H₂S gasochromic effect of mixed ammonium salts of phosphomolybdate nanoparticles synthesized by microwave assisted technique

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Abstract

In the present paper, new H₂S gasochromic nanomaterial of mixed silver nickel ammonium phosphomolybdate synthesized by microwave assisted technique is reported. The microwave treatment was performed in the solid phase using urea and ammonium nitrate as the promoter and oxidizer agents. The designed process allows rapid synthesis of large amounts of this product in nanosized particulate morphology. Morphological and structural features of the prepared products were studied in detail. Chemical analyses indicated a stoichiometry of (NH₄)_{0.5}Ni_{0.75}AgPMo₁₂O₄₀·4H₂O revealing a Keggin-type framework with substitution of silver and nickel cations in its secondary structure. A home-made set-up was used to test gasochromic effect *via* monitoring light intensity variations passing through the samples based on their color change during exposure to different H₂S gas concentrations. Response in coloration was obtained about 12 % to 61.8 % for concentrations from 8.5 to 100 mg·L⁻¹. It is suggested that the presence

of Ag and Ni ions (especially silver as counter cations) in the secondary structure of a Keggin ion plays an important role in the coloration effect of the substituted phosphomolybdate compared with the un-substituted one. In fact, color centers can be originated from the interaction of these cations of the phosphomolybdate network with thiol functional group of H₂S molecules.

Keywords: H₂S gas sensor; Polyoxometalate; Gasochromic.

1. Introduction

Gasochromic compounds are a promising generation of smart materials in the fabrication of gas sensors, which work based on color change during exposure to some gases. They can detect various inflammable and hazardous gases such as H₂, CH₄, H₂S, SO₂ and NO₂ [1-6]. Among these gases, hydrogen sulfide which exists in fossil fuels, natural gas and sewage treatment facilities has a highly toxic effect for living organisms and humans [7, 8]. The high concentration of H₂S gas in the environment (higher than 250 ppm) is very harmful to the human body and may cause death [9, 10]. On the other hand, the presence of high concentrations of this gas in the environment causes air pollution, acid rain and subsequently corrosion of metallic equipments. Therefore, detection and monitoring of its leakage is essential for human health, industrial processing and environmental protection [8-11]. Despite the high importance of H₂S detection, few studies on this gas, compared with other gases, have been performed due to the complication in fabrication of a reliable system as a result of corrosion of electrical contacts and problems in sensor recovery resulting from sediment of sulfur species on the sensing surface [7, 12]. Optical sensing technique that is normally based on non-electrical contact method using gasochromic materials can be a helpful approach to enhance stability of the sensor. WO₃ or MoO₃ doped with

noble metals of Pt or Pd as catalysts are the most studied gasochromic systems, which have been widely reported for H₂ gas [13-19] while a few materials have been found for H₂S gas [6]. Amongst them, heteropoly compounds (HPCs), a known class of inorganic mixed metal oxide, can be considered due to its capability in acceptance of electrons from gas molecules, transferring them and formation of colored mixed-valence species [20]. Since the rapid advancement of nanoscience and nanotechnology, nanostructures of this material have attracted a lot of attention in various applications such as catalysis, photocatalysis, gas sensing and medical applications [21-25]. The most common category of HPCs is molybdophosphoric polyacids with a ‘Keggin’ structure [25, 26]. Although this compound is introduced as the effective material in various applications, it suffers from low structural stability and multi-stage complex synthesis methods. Formation of substituted salts of this polyoxometalate by incorporation of different metals as counter cations and makes its activity stable compared with its acidic parent [26, 27]. Common synthesis techniques including co-precipitation [28-30], hydrothermal/solvothermal [27, 31], reflux reaction [32] require severe acidic condition, complex equipments, high temperature and pressure that restrict their applications in industry [27, 31]. Due to growing demand for application of such compounds, introduction of a simple, safe, low cost and high efficient synthesis strategy is favored. Microwave heating method in solid phase can be a promising technique because it is rather fast, simple, low-cost, safe and eco-friendly [33]. Such microwave treatment can accelerate interaction between reactants using organic driving agents such as glycine, urea, etc [33, 34]. They act as capping agents due to functional groups in their structure to control resulting morphology and nano-sized architecture in solid phase [33].

In the present work, Keggin-type mixed ammonium salt of phosphomolybdate nanoparticles by incorporation of Ag⁺ and Ni²⁺ counter ions were synthesized by a facile and rapid microwave

assisted reaction in solid state. An optical photovoltaic home-made set-up was used to study gasochromic properties of the prepared product. The gasochromic sensing properties were investigated for the prepared sensing work-pieces in exposure to H₂S gas in different gas concentrations from 8.5 to 100 mg · L⁻¹ at room temperature.

