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Electronic supplementary information

A biopolymer gel decorated cobalt molybdate nanowafer: Effective graft polymer cross-linked with an organic acid for better energy storage

Ramya Ramkumar and Manickam Minakshi Sundaram*

School of Engineering and Information Technology, Murdoch University, WA 6150, **Australia**

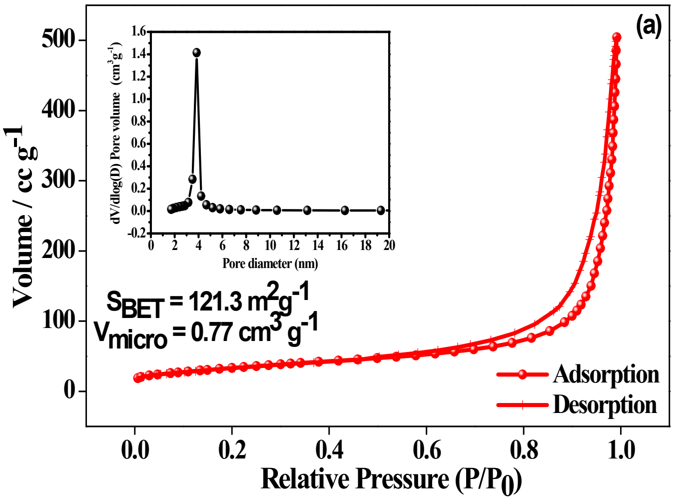
The chemical and polymer modified $CoMoO_4$ sample preparation parameters i.e. such as the role of surfactant and its optimised concentration, chitosan concentration in organic acids and the ratio of cobalt molybdate and chitosan/acid solution that has been used to generate data shown in Figures 1 to 20 are detailed below.

An insight into the role of surfactant and crosslinking agent for the grafting of chitosan onto $CoMoO_4$

Surface-active molecules (surfactants) are a kind of soft template that can assist the growth of parent compound, $CoMoO_4$. The soft template approach has the merits including inexpensive and large yield, which is suitable for scalable productions through facile approach.[1] Meanwhile, other dispersions like microemulsion and reversed microemulsion have also been reported[1] that found wide application for synthesizing conductive polymer through interfacial reactions. The drawback of the soft template method in battery / capacitor application rises from the discrete morphology of particles (shown in Figs. 7 and 8 of the main article) for the chemical $CoMoO_4$, which could increase the electronic impedance to a certain extent.[1] Hence, alternatively, a polymer approach is also being undertaken and discussed.

Chemical modified $CoMoO_4$: The concentration of the surfactant (CTAB) is important for preparing the chemical modified $CoMoO_4$ composite because of the formation of aggregates or micelles at a critical concentration, which is known as critical micelle concentration (CMC).

The effect of concentration of CTAB in $CoMoO_4$ as a precursor was studied and optimized at a slightly lower concentration than the CMC value which is 0.25 mg mL^{-1}. This concentration tends to form micelles around which the hydrophilic particles aggregate forming nanoflake like morphologies. When we tried with higher concentration (> CMC), however the formation of micellar takes place, but due to slow diffusion of ions from the electrolyte to the interface it resulted in lower energy storage capability. Not only that but also the surface electric field is reversed at higher concentration resulting in surface aggregation. The role of CTAB is further corroborated with BET measurements. The nitrogen adsorption desorption isotherms of the $CoMoO_4$ in the absence and presence of surfactant are shown in Fig. S1.



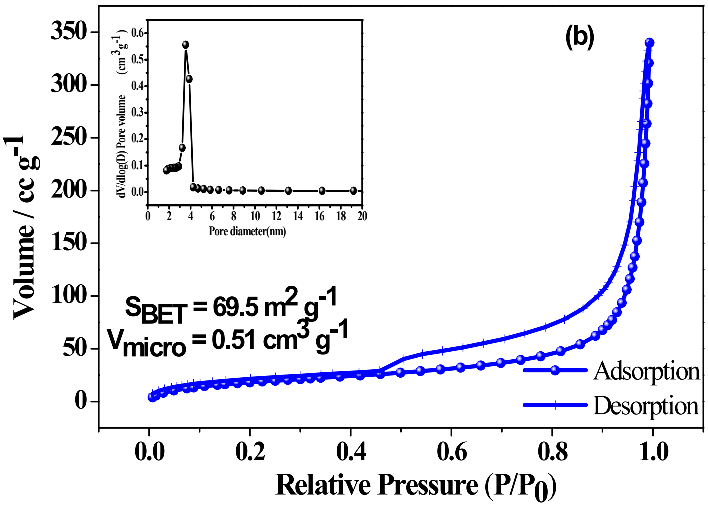


Figure S1 N_2 adsorption – desorption isotherms and pore size distribution of the (a) as-prepared and (b) chemical modified $CoMoO_4$.

