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Gasochromic effect in colloidal nanoparticles of tungsten oxide dihydrate synthesized via a simple anodizing method

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ABSTRACT

This paper reports the gasochromic effect in colloidal nanoparticles of tungsten oxide dihydrate synthesized via a simple electrochemical anodizing of tungsten in an electrolyte composed of 0.02 M HCl. The anodizing caused the electrolyte to convert to a light yellowish colloidal solution consisting of tungsten oxide dihydrate. The ultimate gasochromic colloidal solutions were obtained just by addition of different volumes of 0.2 g/l $PdCl_2$ solution as a source of hydrogen catalyst into the primary colloidal tungsten dihydrate solution. Different tools involving, X-ray diffraction (XRD), high-resolution transmission electron microscope (HRTEM), X-ray photoelectron spectroscopy (XPS), and furrier transformed infrared (FTIR) spectroscopy characterized the colloidal nanoparticles. XRD measurements revealed that the as-prepared nanoparticles are monoclinic $WO_3 \cdot 2(H_2O)$ and were converted to monoclinic WO_3 by annealing at temperatures above 300 °C. XPS showed that the hydroxyl groups and W^{5+} states are dominant in as-prepared sample and lower after annealing or loading $PdCl_2$. It was observed that the Pd-$WO_3 \cdot 2(H_2O)$ solutions which were colorless initially, turned into blue color after dilute hydrogen insertion and then into the colorless state by spontaneously bleaching in ambient air. Moreover, no coloring was observed for colloidal solution composed of monoclinic WO_3. The optical absorption spectra of colloidal samples in colored states were composed of three certain distinct absorption peaks located at 1.3, 1.6 and 1.9 eV. The intensities of first and third peaks were comparable and dominant at deep blue states but, upon bleaching, the second one gradually overcomes them. We attributed this dynamical behavior to the possible surface and bulk phenomena. Finally, the obtained optical absorption results were compared with the small polaron hopping model.

1. Introduction

Recently tungsten oxide nanostructures have attracted more interests from scientific and technological viewpoints because of their sensing and catalytic properties as well as their electrochromic [1] and gasochromic [2] potential applications. In the gasochromic effect tungsten oxide thin films activated with a thin Pd or Pt layer switch from an optical colorless state to a dark blue absorbing state when they are exposed to dilute H_2 gas. This process is often reversible, because the colored films turn reversibly into the colorless state when H_2 is replaced with O_2 [2]. In addition to this observation, it should be noted that almost all the existing reports are commonly related to this effect with thin-film-type gasochromic devices.

Gasochromically or electrochemically colored films of tungsten oxide often show an optical absorption in the near infrared (NIR), which is a desirable effect for heat absorption applications in the solar systems such as thermal filters and building windows (smart windows) [3]. Most of the literature reports that focus their attention on the optical properties of colored films, declare that the NIR absorption includes a broad asymmetric peak at 1–1.5 eV range and various attempts have been made to find a valid explanation for it via peak-deconvolution by two or three multi-peaks [4].

Recently, we have introduced for the first time a gasochromic liquid composed of colloidal tungsten oxide nanoparticles as a new gasochromic system which has unique NIR absorption bands consisting of three main distinct peaks located at around 1.3, 1.6 and 1.9 eV [5]. Based on this observation, colloidal-type tungsten oxide seems to be more capable of acting than thin-film-type to assist basic studies of the gasochromic and hydrogen intercalation phenomena. In that study, crystalline tungsten oxide nanoparticles of about 40 nm average size have been directly

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synthesized by pulsed laser ablation (PLA) method inside DI water and were activated against hydrogen gas by addition of small quantity of palladium salt ($PdCl_2$). Although PLA is a clean technique due to direct interaction of light with matter, but there are some disadvantages with this method such as the broad size distribution of produced nanoparticles, need for expensive equipments, and laser light attenuation as the liquid being opaque due to formation and spreading of nanoparticles.

The scope of this study is to extend the subject of gasochromic liquids into simpler, chipper and more productive synthesis methods. Moreover, to push the criteria toward understanding of fundamentals of the gasochromic mechanism, it is noteworthy that hydrate forms of tungsten oxide can be good candidates owing to their property of high proton transportation. For example, tungsten oxide dihydrate ($WO_3 \cdot 2(H_2O)$) lies in the series of good proton conductors at low operating temperatures and high humidity conditions [6].

Until now, different methods have been used for the synthesis of tungsten oxide nanoparticles including sol–gel [7], thermal oxidation [8], laser ablation in liquid [9], and wire explosion [10]. On the other hand, it has been demonstrated that electrochemical anodizing of tungsten sheets (plates and films) in certain (corrosive) media leads to formation of tungsten oxide hydrate surfaces over the sheets with porous structures and high surface/volume ratio on nanometer size scale. Anodizing has been vastly used for the fabrication of porous WO_3 films through an electrochemical process [11]. In the anodizing process we often deal with a working electrode (anode), reference electrode (cathode) and an electrolyte [12]. Applying electric field between the anode and cathode leads to anode corrosion through an oxidation process. To the best of our knowledge, the most studied electrochemical anodization trials of tungsten have been used for fabrication of a porous WO_3 layer over the anode surface [13–15]. In this study, we focus not on the anode surface, but instead on the materials released into the electrolyte medium from corrosive oxidation of the anode. The obtained solutions containing colloidal nanoparticles were used as the base of gasochromic liquid. Noble metals like palladium and platinum are well-known hydrogen catalysts. To make the system sensitive to hydrogen gas $PdCl_2$ aqueous solutions, as a palladium precursor, of different concentration was added into the above colloidal solutions. These mixtures were found to have gasochromic switching capability and were investigated in the current study by XRD, TEM, XPS, FTIR and UV–vis spectrophotometry.

