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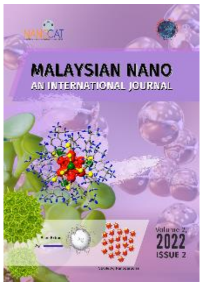

Research article

Synthesis of ammonium oxonium dodeca-molybdophosphate nanostructures for supercapacitor application

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Abstract

Supercapacitors and ultracapacitors are considered potential candidates in the field of energy storage devices for future generations. In this work, Ammonium oxonium dodeca-molybdophosphate nanospheres were successfully prepared using the co-precipitation method. The XRD pattern confirms that the material has a cubic crystal structure. The functional groups of the nanoparticles were analyzed using FTIR spectroscopy. The optical properties were studied using UV absorption spectroscopy. SEM images were used to confirm the morphological variations of the materials. CV and charge/discharge studies were conducted to investigate the electrochemical performance of the nanospheres.

Keywords: Ammonium oxonium dodeca-molybdophosphate, Nanospheres, Co-precipitation method, Electrochemical performance and Supercapacitors application.

1. Introduction

Energy harvesting from renewable energy sources has been the primary goal of the research community in recent times due to energy scarcity [1]. A supercapacitor is an electrochemical energy storage device that can increase the surface area of static electron storage as the energy levels rise [2]. Supercapacitors are thought to be superior electric storage devices because of their faster and simpler charging and faster charge delivery [1]. They also have a higher energy density than conventional capacitors and a longer cycle life than batteries [3]. Batteries excel at storing energy, whereas supercapacitors excel at power storage. This means that supercapacitors are better at quickly discharging their stored energy, whereas batteries save more energy using the same amount of material. It can store a large amount of energy, typically 10 to 100 times more energy per unit mass or volume than electrolytic capacitors [4-5]. Supercapacitors use nanoelectrode material, which is essentially made up of nanotubes / activated carbon/metal oxides/sulfides/phosphates / conducting polymers / composite materials [6-10]. Among them, phosphate-based electrode materials have become effective, economical, and environmentally friendly. Depending on the interaction of phosphate with organic and inorganic components, and microbial communities, it may have some advantages. Further, phosphates, as one of the newly developed materials, show great promise for supercapacitors, with various advantages. In this work, various morphological Ammonium oxonium dodeca-molybdophosphate was synthesized using the chemical precipitation method and extensive characteristics were studied using XRD, SEM, and electrochemical workstation.

2. Experimental Section

2.1. Synthesize of Ammonium Oxonium Dodeca-molybdophosphate

Ammonium oxonium dodeca-molybdophosphate was synthesized using a chemical precipitation method. The following reagents were used to synthesize the ammonium oxonium dodeca-molybdophosphate nanomaterial. Ammonium heptamoloybdate $(NH_4)_6MO_7O_{24}$ and ammonium dihydrogen phosphate $(NH_4H_2PO_4)$ were purchased from Modern Scientific Company. Oxalic acid and double-distilled water were acquired from Sigma-Aldrich. The chemicals were of analytical grade and were used without any purification. Ammonium heptamolybdate (0.2 M) was dissolved in 30 ml of double-distilled water and stirred for 10 min at 60 °C. Ammonium dihydrogen phosphate (0.4 M) was added to the solution and continuously stirred. During stirring, 10 ml of oxalic acid was slowly added dropwise. The prepared solution was then filtered and washed several times using a centrifuge with double distilled water and ethanol to eliminate impurities.

The prepared solution was heated at 80 °C for 2 h in a hot-air oven. Finally, the material was annealed at 350 Â °C for 2 h.

2.2. Characterization techniques

The crystal structure and formation of the synthesized material were analyzed using a RigakuUltima III powder X-ray diffractometer with CuKα1 radiation (XRD), and JASCO FT-IR460 plusin the range of 4000-400 cm^{-1}, and the morphology of the as-prepared and annealed material was recorded using a ZEISS EVO-18 Research scanning electron microscope (SEM).