2. Technical details

2.1. Materials

Ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, 99.9%), ammonium phosphate ((NH₄)₃PO₄, 99.9%), silver nitrate (AgNO₃, 99.9%), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99.9%), urea (CH₄N₂O, 99.9%), ammonium nitrate (N₂H₄O₃, 99%), hydrogen chloride (HCl, 37%), and iron sulfide (FeS, 99%) were purchased from Merck Co. and used without further purification.

2.2. Synthesis procedure

To prepare (NH₄)₃PMo₁₂O₄₀ heteropoly compound (NPMo₁₂), the stoichiometric amounts of (NH₄)₆Mo₇O₂₄·4H₂O and (NH₄)₃PO₄ were mixed to each other in the presence of urea and ammonium nitrate as driving agents in solid phase. The mixture was transferred into an alumina crucible and put into a domestic microwave oven with a power of 360 W for 7 min. The yellow product was collected and analyzed. Mixed ammonium salts of XNPMo₁₂ (X= Ag⁺ and Ni²⁺) were obtained *via* running the aforementioned reaction accompanied by the desired amounts of silver and nickel sources at the same conditions. The obtained samples were analyzed by Fourier Transform Infrared (FT-IR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Diffuse-Reflectance Spectra (DRS), CHN, Inductively Coupled Plasma Spectrometry (ICP) and Energy-Dispersive X-ray Spectroscopy Analysis (EDX) techniques.

2.2. Gasochromic set-up

A simple home-made set-up with the ability of monitoring light intensity variations passed through the samples during coloration was used to study gas sensing experiments for H₂S gas. Fig. 1 depicts a scheme of the set-up containing a sealed chamber as so-called gascell integrated with gas inlet and outlet, light sources (commercial high brightness LED, sensitive to wavelength of 400–600 nm and center peak in 520 nm) and detector (commercial silicon photodiode S1337-Hamamatsu, wavelength of 190-900 nm). The gascell includes a cylindrical chamber with a content of 150 mL that the gasochromism samples are hanged into the cell medium by a holder aligned with light source and detector. Two light sources marked as LED (2) and (3) were also devised with incidence angle of 45° in the gascell body to provide reflection response for low optical transparent films.

2.3. Gasochromic test

H₂S gas for sensing experiments was prepared by reaction of $2\text{HCl} + \text{FeS} \rightarrow \text{H}_2\text{S} + \text{FeCl}_2$. A certain quantity of the prepared H₂S gas was injected into the gascell so as to yield a desired concentration from 8.5 to 100 mg·L⁻¹. The gasochromic films were provided on glass substrates and the photo-voltaic sensing response was recorded as a function of time during coloration using a data logger connected to a computer. The samples were also studied by UV-Vis spectroscopy before and after coloration by gas.

2.4. Characterizations

The X-ray diffraction (XRD) patterns were recorded by a STOE powder diffraction system using Cu K α_1 radiation (wavelength, $\lambda=1.54060$ Å). FT-IR spectra were recorded on a Shimadzu-8400S spectrometer in the range of 400–4000 cm⁻¹ using KBr pellets. SEM images and EDXdata were taken on VEGA\TESCAN S360 with gold coating. DRS data were prepared via a Shimadzu (MPC-

2200) spectrophotometer in the wavelength range of the 190–800 nm. Elemental analysis was performed by utilizing a FOSS Heraeus CHN microanalyser and ICP analysis on sequential plasma spectrometer, Shimadzu (ICPS-7000 ver. 2).

3. Results and Discussion

3.1. Structural and morphological description

The recorded XRD patterns of the synthesized samples shown in Fig. 2 represent a similar pattern with cubic lattice of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot 4\text{H}_2\text{O}$ according to JCPDS Card No. 09-0412. Diffraction peaks at 2θ values of 10.71° , 13.12° , 15.15° , 18.62° , 21.56° , 24.17° , 26.48° , 28.58° , 30.67° , 32.53° , 36.11° , 39.40° , 43.92° , 47.98° , 50.68° , 51.97° , 55.68° , 57.94° , 62.62° and 64.78° match with 110, 111, 200, 211, 220, 310, 222, 321, 400, 411, 332, 510, 440, 532, 541, 622, 550, 552, 732 and 554 planes of cubic phase with a space group of Pn3m. A slight shift is observed in most of the diffraction lines of the substituted products compared with the un-substituted sample (for instance, shift in diffraction line of 222 that is shown in the insert of Fig. 2). These shifts can be attributed to the occupation of counter positions in the Keggin framework by the Ag^+ and Ni^{2+} or both ions in the prepared samples. In fact, substitution of the ammonium unit by these cations causes a rearrangement of secondary structure of the Keggin ion while its primary structure is preserved [35, 36]. These results show successful formation of the crystalline phase of homogeneous heteropoly salts of mixed silver, nickel and silver/nickel ammonium phosphomolybdates.

