Synthesis and Electrochemical Performance of Keggin-type Polyoxometalate Gels

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Abstract. Three Keggin-type vanadium-substituted polyoxometalate gels, $[PyPS]_6PW_9V_3O_{40}$, $[PyPS]_4PW_{11}VO_{40}$ and $[PyPS]_4PMo_{11}VO_{40}$ have been synthesized and characterized. The relationship between the component elements of the vanadium-substituted polyoxometalate gels and their electrochemical performance has been investigated. The results show that $[PyPS]_4PMo_{11}VO_{40}$ has stronger oxidability than $[PyPS]_6PW_9V_3O_{40}$ and $[PyPS]_4PW_{11}VO_{40}$.

1. Introduction

Polyoxometalates (POMs), a class of nano-sized inorganic transition-metal oxide clusters with a diverse range of fascinating properties, have attracted special interest in the fields of catalysis, medicine, biology and materials science [1-6]. POMs can be modified by some other series of cations, such as quaternary ammonium cations, to prepare many novel types of gel-type hybrid materials [7-10]. Such POM-based gel-type materials can be easily shaped, and can maintain some significant physical characteristics such as temperature-responsive behavior. Therefore, they have remarkable potential applications, such as electrochemical supercapacitors and fuel cells [11, 12].

Herein, we report the synthesis and electrochemical performance of three Keggin-type vanadium-substituted polyoxometalate gels, $[PyPS]_6PW_9V_3O_{40}$, $[PyPS]_4PW_{11}VO_{40}$ and $[PyPS]_4PMo_{11}VO_{40}$.

2. Experimental

2.1. Instruments and reagents

Infrared (IR) spectra were recorded on a NICOLET NEXUS 470 FT/IR spectrometer over the wavenumber range 400–4000 cm^{-1} using KBr pellet. X-ray powder diffraction analysis was obtained on a BRUKER D8 ADVANCE X-ray diffractometer using a Cu tube operated at 50 kV and 200 mA in the range of 2θ =4–40° at a scanning rate of 0.02° s^{-1}. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was determined on a Shimadzu V-1012 ICP-MS spectrometer. Electrochemical experiments were performed with a CHI660E Electrochemical Workstation in a conventional three-electrode electrochemical cell using glass carbon (5 mm in diameter) as the working electrode, platinum as the counter electrode, and a saturated calomel reference electrode in organic media. The density of substrate was 0.25 mM and 0.2 M $NaClO_4$ was assigned as electrolyte.

All reagents were analysis grade and purchased from Aladdin, without further purification.

2.2. Synthesis of polyoxometalate gels

1-(3-sulfonic group) propyl-pyridine (PyPS) was synthesized according to the literature [13]. $H_6PW_9V_3O_{40}$, $H_4PW_{11}VO_{40}$ and $H_4PMo_{11}VO_{40}$ were synthesized by modification of the method according to the literatures [14-16]. The pre-synthesized PyPS and phosphorus-containing HPA, $H_6PW_9V_3O_{40}$, $H_4PW_{11}VO_{40}$ and $H_4PMo_{11}VO_{40}$ were taken in 6:1, 4:1 and 4:1 mole ratio to give one mole of $[PyPS]_6PW_9V_3O_{40}$, $[PyPS]_4PW_{11}VO_{40}$ and $[PyPS]_4PMo_{11}VO_{40}$. PyPS was added to an aqueous solution of HPA, and then the mixture was stirred for 10 h at room temperature. Water was first evaporated in a 40°C water bath and then removed under vacuum to give highly viscous even gel-state products. The obtained compounds are highly insoluble in tetrahydrofuran, acetone or ethyl acetate, but soluble in water, N, N-dimethylformamide and dimethyl sulfoxide.

Carbon, nitrogen, sulfur, phosphorus, tungsten, molybdenum and vanadium were analyzed by elemental analysis. The results indicate that the actual measurement values are consistent with the calculated values, which confirms the composition of three POM-Gels.

3. Results and discussion

3.1. IR spectra

Table 1. The assignment of the vibration modes in the IR spectra of the gels.