The typical behaviour exhibits type IV isotherm with a H1 (Fig. S1a) and H2 (Fig. S1b) type hysteresis loop in the intermediate relative pressure range (0.7 – 0.9) which is a characteristic of mesoporous materials. The pore size (shown in the inset) distribution shows mesopores with the extent being more for the surfactant added $CoMoO_4$ (Fig. S1b). The observed lower pore distribution of the chemical $CoMoO_4$ could promote the ionic transport in the host matrix while improving the rate performance of the device. The as-prepared sample show the highest surface area of 121.3 m^2g^{-1} in comparison with CTAB sample, which shows a surface area of 69.5 m^2g^{-1}. This confirms that the role of surfactant as a precursor during synthesis leaves carbon residue than influencing an increase in surface area. The presence of carbon in the synthesized $CoMoO_4$ is supported by surface analysis using XPS (Fig. 2b in the main article) and PIXE techniques (Fig. S2).

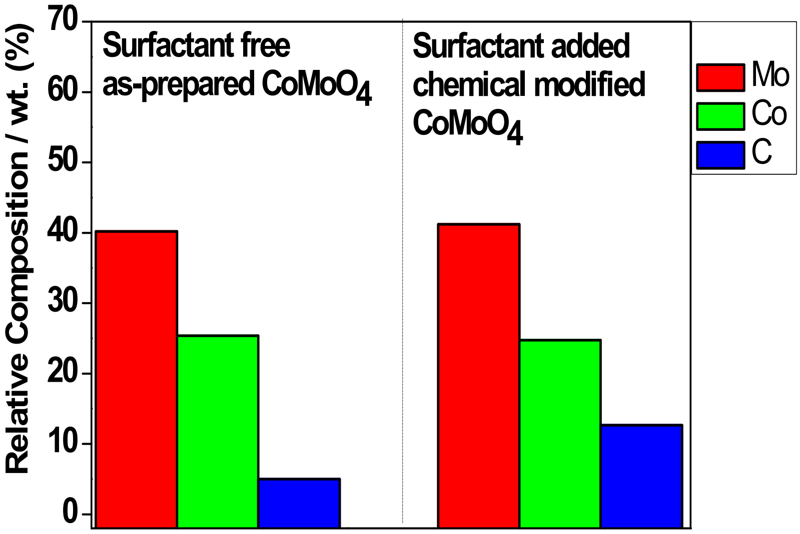


Figure S2 Simultaneous PIXE and RBS analyses of the possible elements present in the synthesized $CoMoO_4$ samples in the absence and presence of CTAB as surfactant.

A typical bar chart corresponding to elements present in $CoMoO_4$ and C is given in Fig. S2. There is no variation in the quantity of Co and Mo across the electrodes for the as-prepared and chemical modified samples. However, it is important to see the relative change in the concentration of carbon for the chemical modified sample. For the as-prepared sample, the observed 5 wt. % of carbon comes from the decomposition of urea as a fuel during combustion process. In the case of CTAB added sample, the observed increment in carbon (at least twice the amount) is the residual carbon from the surfactant. In summary, the absence of CTAB (as-prepared) is shown to have less amount of carbon and different morphology, whereas, an excess of CTAB could disrupt the host structure.

***Specific capacitance vs. concentration of surfactant**:* Once the precursors (surfactants and molybdates) uniformly organize around the optimised amount of surfactant (CMC value; ~ 0.20 mg mL^{-1}) and then heat treating the sample at a mild temperature around 300 °C, the surfactant gets evaporated but the organized monomers form nanoflakes arising out of the hemispherical micellar formations. But on the other hand, CTAB has no effect on the growth at concentrations below the CMC value. The $CoMoO_4$ was synthesized by varying the concentration of CTAB during the synthetic preparation but all samples were heated at identical conditions. The $CoMoO_4$ electrodes prepared at different concentrations of CTAB were subjected to charge-discharge and the obtained capacitance values are plotted in Fig. S3.

