.1	2670.5	0.88	0.03
rGO-POM ₁₀	237.5	-	984.1	1127.5	1331.7	1600.7	2667.1	0.89	0.03
rGO-POM ₂₀	232.5	-	1015.5	1128.5	1331.8	1599.5	2662.0	0.93	0.02
rGO-POM ₄₀	239.2	-	1003.8	1121.4	1330.7	1599.5	2658.2	0.98	0.02
rGO-POM ₅₀	245.7	-	984.5 (1010.2)	1135.3	1331.7	1599.1	2652.5	1.09	0.02
rGO-POM ₆₀	243.0	-	984.7	1128.3	1331.7	1599.1	2651.6	1.15	0.01
rGO-POM ₈₀	243.9	-	980.2	1131.5	1331.7	1599.1	2650.2	1.23	0.01

Table S2. Summary of Raman spectral positions (in cm^{-1}) of POW, D, G and 2D bands and I_D/I_G and I_{2D}/I_G ratio for pristine rGO and hybrids.

Electrode Material	ν_s (W-O _a)	ν_s (P-O _a)	ν_s (W=O _d)	ν_{as} (W=O _d) and (W-O _b -W)	D band (cm^{-1})	G band (cm^{-1})	2D band (cm^{-1})	I_D/I_G	I_{2D}/I_G
POW	218.0 (238.8)	938.1	993.3	1007.2	-	-	-	-	-
rGO	-	-	-	-	1341.1	1602.7	2661.8	1.12	0.38
rGO-POW ₅	216.6	-	998.2	1008.7	1340.1	1602.1	2659.8	1.09	0.35
rGO-POW ₁₀	229.5	-	-	-	1340.1	1601.2	2658.0	1.05	0.36
rGO-POW ₂₀	224.9	-	1001.2	1016.6	1338.4	1600.2	2654.4	0.98	0.33
rGO-POW ₄₀	215.6 (229.5)	926.1	996.7	1007.9	1340.8	1602.7	2660.1	0.94	0.37
rGO-POW ₅₀	213.5 (229.4)	931.4	984.7	1002.6	1335.2	1599.3	2660.5	0.89	0.34
rGO-POW ₆₀	213.4 (234.3)	942.5	991.2	1005.1	1335.2	1598.2	2659.7	0.84	0.27
rGO-POW ₈₀	213.4 (236.4)	942.5	995.8	1007.7	1335.2	1598.0	2659.2	0.81	0.21

Table S3. Summary of electrochemical impedance spectroscopy simulations with fitted circuit element parameters.

Electrode Material	R_s (Ω)	Q (F)	n	R_{ct} (Ω)	Z_w (Ω)	L_w (H)	χ^2 Error (%)
rGO-POM ₅	1.997	0.00383	0.80	0.3903	0.01146	7.00E-07	1.1
rGO-POM ₁₀	0.3517	0.001944	0.75	9.069	0.1785	7.00E-07	1.8
rGO-POM ₂₀	0.8776	0.000139	0.89	510.7	0.005078	7.00E-07	0.6
rGO-POM ₄₀	0.7742	0.000363	0.76	12.42	0.0766	7.00E-07	0.8
rGO-POM ₅₀	1.224	0.004774	0.73	12.56	0.1465	7.00E-07	1.4
rGO-POM ₆₀	0.002	0.000241	0.82	39.91	0.02672	7.00E-07	3.7
rGO-POM ₈₀	0.005	0.01193	0.66	2.56	0.003763	7.00E-07	0.4
rGO-POW ₅	1.47	0.004244	0.72	20.9	0.06798	7.00E-07	3.2
rGO-POW ₁₀	1.896	0.004729	0.65	2.702	0.2074	7.00E-07	7.0
rGO-POW ₂₀	1.085	0.007377	0.60	5.834	0.1127	7.00E-07	4.5
rGO-POW ₄₀	1.9	0.002689	0.70	82.73	0.02437	7.00E-07	2.0
rGO-POW ₅₀	1.215	0.002776	0.70	13.64	0.09469	7.00E-07	6.9
rGO-POW ₆₀	0.3225	0.005315	0.65	27.43	0.04042	7.00E-07	2.5
rGO-POW ₈₀	0.002169	0.001996	0.75	15.26	0.03163	7.00E-07	4.8

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