2.3. Electrochemical studies

The electrochemical performance of ammonium oxonium dodecamolybdate was studied using a CHI660C electrochemical workstation. The working electrode material was prepared by mixing carbon black, the active material, and PVDF in a ratio of 8:1:1. The mixed slurry of the active material was coated onto a Ni foam substrate and dried at 60 °C for 5 h. Dried Ni foam was used as the working electrode. Ag/AgCl and Platinum wire were employed as the reference and counter electrode respectively.2 M Na_2SO_4 was used as the electrolyte to study the cyclic voltammetric, charge/discharge, and electrochemical impedance spectroscopic measurements of the prepared working electrode material.

3. Results and discussion

3.1. Structural and morphological studies

The XRD pattern of the Ammonium Oxonium DodecaMolybdophosphate nanoparticles is shown in Fig.1. The 2θ values of the peaks corresponding to the Miller indices (011), (111), (002), (112), (222), (013), (221), (123), (033), (233), (115), (156), and (118) confirmed the formation of the cubic crystal structure of the ammonium oxonium dodecamolybdenum phosphate nanomaterial($(NH_{4})_{2.6}(H_3O)_{0.4}(PMo_{12}O_{40})$).

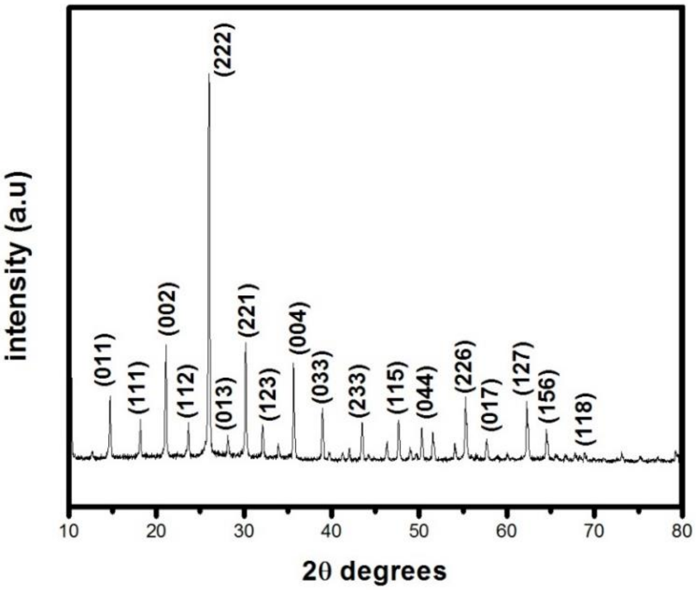

Figure 1: XRD pattern of the $(NH_4)_{2.6}(H_3O)_{0.4}(PMo_{12}O_{40})$ porous nanospheres