Fig. 3 indicates the FT-IR spectra of the prepared ammonium phosphomolybdate (NPMo_{12}) (Fig. 3a) and the substituted samples (AgNPM_{12} , NiNPMo_{12} and AgNiNPMo_{12}) (Fig. 3b-d). The observed peaks in all spectra especially in the range of $1100\text{--}500\text{ cm}^{-1}$ that are very similar

clearly indicate the formation of the Keggin-type structure of ammonium molybdophosphate [21, 35]. The characteristic bands of the Keggin ion at 1062, 962, 864 and 788 cm^{-1} , which are uniformly observed in all samples, are attributed to asymmetric stretching vibrations of P-O_a , Mo-O_d , $\text{Mo-O}_b\text{-Mo}$, $\text{Mo-O}_c\text{-Mo}$, respectively. The marked oxygen atoms of O_a , O_b , O_c and O_d (shown in Fig. 4) refer to constitutive oxygen atoms of the Keggin architecture; O_a indicates the O atom shared between PO_4 tetrahedron and a trimetallic group, O_b is the oxygen atom linking two trimetallic groups, O_c is the oxygen atom linking two MoO_6 octahedral group inside a trimetallic unit and O_d refers to the terminal oxygen atom of this structure [35, 36]. Characteristic band at 595 cm^{-1} is related to P-O bending vibration frequency. A broad peak at 3207 cm^{-1} and a sharp band at 1413 cm^{-1} are assigned to feature absorptions of the -NH_4^+ unit. The observed peaks at 3425 and 1625 cm^{-1} are related to stretching and bending vibration frequencies of O-H group, respectively. It is an evidence for the presence of the adsorbed H_2O molecules in the samples [35-37]. In the literature, a split of the P-O_a stretching band as a shoulder on this band and a change of FT-IR spectral data by substitution of any transition metal ion instead of Mo in the Keggin ion due to a decrease of the oxoanion symmetry have been reported [36]. We did not observe any splitting of this band in the FT-IR spectra of the substituted products. Since no significant difference was observed in spectra, it can be concluded that the primary Keggin structure has been preserved and the silver and nickel cations were incorporated instead of ammonium units in the secondary structure of NPMo_{12} .

The elemental analysis of EDX (shown in Fig. 5) revealed the presence of Mo, N, P, Ni and Ag elements in these products. The percentages of Ag and Ni, Mo, P, N and H in product structures were also obtained from ICP and CHN elemental analyses data. The resulting data are summarized in Table 1.

Therefore, the molecular formulae of the synthesized samples, (NPMo₁₂), (AgNPMo₁₂), (NiNPMo₁₂) and (AgNiNPMo₁₂), are (NH₄)₃PMo₁₂O₄₀·4H₂O, (NH₄)₂AgPMo₁₂O₄₀·4H₂O, (NH₄)_{1.5}Ni_{0.75}PMo₁₂O₄₀·4H₂O and (NH₄)_{0.5}Ni_{0.75}AgPMo₁₂O₄₀·4H₂O, respectively.

The SEM observations revealed a particulate morphology for all samples (Fig. 6). It was found that the presence of silver, nickel or both ions causes a decrease of particle size from about 150 nm in the NPMo₁₂ sample (Fig. 6a) to average values of 72, 89 and 48 nm in the NiNPMo₁₂ (Fig. 6b), AgNPMo₁₂ (Fig. 6c) and AgNiNPMo₁₂ (Fig. 6d) samples, respectively.

We suggest as a conceptual model of the synthesis pathway, ammonium nitrate and also, nitrate units of the metal sources accompanied by urea, turn on a combustion reaction *via* burning during reactants-microwave interactions. This causes continuous gas escape from the system, exchange of counter units and nano-particulate phosphomolybdate framework product in solid phase.

3.2. Gasochromic property of the samples

To investigate the gasochromic effect, many films of the products were prepared by dispersion of the synthesized materials in water and coating on glass substrates. A Cross-section microscopic image of a typical AgNiNPMo₁₂ film that revealed a thickness of about 1.5 μm is shown in Fig. 6e.