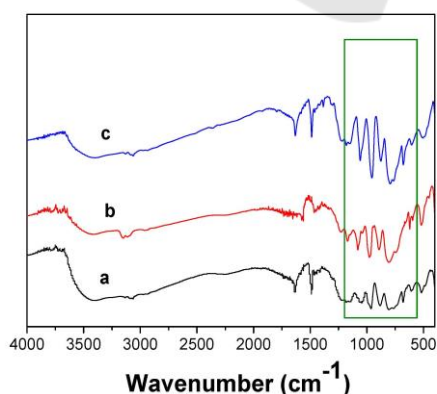| Vibration modes	Wavenumber (cm^{-1})		
	$[PyPS]_6PW_9V_3O_{40}$	$[PyPS]_4PW_{11}VO_{40}$	$[PyPS]_4PMo_{11}VO_{40}$
O-H stretching	3420	3413	3425
-CH_2 stretching	2953	2951	2935
H-O-H bending	1633	1637	1635
-CH_2 scissoring	1468	1488	1482
S=O bending	1171	1163	1148
P-O_a stretching	1055	1053	1051
M-O_d stretching	971	963	956
M-O_b-M stretching	892	891	878
M-O_c-M stretching	806	808	798

Figure 1. IR spectra of the products: (a) $[PyPS]_6PW_9V_3O_{40}$, (b) $[PyPS]_4PW_{11}VO_{40}$, (c) $[PyPS]_4PMo_{11}VO_{40}$.

Compared with the pure acid, the characteristic bands of polyoxoanions have shifted (Figure 1). The pure stretching vibration, $M-O_d$ vibrations, where the vibration frequency is influenced by the anion-anion interactions, have decreased when sulf-group grafted ammoniums have been added with HPA to make gel-type compounds. This is due to the weaker anion-anion electrostatic interaction as the anion-anion distance increases. As $M-O_b-M$ and $M-O_c-M$ vibrations are not pure and cannot be free from bending character, there is perhaps a competition of the opposite effects, which leads to an increase in the vibratation comparing to the pure acid. The result reveals that this series of compounds still maintain POM structures, which is consistent with those reported in the literature.

In the high wavenumber region, each spectrum of the gels exhibits two other peaks at around $3420 cm^{-1}$ and $1630 cm^{-1}$. These are assigned to the stretching vibration of O-H bonds and the bending vibration of H-O-H bonds, respectively.

In addition, there are some other characteristic peaks of sulf-group grafted ammoniums such as $\nu_{S=O}, \nu_{C-H}$ of CH_2. These sulf-group grafted ammoniums cations also maintain their structure, which indicates the successful assembly and existence of the POM structure units and organic ammonium cations in the compounds without depolymerization or degradation.
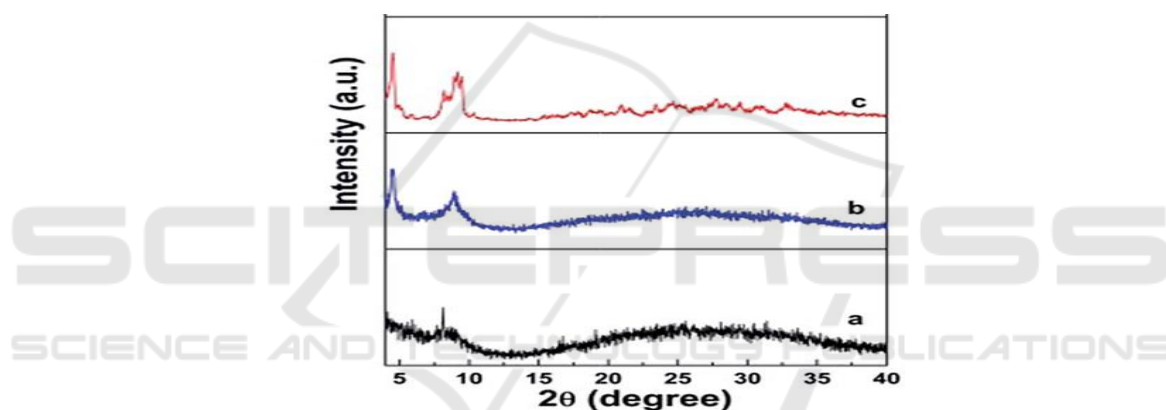
3.2. XRD patterns

Figure 2. XRD patterns (a) $[PyPS]_6PW_9V_3O_{40}$, (b) $[PyPS]_4PW_{11}VO_{40}$, (c) $[PyPS]_4PMo_{11}VO_{40}$.

Figure 3. Schematic illustration of organized structures of the POM-type layered materials.

The XRD patterns (Figure 2) of [PyPS]$_6$PW$_9$V$_3$O$_{40}$, [PyPS]$_4$PW$_{11}$VO$_{40}$ and [PyPS]$_4$PMo$_{11}$VO$_{40}$ are in marked contrast to that of the pure heteropoly acids and consistent with the gel-state appearance. According to the recent paper and considered intense peaks in the XRD patterns of these compounds in small angles area, we can assume that an organized layer-type structure exists in this series of compounds, as illustrated in Figure 3, and the height of each layer can be calculated by the intense peaks in small angles area. Meanwhile, the strong diffraction peak at 7~10 ° can be considered as the POM anion structure and a wide diffraction peak appears in the wide-angle region, indicating that these compounds have a gel-type phase at room temperature, which is caused by weak connections of the layers, rather than an identified shape in total like the pure acid.

