A molecular hybrid polyoxometalate-organometallic moieties and its relevance to supercapacitors in physiological electrolytes

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HIGHLIGHTS

- Ruthenium bipyridine—phosphomolybdate is formed with/without potassium iodide.
- Hybrids characterized by CHN analysis, TEM, FT-IR, TGA, XRD and electrochemistry.
- The hybrid synthesized with KI has excess Ru(bpy) moieties.
- Hybrid with excess Ru(bpy) is better for capacitors in physiological electrolyte.
- 125 F g^{-1} and 68 F g^{-1} are obtained for hybrids formed with and without KI.

GRAPHICAL ABSTRACT
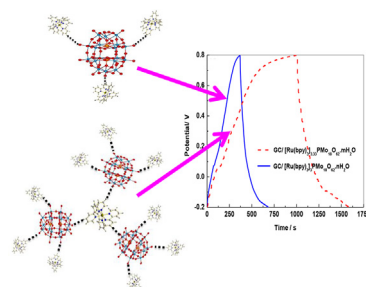
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ABSTRACT

Supercapacitors operating in physiological electrolytes are of great relevance for both their environmentally friendly aspect as well as the possibility to be employed for powering implantable microelectronic devices using directly biological fluids as electrolytes. Polyoxometalate (POMs) have been proven to be useful for supercapacitors in acidic media. However, in neutral pH, POMs are usually not stable. One relevant alternative is to stabilize POMs by pairing them with organic moieties to form hybrids. In this study, we combined $K_6P_2Mo_{18}O_{62}\cdot12H_2O$ (P_2Mo_{18}) with $Ru(bpy)_3Cl_2\cdot6H_2O$ (Ru(bpy)). The synthesis was carried out with and without the mild reducing agent KI. The hybrids were characterized by CHN analysis, TEM, FT-IR, XRD, TGA and cyclic voltammetry. CHN elemental analysis revealed that one mole $[P_2Mo_{18}O_{62}]^{6-}$ is paired with 3 mol $[Ru(bpy)_3]^{2+}$ to form $[Ru(bpy)_3]_3PMo_{18}O_{62}\cdot nH_2O$. With KI present, $[P_2Mo_{18}O_{62}]^{6-}$ is linked to 3.33 mol to yield $[Ru(bpy)_3]_{3.33}PMo_{18}O_{62}\cdot mH_2O$. Excess of Ru(bpy) in $[Ru(bpy)_3]_{3.33}PMo_{18}O_{62}\cdot mH_2O$ was further confirmed by TEM, FT-IR, XRD, TGA and cyclic voltammetry. In turn, hybrid composition is found to strongly influence the supercapacitor behavior. The hybrid rich in Ru(bpy) is found to perform better for supercapacitors in physiological electrolytes. 125 F g^{-1} and 68 F g^{-1} are the capacitance values obtained with $[Ru(bpy)_3]_{3.33}PMo_{18}O_{62}\cdot mH_2O$ and $[Ru(bpy)_3]_3PMo_{18}O_{62}\cdot nH_2O$, respectively. In terms of specific energy densities, 3.5 Wh kg^{-1} and 2 Wh kg^{-1} were obtained for both hybrid simultaneously. The difference in supercapacitor performance between both hybrids is also noticed in impedance spectroscopy which showed that $[Ru(bpy)_3]_{3.33}PMo_{18}O_{62}\cdot mH_2O$ has lower electron transfer resistance if compared to $[Ru(bpy)_3]_3PMo_{18}O_{62}\cdot nH_2O$. Finally, if compared of parent $K_6P_2Mo_{18}O_{62}\cdot12H_2O$, the stability of both hybrids is found to be highly improved.

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1. Introduction

Supercapacitors are energy storage devices, with the ability to deliver huge amount of energy in a short period of time [1]. Unlike batteries, supercapacitors have low energy densities (<10 Wh kg^{-1}) [2,3]. Hence, current research in supercapacitor is focused on exploring new materials that could increase the energy density. There have been lots of reports dealing with high surface carbon based supercapacitors [4–9]. Although high specific capacitance was achieved for some materials, energy density is still not as comparable with batteries. Transition metal oxides are another promising material called pseudocapacitors as they can store energy in the form of redox reactions in addition to the double layer capacitance [10–15]. These materials can deliver higher energy densities through Faradaic reactions occurring on the electrode surface. Among the numerous investigated metal oxides, RuO_2 [16] and MnO_2 [17] showed to be the most relevant for supercapacitors. Though, metal oxide based pseudocapacitors could deliver high energy densities than carbon based double layer capacitors, they still have problems with cycle life and stability of the materials. Also, these materials require strong acidic or alkaline electrolytes and marginal activities are expected in neutral and physiological electrolytes.