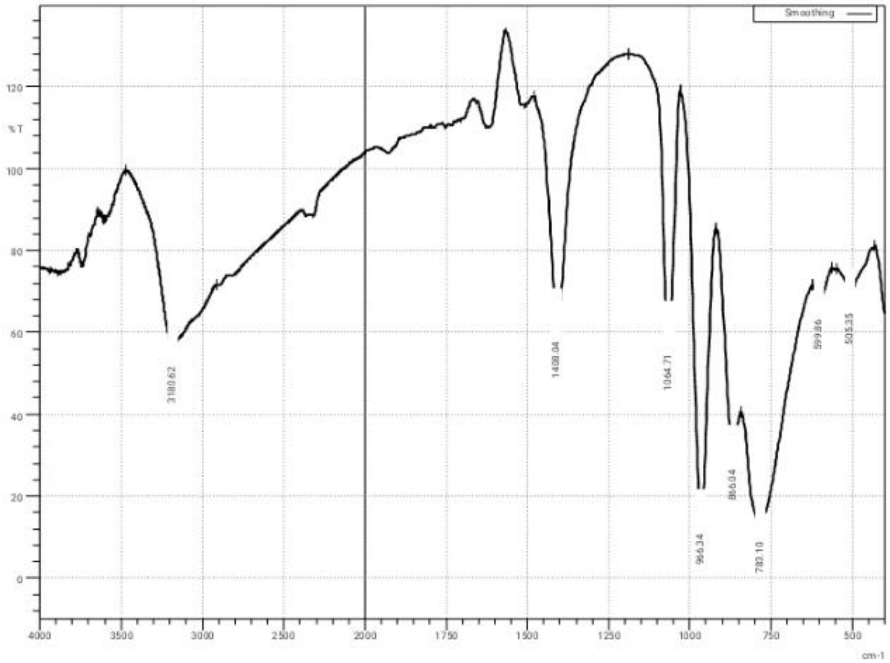

Figure 2: FTIR spectra of the $(NH_4)_{2.6}(H_3O)_{0.4}(PMo_{12}O_{40})$ porous nanospheres

FTIR analysis was used to determine the functional groups of the synthesized $(NH_4)2.6(H_3O)0.4(PMo_{12}O_{40})$ porous nanoparticles. The FT-IR spectra were recorded in the range of 3200-400 cm-1 as shown in Figure 2. The absorption peaks and corresponding functional groups of $(NH_4)2.6(H_3O)0.4(PMo_{12}O_{40})$ are presented in Table 1.

Table 1: Various functional groups are prepared samples

S.No	**Wave number (cm^{-1})**	**Functional Group**
1	505	PO_4^{3-}
2	599	Mo=O
3	783.10	C-H
4	866.04	Ar-C
5	966	O=P-O
6	1062.78	C-C, C-O, C-O

The optical properties of the ammonium oxonium dodecomolybdophosphate nanostructures were studied in terms of absorbance spectrum in the UV-visible spectral range is 300-800 nm. The absorption spectra of the prepared materials are shown in Figure 3 (a) and Figure 3b shows the band gap measurements from the absorption spectra. The band gap value of the material was calculated using Taue's equation and the calculated value is 4.03 eV.

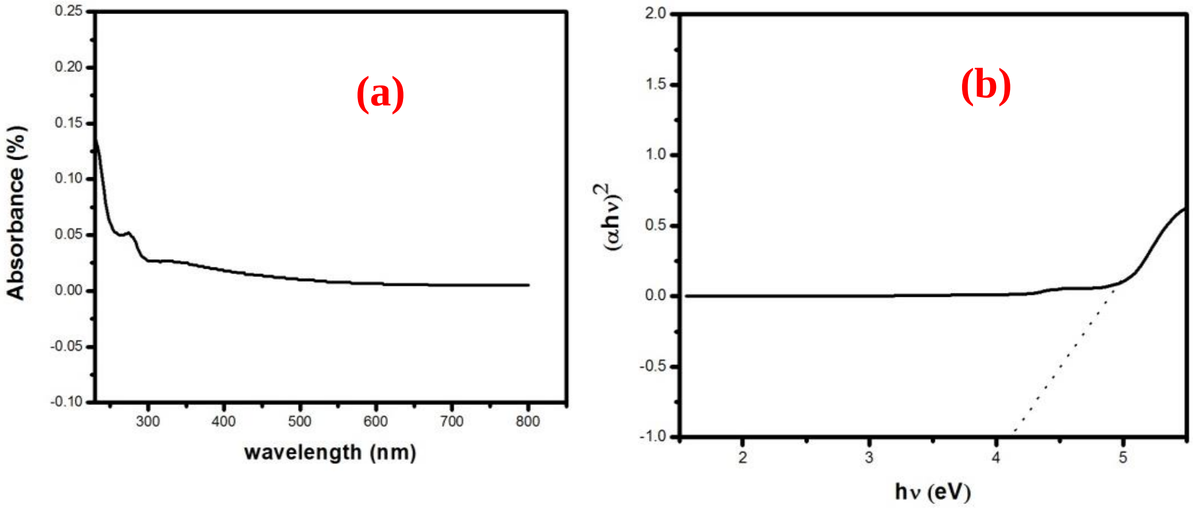

Figure 3: (a) UV-Vis spectra of the $(NH_4)_{2.6}(H_3O)_{0.4}(PMo_{12}O_{40})$ porous nanospheres (b) bandgap measurement