3.3. The cyclic voltammetry

The cyclic voltammetry studies of [PyPS]$_4$PW$_{11}$VO$_{40}$, [PyPS]$_6$PW$_9$V$_3$O$_{40}$ and PyPS]$_4$PMo$_{11}$VO$_{40}$ are shown in Figure 4 and Table 2.
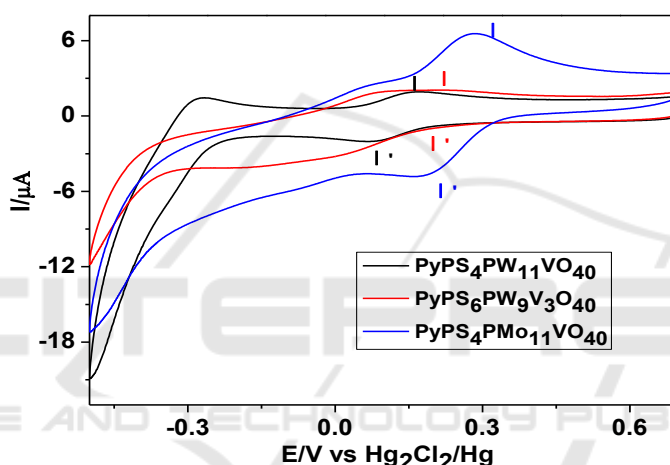
Figure 4. Cyclic voltammetry of [PyPS]$_4$PW$_{11}$VO$_{40}$, [PyPS]$_6$PW$_9$V$_3$O$_{40}$ and [PyPS]$_4$PMo$_{11}$VO$_{40}$ with a scanning rates of 50mv·s^{-1} in DMF.

Table 2. The half-wave potentials, E$_{1/2}$, for the redox couples observed in Figure 4.

Compounds	E$_{1/2}$ (I/ I') [mv]
[PyPS]$_4$PW$_{11}$VO$_{40}$	131
[PyPS]$_6$PW$_9$V$_3$O$_{40}$	206
[PyPS]$_4$PMo$_{11}$VO$_{40}$	245

In [PyPS]$_4$PW$_{11}$VO$_{40}$, [PyPS]$_6$PW$_9$V$_3$O$_{40}$ and [PyPS]$_4$PMo$_{11}$VO$_{40}$, the reduction of the vanadium is shown as follows: .

$$PW_{11}V(V)O_{40}{}^{4-} + e^- \rightarrow PW_{11}V(IV)O_{40}{}^{5-} \qquad I\ /\ I\ '$$

$$PW_9V_3(V)O_{40}{}^{6-} + 3e^- \rightarrow PW_9V_3(IV)O_{40}{}^{9-} \qquad I\ /\ I\ '$$

$$PMo_{11}V(V)O_{40}{}^{4-} + e^- \rightarrow PMo_{11}V(IV)O_{40}{}^{5-} \qquad I \, / \, I \,'$$
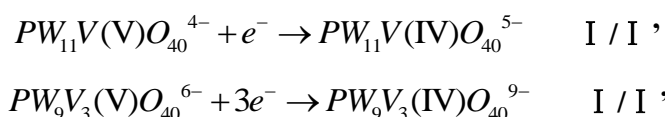
Table 2 reveals that $[PyPS]_4PMo_{11}VO_{40}$ has stronger oxidability than $[PyPS]_6PW_9V_3O_{40}$ and $[PyPS]_4PW_{11}VO_{40}$, while the tri-substituted compound, $[PyPS]_6PW_9V_3O_{40}$, has stronger oxidability than the mono-substituted one, $[PyPS]_4PW_{11}VO_{40}$. In other words, it can be concluded that when it comes to the vanadium-substituted molybdophosphorates and tungstophosphorates, it is the POM component elements that mainly determine the oxidability rather than the number of the substituted atoms, as $[PyPS]_4PMo_{11}VO_{40}$ has stronger oxidability than $[PyPS]_6PW_9V_3O_{40}$ and $[PyPS]_4PW_{11}VO_{40}$, while there are more vanadium atoms in $[PyPS]_6PW_9V_3O_{40}$.

4. Conclusions

In this paper, we have mainly reported the synthesis and electrochemical performance of a series of POM-type gels, $[PyPS]_6PW_9V_3O_{40}$, $[PyPS]_4PW_{11}VO_{40}$ and $[PyPS]_4PMo_{11}VO_{40}$. The relationship between the component elements of the vanadium-substituted polyoxometalate gels and their electrochemical performance has been investigated. The results show that $[PyPS]_4PMo_{11}VO_{40}$ has stronger oxidability than $[PyPS]_6PW_9V_3O_{40}$ and $[PyPS]_4PW_{11}VO_{40}$. They can be promising materials for supercapacitors.

Acknowledgements

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