Nowadays, there is huge interest to create micro sized energy storage devices to power implantable biomedical devices like sensors transmitters or micro-artificial organs. For that, it is important to investigate the performance of supercapacitors in physiological electrolytes. Transition metal oxides are not as active in physiological electrolytes as they are in acidic or alkaline solutions. Hence, it is important to explore new materials that may perform better in physiological electrolytes. Polyoxometalates (POMs) are molecular oxides formed between transition metal centers and oxygen [18]. Most POMs are highly stable in acidic media and undergo fast, quasi-reversible, multi redox reactions [19,20]. In acidic media, POMs have been shown to be relevant for supercapacitors either as electrolytes or even when they are deposited on electrodes [21–26]. Available reports on POMs for supercapacitor studies involved specially composites

with conducting polymers, and carbon based materials like carbon nanotubes and graphene tested and studied in acidic solutions. For example, by anchoring POMs onto electrochemically grown polyaniline, Romero et al. reported a stable capacitance of 120 F g^{-1} [23,24]. The same group utilized two different conducting polymers polyaniline and PEDOT to yield a stable capacitance of 168 F g^{-1} and 80 F g^{-1}, respectively [25]. Similarly, Michael et al. anchored POMs on electrochemically deposited polypyrrole and PEDOT, they assembled a cell in asymmetric configuration that resulted in 30 F g^{-1} at 10 mA and energy density of 3.9 Wh kg^{-1} at 1 kW kg^{-1} [26]. Recently Cui et al. functionalize the graphene with polyaniline and Keggin based POM (PMo_{12}) to obtain higher capacitance of 587 F g^{-1} at 0.1 mA g^{-1} [27]. In other studies, POMs are immobilized onto graphene surface through ionic liquid to yield a stable capacitance of 408 F g^{-1} at a current density of 0.5 A g^{-1} [28]. However, it is important to remind that all these studies are carried out using strong acidic electrolytes, where higher capacitance values are expected. On the other hand, it is well known that when pH increases, most POMs tend to decompose and their structural arrangements collapse and hence lose their properties [20]. The latter can be improved by combining POMs with organic moieties like ionic liquids to form hybrids [29–31]. These hybrids are usually more stable at neutral pH but not yet investigated in physiological electrolytes and serum. On the other hand, a handful of recent reports appeared on various materials in physiological electrolytes or simply at neutral pH of which depending on the material perform more or less for supercapacitor applications [32–36].

In this paper, we have investigated the possibility for supercapacitor electrodes in the physiological electrolyte using hybrids formed between the Dawson type $K_6[P_2Mo_{18}O_{62}] \cdot 12H_2O$ and $Ru(bpy)_3 \cdot 6H_2O$. A Ru based organic moiety is selected because Ru is usually relevant for supercapacitor application and may enhance the activity of the POM. The hybrids were synthesized and characterized by various analytical techniques including CHN analysis, TEM, FT-IR, XRD, TGA and cyclic voltammetry. The performance of the deposited hybrids on electrodes are evaluated for supercapacitor use in physiological electrolytes.
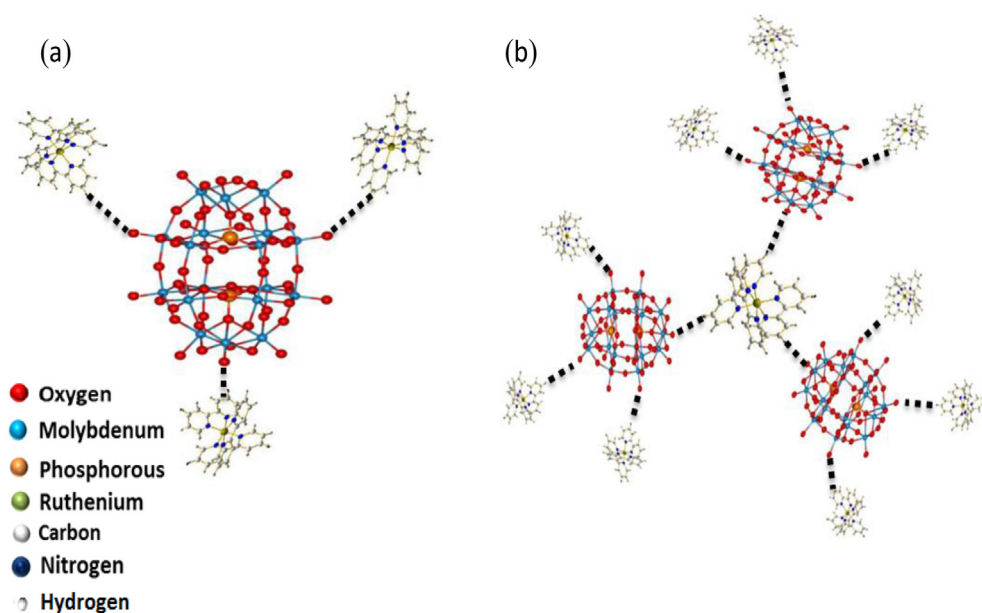

Fig. 1. Schematic representation of the two formed hybrids $[Ru(bpy)_3]_3PMo_{18}O_{62} \cdot nH_2O$ (a) and $[Ru(bpy)_3]_{3.33}PMo_{18}O_{62} \cdot mH_2O$ (b) estimated from CHN analysis. Interaction between Ru(bpy) and P_2Mo_{18} via hydrogen bonding is represented in dotted line.