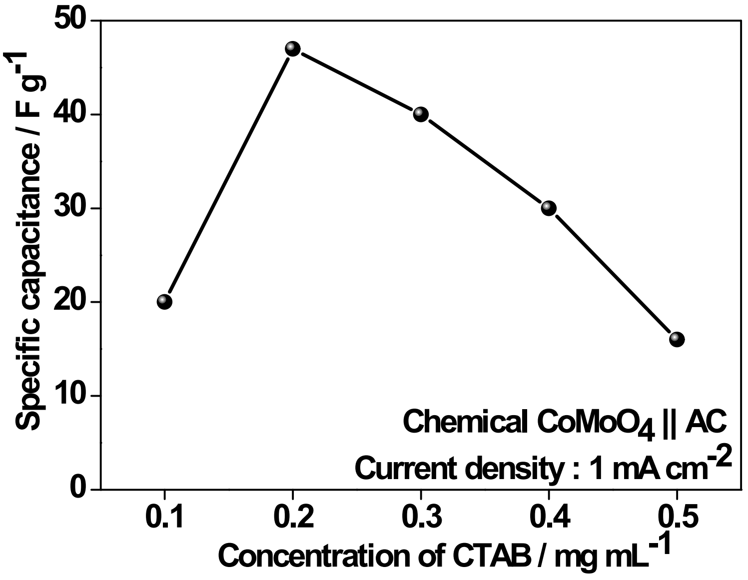


Figure S3 Dependence of specific capacitance of chemical modified $CoMoO_4$ on the concentration of CTAB present in $CoMoO_4$ as a precursor before heat treatment.

Variation of the discharge capacitance at a current rate of 1 mA cm^{-2} is displayed. Initially there is an increase in the capacitance from 0.1 to 0.2 mg mL^{-1} (from 20 to 47 F g^{-1}) then there is a steady decrease in capacitance before falling to a very low value of 17 F g^{-1} at 0.5 mg mL^{-1}. Compared to surfactant free (39 F g^{-1}; see table 2 in the main article) the obtained better discharge capacity (47 F g^{-1}) can be ascribed to the effective residual carbon, nanoflakes morphology and lower ohmic resistance as evidenced from EIS plot in Fig. 18 in the main article. Hence the concentration of CTAB for $CoMoO_4$ was optimized at 0.2 mg mL^{-1} for all our investigations.

Polymer modified $CoMoO_4$: The precise control of morphology, bonding and electrochemical properties of $CoMoO_4$ is of great importance for their use in capacitor applications. Hence, to obtain colloidal particles, a polymer approach has been taken. Chitosan, produced by enzymatic deacetylation of chitin, is selective to the sorption of metal ions.[2] Importantly, it is reported that chitosan does not take sorption of alkali and alkali earth metal ions[57] but it collects cobalt/molybdate metal ions from the aqueous solution. The properties of chitosan dispersed in acetic acid are widely studied in literature including the solubility factor and the extent of gel formation while varying concentrations of acetic acid. We have observed that chitosan in weak acetic acid (CH_3COOH) becomes a polyelectrolyte due to the protonation of the $–NH_2$ groups. As reported by Rinaudo[3-4], amino groups of chitosan take the protons available in aqueous solution and the following equilibrium state can be considered:

$$\mathrm{Chit}-NH_2 + H_3O^{+} \leftrightarrow \mathrm{Chit}-NH_3^{+} + H_2O \quad \text{(protonated chitosan)} \qquad (1)$$

$$\mathrm{Chit}-NH_2 \quad M^{2+} + H^{+} \leftrightarrow \mathrm{Chit}-NH_3^{+} + M^{2+} \text{ (uptake of } Co^{2+} \text{ ions)} \quad (2)$$

The reaction in *Eq*. (2) shows that the mechanism of chitosan dissolution is not only protonation of the amino group, but also includes interactions between chitosan and the uptake of metal ions. These metal ions in the chitosan matrix are energetically favourable for reversible redox reactions. Complete solubilisation of chitosan in acetic acid is obtained at 10 g L^{-1}. The degree of protonation initially increases involving a progressive solubilisation of chitosan and then stabilises around 0.2 M. The excessive addition or large acid concentrations hasn’t affected either the cross-linking or the energy storage performance, this could be due to complete protonation associated with the low degree of dissociation strength. Chitosan has a unique property of adsorbing metallic ions (Co) from acidic medium that has motivated the production of chitosan cross-linked $CoMoO_4$ using citric acid as crosslinking agent. The role of the chitosan and citric acid reaction along with $CoMoO_4$ for storing energy storage applications has not been reported yet. This homogenous cross-linking process obtained by the dissolution of chitosan in acetic acid or citric acid solution enhanced the energy storage capability through an increased adsorption capacity of metal ions.[5] Whereas, in the case of stronger acid like Citric acid (CA), there was a lower viscosity, due to the screening effect of anionic group in solution. For an instance, this screening effect may increase with increasing acidity of acid (AA < CA < HCl) or decreasing pH value of solvent. The citric acid is able to minimise the distance between charged particles by adsorbing suitable charged ions and eliminate surface hydration water.[6] On the other hand, excess CA acts as an inhibitor and hence the level is optimised at 20 g L^{-1} concentration.

