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Blue colloidal nanoparticles of molybdenum oxide by simple anodizing method: decolorization by $PdCl_2$ and observation of in-liquid gasochromic coloration

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ABSTRACT

In this study, colloidal nanoparticles of molybdenum oxide were prepared through a simple electrochemical anodizing of molybdenum sheets in 0.02 M HCl electrolyte. The initial transparent electrolyte turned into a long-term stable dark blue color during the anodizing process. The blue liquid exhibited several optical absorption peaks and shoulders at photon energies of 1.2, 1.4, 1.6 and 1.9 eV. However, to examine the gasochromic coloration in the liquid phase, the colloidal solution must be initially colorless. Moreover, the liquid with gasochromic property is required to be catalytically active against hydrogen gas. These tasks were performed by adding precursor $PdCl_2$ solution. It was observed that $PdCl_2$ not only activates the liquid for gasochromic coloration, but also removes the initial blue color. General characterizations were performed on drop-dried samples by means of transmission electron microscopy (TEM), UV–vis spectroscopy and X-ray photoelectron spectroscopy (XPS). The decolorized colloidal molybdenum oxide samples exhibited unique in-liquid gasochromic colorations by diluted hydrogen bubbling, which converted the colorless solutions back to the dark blue color. The gasochromically colored samples showed absorption bands analogous to those of as-prepared blue samples along with an extra shoulder at around 3 eV. The coloration mechanism was described according to two existing models; small polaron and charge transfer models.

1. Introduction

Gasochromic coatings and glazing of transition metal oxides have been investigated for several decades [1–4]. In the gasochromic phenomenon, an electrochromic film such as tungsten oxide covered with a thin Pd or Pt layer (4–5 nm thickness) is able to switch from a bleach or transparent state to a dark blue absorbing state when they are exposed to hydrogen gas. Meanwhile, the color switching can occur between transparent and mirror states too, which have been observed for thin films of certain metal hydrates such as MgNi alloys [5,6]. For each kind, this process is often reversible; when H_2 is replaced with O_2, the colored state reversibly turns to bleach. Gasochromic coating have been used for different applications such as optical hydrogen gas sensing, hydrogen leak detecting, smart mirrors and windows [7–9].

Up to now, the main objectives have focused on thin films of gasochromic materials and little has been done on new systems like colloidal solutions. Moreover, gasochromic thin films often exhibit a single broad absorption peak in NIR when they are colored [10–14]. This broad peak is unable to entirely interpret the chromic phenomena in details and must be de-convoluted manually into some constructing narrower peaks. Moreover, hydrogen transfer into the lattice as the first step of gasochromic coloration is limited in a rigid thin solid film due to one dimensional diffusion across the layer. Nevertheless, colloidal nanoparticles provide greater diffusion constants for a gas as they are dispersed in a fluid and absorb incoming hydrogen faster as they have great surface to volume ratio. In the gasochromic system, the hydrogen catalyst (Pd or Pt) plays critical role because it controls hydrogen dissociation rate under the spill-over mechanism [15,16]. One more advantage of colloidal systems is that the adding of the salt solution of the noble metals Pd and Pt into the gasochromic colloids creates the activation against hydrogen gas simply. Studying on tungsten oxide colloidal nanoparticles prepared by laser ablation [17] or anodizing [18] in the liquid and activated by palladium chloride, we have recently demonstrated that colloidal forms of gasochromic materials have the capability of in-liquid gasochromic coloration with unique optical properties demonstrating distinct optical absorption bands instead of one NIR region broad peak. Up to now, the most studied material for gasochromic is

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tungsten oxide films with a variety of texture, morphology and composition, which have shown fast coloring, durability and good reversibility. However, molybdenum oxide is one another material with great ability of gasochromic coloration and has been known as a good photochromic material. Few reports on gasochromic coloration of molybdenum oxide thin films exist in literature [19–21] and most of which has not shown coloring reversibility. Additionally, to the best of our knowledge, no report on in-liquid gasochromic coloration of a colloidal molybdenum oxide has emerged up to now. For that reason, it is of scientific and technical benefit to explore the gasochromic coloration of the colloidal solutions of molybdenum oxide. Meanwhile molybdenum oxide has recently attracted much attentions for its applications in gas sensing [22,23], field emission [24] cathode of batteries [25,26] electrochromic [27] and photochromic [28].