2. Experimental

Nanoparticles of tungsten oxide dihydrate were fabricated by anodizing tungsten rods in diluted HCl. For this purpose, two tungsten rods were put 1 cm parallel to each other into a 0.02 M HCl electrolyte. Then a 60 V DC bias voltage were applied to the two ends of rods for 5 min (Fig. 1). By applying voltage, the anode surface began to corrode and was released gradually into the electrolyte. A $PdCl_2$ solution was prepared by adding 0.02 g of $PdCl_2$ powder (99.99% purity) into a mixture of 99.9 cc DI water and 0.1 cc HCl. This composition was kept in ultrasonic bath until $PdCl_2$ was dissolved and a uniform yellowish solution of 0.2 g/l $PdCl_2$ was obtained after 3 h. Then, various amounts of this solution including 0, 0.2, 0.4, 0.6, 0.8 and 1 cc, were added to 10 cc of as prepared colloidal solution of tungsten dihydrate. These obtained samples were named as WT5, WP0.2, WP0.4, WP0.6, WP0.8, and WP1 (Table 1). In order to perform some characterizations, samples were prepared by drop-drying the nanoparticles from their colloidal solution onto silicon or glass substrates. The crystalline structures were analyzed by X-ray diffraction ($Cu_{k\alpha}$, $\lambda = 0.1544$ nm, model Philips XPERT). Chemical bonds of the samples were obtained by FTIR spectroscopy in the mid-infrared range (600–4000 cm^{-1}) using Bruker FTIR (model Tensor27) system. The XPS analysis was done in an ESCA/AES system. The system is equipped with a concentric hemispherical analyzer (CHA, Specs model EA10 plus) suitable for auger electron spectroscopy and XPS. For exciting the X-ray photoelectrons, an AlK_α line at 1486.6 eV was used. The energy scale was calibrated against the carbon binding energy (284.8 eV). Optical properties of liquids before and after hydrogen intercalation were measured in the 190–1100 nm wavelength range using Perkin Elmer spectrophotometer (Lambda 25). The gasochromic experiments were carried out by alternatively bubbling 10%H_2/Ar (flow = 60 l/h) or O_2 (flow = 30 l/h) gases through a tiny stainless steel pipe into a quartz cell containing the colloidal samples.

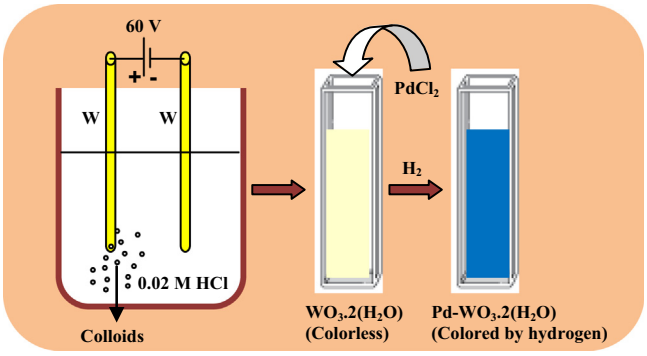

Fig. 1. Schematic representation of synthesis of $WO_3 \cdot 2(H_2O)$ colloidal solution by anodizing method, activation against hydrogen gas by $PdCl_2$ and gasochromic coloring by insertion of diluted hydrogen gas.

Table 1
Sample names and their preparation conditions.

Sample name		WT5	WP0.2	WP0.4	WP0.6	WP0.8	WP1
Anodizing time	(min)	5	5	5	5	5	5
$WO_3 \cdot 2(H_2O)$	(cc)	10	10	10	10	10	10
	(mmol/l)	2.5	2.5	2.5	2.5	2.5	2.5
$PdCl_2$ (0.2 g/l)	(cc)	0	0.2	0.4	0.6	0.8	1
	(μmol/l)	0	10	20	30	40	50

3. Result and discussion

3.1. Crystal structure

Fig. 2(a–g) shows the XRD patterns of as-prepared sample (WT5) before and after annealing at different temperatures of 100, 200, 300, 400 and 550 °C for 2 h in air. All the diffraction peaks of sample WT5 agree well with the monoclinic tungsten oxide dihydrate (PDF 00–016-0166), $WO_3 \cdot 2(H_2O)$. However, no intense diffraction peak has been detected after annealing at 100 °C. In addition, there are some weak peaks which could not be indexed, and are believed to be from the formation of an intermediate compounds during phase transition; likely orthorhombic tungsten oxide monohydrate with formula $WO_3 \cdot (H_2O)$. New diffraction peaks, however, appear in XRD pattern when annealing temperature increases to 200 °C. This pattern contains the diffraction peaks of the monoclinic WO_3 (PDF 00–005-0364) and indicates a significant crystalline transformation from the