The films were used to record coloration response in exposure to different concentrations of H₂S gas from 8.5 to 100 mg·L⁻¹. All gasochromic tests were carried out in the home-made set-up shown in Fig. 1.

Fig. 7 presents the recorded voltage vs. time in seconds as coloration step based on light intensity passing through a sample placed in various concentrations of the target gas.

The results indicated an intense decline of voltage variations due to reduction of light intensity passing through the colored samples. They present enhancement of sample response by increasing gas concentration. The silver and nickel incorporated samples displayed enhanced coloration effect compared with un-substituted samples (Fig. 7a-d). Fig. 8 presents the response factor under different gas concentrations at room temperature of 25-28°C. Sensing response factor in percentage, R_f , is defined as the following equation [38]:

$$\text{Response factor (\%)} = \frac{V_f - V_i}{V_i} \times 100 \quad (1)$$

where, V_f is photovoltaic read out after exposure to H_2S gas and V_i is the initial recorded voltage before gas injection. The response value of Ag/Ni substituted sample is comparatively high and shows an increase from 12.5 % up to 61.8 % by increasing gas concentration from 8.5 to 100 $mg \cdot L^{-1}$. We also measured UV-Vis diffuse reflectance (DR) spectra of AgNiNPMo₁₂ nanoparticles in wavelength range of 190-800 nm before and after exposure to different concentrations of H_2S gas (Fig. 9). Before gas exposure, a wide absorption band constituted of two components is observed which belongs to different charge-transfer (CT) energies of $O^{2-} \rightarrow Mo^{6+}$ in the Keggin structure [39]. Intensity in the range of lower wavelength is decreased but in higher range increased after exposure to target gas especially in high concentrations. This is probably due light absorption of the transferred electrons between the Keggin network and H_2S molecules. In addition, the spectra above 600 nm indicates the intervalence CT between Mo^{5+} and Mo^{6+} , which is an evidence of converting the yellow heteropoly compound to that of the blue [39, 40]. So the substituted Ag and Ni cations in the secondary structure of the Keggin body play a key role in the coloration effect. The dark green-brown color as presented in the insert of Fig. 9 arises from the co-existence of a blue, yellow and black species. We suggest a reaction model based on physisorption and then, chemisorption of the gas molecules on active sites of the

sensing surface. Scheme 1 indicates a probable pathway for Ag^+ substituted product in exposure to H_2S gas. According to this model the gas molecules are adsorbed on the surface, the counter units in polyoxometalate framework catalyze the cleavage of the H–S bond, H^+ species interact with Mo (VI) ions and produce $\text{H}_x\text{Mo(V)Mo(VI)}$ intermediate species as blue color center. Ag–SH and Ni–SH units are formed as black color centers. Although gas diffusion in the sample and the formation of color centers take several minutes, the bleaching process in ambient conditions requires several days. The recovery process includes the cleavage of Ag–SH and MoO–H bonds made in coloration process. We surmise that the interactions between gas molecules and active sites are of strong physical interactions, which causes the recovery process prolongs for several days.

To study the repeatability and aging of the prepared samples, we carried out a series of coloration-bleaching processes for AgNiNPMo_{12} nanoparticles under similar conditions in exposure to $70 \text{ mg}\cdot\text{L}^{-1}$ of H_2S gas. The results indicated that the dark green color of the exposed film gradually returns initial yellow color after several days at room temperature in air or even flow of oxygen gas. To obtain rapid bleaching process, the colored sample was introduced in oxygen flow passed over H_2O_2 in a bottle for about 20 min till turned yellow color but with weak response. To increase sensing response we found that heat treatment of the bleached sample about 70°C a few hours in air can improve recovery process. Fig. 10 presents the recorded voltage variations (ΔV) in 5 cycles of coloration/bleaching process.

We determined the response time of the products to different concentrations of target gas by fitting the recorded voltage variations to a first order exponential function using the following equation 2 [41]:

$$V(\tau) = (V_i - V_f) \exp \frac{t}{\tau} \quad (2)$$

Where, V_i and V_f are initial and final responses in voltage, respectively, t is sensing time and τ is the time constant for the response step as response time, which is defined as the sensor sensing time to reach to 36% of the original value of the response. Fig. 11 indicates the calculated response times for the coloration step under different concentrations of the target gas. It is observed that it decreases by increasing gas concentration, due to higher number of absorbed gas molecules. As a typical example, the AgNiNPMo_{12} sample displays a decrease of response time from about 187 to 85 s by increasing gas concentration from 8.5 to 100 $\text{mg}\cdot\text{L}^{-1}$.