***Specific capacitance vs. concentration of biopolymer chitosan**:* Chitosan dispersed in strong citric acid and its specific capacitance as a function of chitosan content is depicted in Fig. S4.

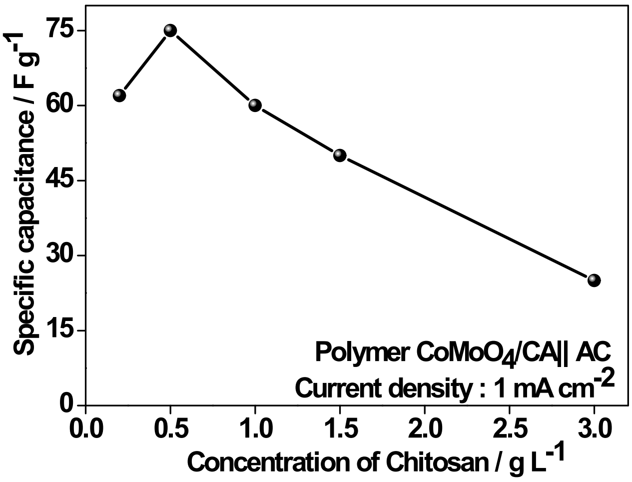


Figure S4 Dependence of specific capacitance of polymer modified $CoMoO_4$ as a function of chitosan concentration in a constant citric acid concentration.

The specific capacitance was initially low (60 F g^{-1}) at a lower concentration of 0.1 g L^{-1} chitosan. However, the capacitance increased significantly to 75 F g^{-1}, when the chitosan content was 0.5 g L^{-1} and then steeply decreased for further higher concentrations ($\geq$ 0.5 g L^{-1}) indicating that the concentration of chitosan from 0.1 to 3 g L^{-1} was optimized with the specific capacitance values. It has been showed that there is a consequential improvement in specific capacitance through chitosan solubility and uptake of metallic ions while increasing the number of carboxyl group in citric acid[7], however the concentration is limited to 0.5 g L^{-1}. The reason behind this behaviour may be due to the fact that chitosan dissolves initially in citric acid forming polyelectrolytes and then as the concentration further increases the polymer viscosity, which can prevent the diffusion of $CoMoO_4$ particles and the electrolyte ions to pass through to the electrode. The schematic representation of grafted $CoMoO_4$/chitosan composite in organic acid complex is shown in Fig. S5.

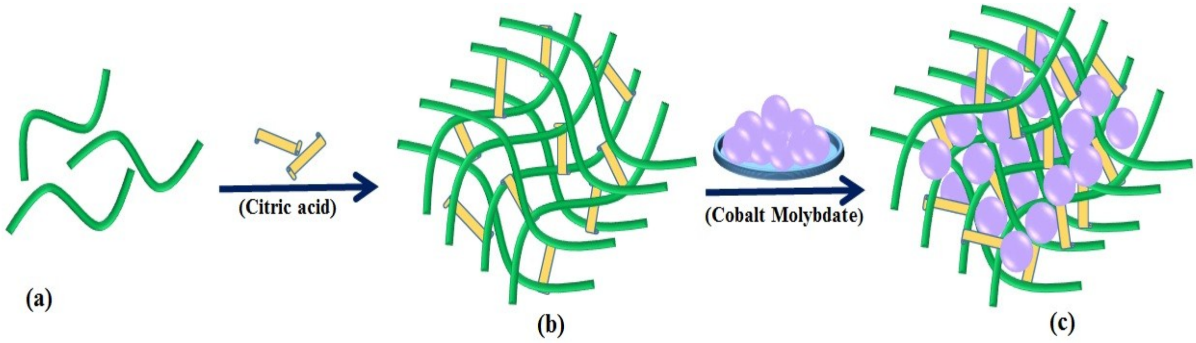


Figure S5 Schematic view of (a) biopolymer chitosan, (b) cross-linked chitosan in the presence of citric acid as a cross linker, and (c) grafted cobalt molybdate - chitosan hybrid structure.

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