The morphological variation of the surfactant-assisted ammonium oxonium dodeca-molybdenum material was recorded using SEM images. Ammonium Oxonium Dodeca Molybdophosphate material was synthesized without using a surfactant, and is showed an aggregated cube-like morphology, as shown in Figure 4. When using a surfactant, the morphology of the material changes from a cube to a nanosphere with a porous nature. Figure 5(a,b) shows the porous nanosphere formation of ammonium oxonium dodecamolybdenum material.

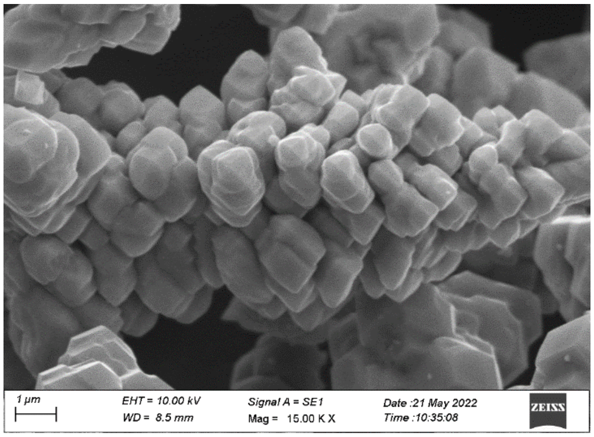

Figure 4: Morphology of the $(NH_4)_{2.6}(H_3O)_{0.4}(PMo_{12}O_{40})$ nanoparticle without using surfactant

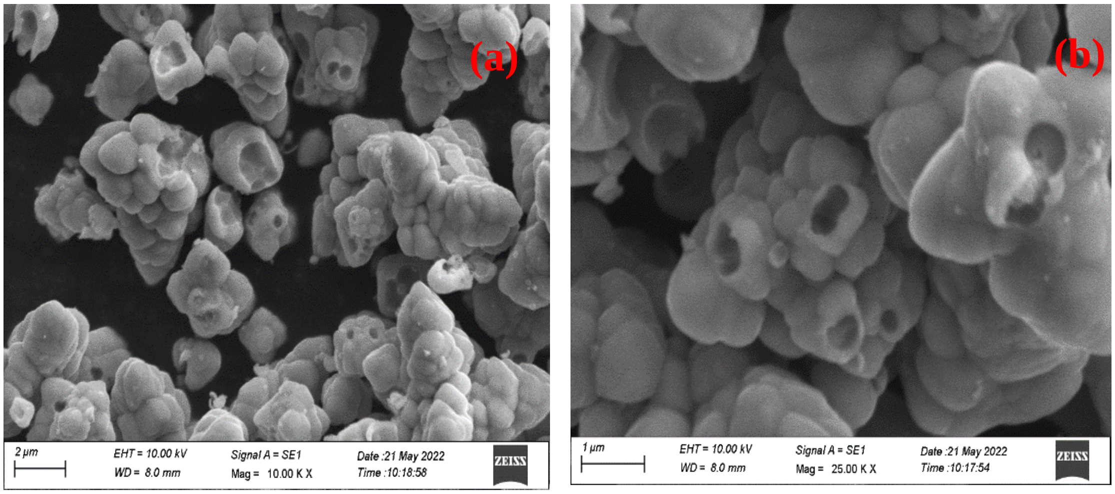

Figure 5: Morphology of the surfactant-assisted $(NH_4)_{2.6}(H_3O)_{0.4}(PMo_{12}O_{40})$ porous nanospheres

3.2. Electrochemical studies

The electrochemical performance of surfactant-assisted ammonium oxonium dodecaolybdophosphate was evaluated using cyclic voltammetry and charge-discharge studies. Cyclic voltammetry studies were carried out in the potential range of 0.0 - 0.6 V at scan rates ranging from 5 to 150 mV/s. Cyclic voltammetry (CV) studies of ammonium oxonium dodecaolybdophosphate at different scan rates are shown in Figure 6a.