In order to evaluate the influence of relative humidity (RH) on the gasochromic response of the prepared films to H_2S gas, the gasochromic tests were performed in different RH levels in constant concentration of gas (70 $\text{mg}\cdot\text{L}^{-1}$). Based on the obtained results shown in Fig. 12, it was observed that the coloration response factor is approximately constant in RH levels up to 50% while for higher levels coloration response decreases due to hydration and blocking of active sites of compound (i.e., Ag^+ and Ni^{2+} units).

Conclusions

In a summary, we developed a solid state microwave assisted technique for rapid synthesis of mixed silver/nickel ammonium phosphomolybdate nanoparticles, which can be easily scaled up for production of various substituted polyoxometalate salts without using any acidic or basic media. The gasochromic behavior of the prepared products was evaluated in exposure to H_2S gas in different concentrations. Tests were performed in a simple set-up with the ability of recording the optical sensing response. A response factor of about 12.5 to 61.8 % obtained for AgNiNPMo_{12} nanoparticles by increasing the gas concentration from 8.5 to 100 $\text{mg}\cdot\text{L}^{-1}$ that it demonstrates a good capability of this product for H_2S sensing. A possible mechanism was suggested to explain the gasochromic property of the as prepared samples in exposure target gas.

Our results open a novel outlook of feasibility of production of new gasochromic materials for sensing various target gases however it requires further investigations.

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Figure captions

Fig. 1. Schematic representation of used home-made gasochromic set-up, marked light source of LED (1) for the transmittance state and LEDs (2) and (3) for the reflection state.

Fig. 2. XRD patterns of the prepared samples. Figure in the insert shows a shift in the diffraction line of (222).

Fig. 3. FT-IR spectra of the prepared samples; (a) NPMo_{12} , (b) AgNPMo_{12} , (c) NiNPMo_{12} and (d) AgNiNPMo_{12} .

Fig. 4. Schematic representation of the Keggin structure of phosphomolybdate anion $(\text{PMo}_{12}\text{O}_{40})^{3-}$: O_a , O_b , O_c , and O_d labeled the four types of oxygen in this structure.

Fig. 5. EDX elemental analysis of the prepared samples; (a) NPMo_{12} , (b) AgNPMo_{12} , (c) NiNPMo_{12} and (d) AgNiNPMo_{12}

Fig. 6. SEM images of NPMo_{12} (a), AgNPMo_{12} (b), NiNPMo_{12} (c), AgNiNPMo_{12} (d) and cross section image of the prepared AgNiNPMo_{12} film.

Fig. 7. Voltage variation vs. time in seconds based on light intensity passing through NPMo_{12} (a), NiNPMo_{12} (b) AgNPMo_{12} (c) and AgNiNPMo_{12} (d) samples in different gas concentrations (from 8.5 to 100 ppm).

Fig. 8. Response factor of sensing products for target gas in different concentrations (8.5-100 $\text{mg}\cdot\text{L}^{-1}$).

Fig. 9. UV-Vis DR spectra of AgNiNPMo_{12} film before and after exposure to H_2S gas in different concentrations, and the digital photographs of samples before and after contact with gas.

Fig. 10. The voltage variation (ΔV) vs. time during 5 cycles coloration/bleaching process.

Fig. 11. Time constant values for response step of the prepared products in different gas concentrations.

Fig. 12. Sensing response factor and time curves of the prepared AgNiNPMo₁₂ film to 70 mg·L⁻¹ H₂S gas in different relative humidifies at room temperature.

Table

Table 1. Elemental analysis of the prepared products

Samples	H (%)		N (%)		P(%)		Mo (%)		Ni (%)		Ag (%)	
	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
NPMO₁₂	1.02	1.13	2.15	2.01	1.56	1.40	59.09	59.19	-	-	-	-
AgNPMo₁₂	0.78	0.80	1.37	1.40	1.52	1.58	56.48	56.44	-	-	5.29	5.13
NiNPMo₁₂	0.71	0.71	1.17	1.06	1.51	1.57	58.42	58.58	2.26	2.23	-	-
AgNiNPMo₁₂	0.60	0.69	0.35	0.38	1.54	1.51	57.58	57.01	2.20	2.26	5.31	5.34

Scheme

Scheme 1. Proposed mechanism of interaction of the synthesized products with H_2S gas molecules.

Figures

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

Fig. 12.