Until now, different methods have been used for production of molybdenum oxide nanoparticles including liquid exfoliation [29], plasma processing [30], soft chemical process [31] and water bath method [32]. In our previous work on tungsten oxide based gasochromic liquid, we have used a simple anodizing method for synthesis of gasochromic tungsten oxide colloids. In the electrochemical anodizing process, the metallic anode is oxidized to a metal oxide, fragmented into very small pieces, is dispersed into the electrolyte and gives a homogenous colloidal solution. It is noteworthy that hydrate forms of metal oxides, which have been obtained by anodizing method, are good candidates owing to their property of high proton transportation. The method of anodizing has been also used in a few papers for synthesis of metal oxides of other elements such as titanium compounds [33,34]. Although people are familiar with this process in electrochemistry or corrosion science, less attention has been paid to it as a method for generation of colloidal solutions and nanoparticles. In the present work, this idea is extended to molybdenum oxide for synthesis of nanoparticles via the anodizing of Mo sheets in an acidic electrolyte and their gasochromic properties in the liquid phase are investigated. Besides, colloidal nanoparticles dispersed in a liquid often exhibit different chromic performance comparing with bulk or thin films types. In the case of molybdenum oxide, for example, the photochromic performance has been observed to be different from molybdenum oxide thin films [35]. This is due to the particles that are separated from each other in solutions and accordingly much effective surface area is available to expose to incoming light. In addition, colloids in nanoscale often present extra absorption bands in optical spectra. This assists better understanding the underlying physical mechanisms. In the work on tungsten oxide, anodizing of tungsten rods in acidic electrolyte led to formation of tungsten oxide dehydrate colloids which were initially transparent (colorless). In this study, however, anodizing of molybdenum led to formation of molybdenum oxide colloids with a dark blue color.

Since gasochromic investigations need primarily colorless samples therefore we had to remove the initial blue color. Accordingly, this will be an important point to be addressed in this paper. We found that addition of palladium salt ($PdCl_2$) solution, which is used in our method as the source of hydrogen catalyst, also leads to gradually decolorization of the as-prepared blue colloidal molybdenum oxide solutions with a salt concentration-dependent decolorization rate. Under hydrogen gas exposure, this composition of colorless colloidal solution was able to be converted nearly to its initial blue color along with an extra shoulder at around 3 eV. The variations of optical absorption in the bleaching process of gasochromically colored samples were interpreted by the small polaron and inter-band transition models. Here, TEM, XPS, and UV–vis spectrophotometer tools were used for characterization of produced nanoparticles. Fig. 1 indicates the process from anodizing to in-liquid gasochromic coloration.

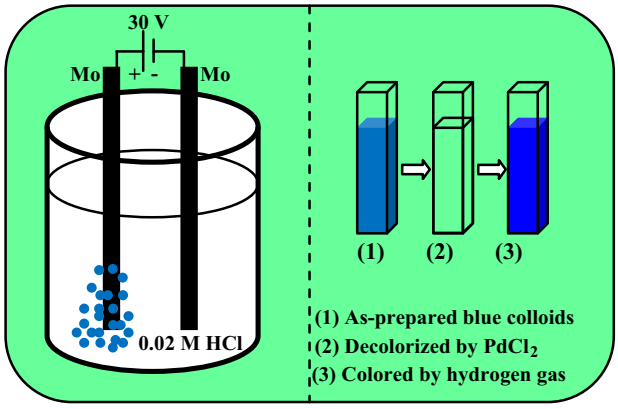

Fig. 1. Schematic representation of synthesis of molybdenum oxide nanosheets by anodizing method, as-prepared blue colloids, decolorization and activation against hydrogen gas by $PdCl_2$ and gasochromic coloring by hydrogen bubbling. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

Colloidal nanoparticles of molybdenum oxide were fabricated via an electrochemical anodizing of molybdenum sheets in a 0.02 M HCl electrolyte. In this process, two molybdenum sheets were put 1 cm apart from each other into a 0.02 M HCl electrolyte. A 30 V DC bias voltage was applied to the two ends of sheets for 5 min (Fig. 1). By applying voltage, the anode began to corrode electrochemically, gradually dispersed throughout the electrolyte and the colloidal solution were obtained. Total dispersion of molybdenum were measured from the weight loss of molybdenum sheets. $PdCl_2$ 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 for 3 h until $PdCl_2$ powder was dissolved entirely and a uniform yellowish solution of 0.2 g/l $PdCl_2$ was obtained. Then, by addition of $PdCl_2$ solution to the colloidal molybdenum oxide, samples of different Pd:Mo ratios (1:20, 1:15, 1:10 and 1:5) were obtained. They were named according to the Pd:Mo ratio (for example $PM_{1:10}$ denotes Pd:Mo = 1:10). In order to perform some characterizations, the certain samples were prepared by drop-drying of colloidal solution onto quartz substrates or TEM girds. TEM imaging was performed using Philips Holland model CM120. The XPS analyses were done using an ESCA/AES system. The ESCA system was 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 AlKα line at 1486.6 eV was used. The energy scale was calibrated against the carbon binding energy (284.8 eV). Optical absorptions were measured in the 190–1100 nm wavelength range using Perkin Elmer spectrophotometer (Lambda 25). Gasochromic investigations were performed using (10%H_2)/Ar mixed gas for coloring and O_2 (purity 99.9%) for bleaching which were alternatively bubbled into the $PM_{1:15}$ colloidal solutions through a tiny glass pipe.

3. Results and discussion

3.1. TEM

Fig. 2(a) shows a typical TEM image and corresponding size distribution histogram of as-prepared sample. Crystallites of polygon-shape are observable in the TEM image that resembles nanosheets in some part of image. In the inset, for example, nanoparticles are placed over each other in such a way so that