Charge/discharge measurements of the Ammonium Oxonium Dodeca Molybdophosphate porous nanospheres were performed at different current densities ranging from 1 A g^{-1} to 15 A g^{-1}, as shown in Figure 6b. The specific capacitance of the electrode material was accurately calculated from the charge-discharge studies. The formula for determining the specific capacitance (Cs) value is,

$$C_s=\frac{i\Delta t}{m\Delta V}$$

Where i (mA) is the discharge current, Δt is the time taken during discharging, m is the mass of the active material and ΔV is the potential window (V). The calculated C_s value of the Ammonium Oxonium Dodeca Molybdophosphate nanosphere electrode material is 109 C/g at a current density of 1 A/g.

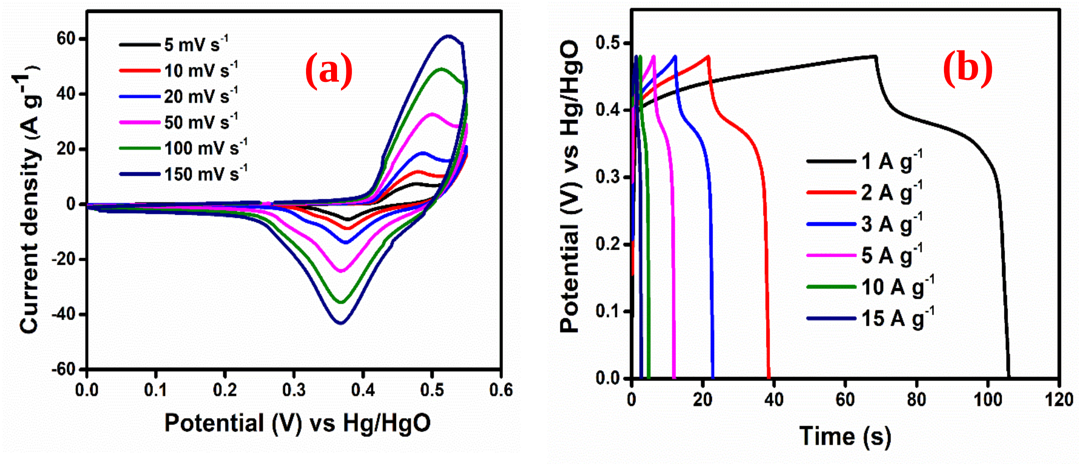

Figure 6: (a) CV analysis of surfactant assisted $(NH_4)_{2.6}(H_3O)_{0.4}(PMo_{12}O_{40})$ porous nanospheres (b) charge/discharge measurement of surfactant assisted $(NH_4)_{2.6}(H_3O)_{0.4}(PMo_{12}O_{40})$ porous nanospheres

4. Conclusions

In summary, a coprecipitation method was used to develop ammonium oxonium dodeca-molybdophosphate nanospheres. XRD analysis confirmed the cubic crystal structure of the prepared sample. The functional groups of the nanoparticles were analyzed (FTIR). The bandgap energy was calculated to be 4.03 eV. SEM analysis showed that the morphology of the material changed from cubic to porous nanospheres. Finally, the maximum specific capacitance of the ammonium oxonium dodecamolybdenum nanospheres was 109 C/g at a current density of 1 A/g, indicating that this material is suitable for supercapacitor applications

Conflicts of interest

The authors declare no conflict of interest.

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