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Combinatorial Electrochemical Synthesis and Characterization of Tungsten-Molybdenum Mixed Metal Oxides

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Abstract−Automated systems for electrochemical synthesis and high throughput screening of photoelectrochemical materials were developed and used to prepare tungsten-molybdenum mixed metal oxides, WO_3-MoO_3. Two-dimensional arrays (library) of diverse composition were synthesized by automated cathodic electrodeposition on Ti foil substrate. Electrolytes were prepared by mixing W-peroxo complex and Mo-peroxo complex. The compositions in films were found to strongly depend on the composition of electrolyte, and found to be relatively independent of deposition voltage. The morphology was found to be very homogeneous. The electrodeposited oxides typically showed n-type behavior. Automated measurement of photocurrent by using a scanning photoelectrochemical cell showed that mixed oxides showed higher photocatalytic activity than pure tungsten oxide or pure molybdenum oxide. Photoactitvities of the mixed oxides were strongly dependent on the film composition.

Key words: Combinatorial Synthesis, WO_3-MoO_3 Mixed Oxide, Electrodeposition, Photocurrent, High Throughput Screening

INTRODUCTION

Tungsten oxide (WO_3) and molybdenum oxide (MoO_3) are indirect bandgap semiconductors with interesting photoconductive behavior. They are presently used in electrochromic devices and chemical sensors and show a promise as low cost materials for solar energy applications [Yao et al., 1996; Granqvist, 2000; Pennisi and Simone, 1992; Faughnan and Crandall, 1977]. Electrochemical deposition methods have been used for WO_3 or MoO_3 deposition by dissolving metal powder in hydrogen peroxide [Meulenkamp, 1997; Hutchins et al., 1999; Monk et al., 1995]. The electrodeposition method has many advantages over other synthesis routes in terms of economics and flexibility for making large surface area metal oxide films.

Combinatorial chemistry involves the deliberate creation and screening of very large numbers of new materials from different combinations of specific building block atoms and molecules [Hanak, 1970; Hanak et al., 1969]. Applied to functional inorganic materials, this method has been used to rapidly investigate large numbers of mixed metal oxides as potential phosphors, catalysts, and dielectric materials [Danielson et al., 1997, 1998]. Automated electrochemical methods for creating and screening collections of compositionally varied materials (libraries) for photoelectrochemical performance have recently been described [McFarland et al., 2001]. Electrochemical methods lend themselves well to the combinatorial synthesis of inorganic materials because of the many synthesis variables under direct control such as voltage, current density, electrolyte, which can be varied programmably, resulting in diversity of structure and composition.

We used methods of automated electrochemical synthesis and screening of WO_3-MoO_3 mixed oxide to address the following questions: 1) Can a combinatorial library of WO_3-MoO_3 mixed oxide be rapidly synthesized and screened electrochemically? 2) What are the photoelectrochemical effects of the compositional changes? 3) Is there any trend in photoelectrochemical activity as a function of composition that might improve our understanding of composition-function relationships?

EXPERIMENTAL

The stabilized Me (W or Mo)-peroxo electrolyte was prepared by dissolving proper amount of tungsten powder or molybdenum powder in 60 ml of 30% hydrogen peroxide solution. The excess hydrogen peroxide was subsequently decomposed with platinum black. The solution was diluted to 50 mM with a 50 : 50 mixture of water and isopropanol.

The films were deposited cathodically under potentiostatic control in a 63-sample combinatorial array. In brief, the assembly consisted of a 30 mm thick polypropylene block with 63-10.8 mm diameter holes. Using independent O-rings for sealing, the block was affixed to the titanium foil substrate forming 63 independent working electrodes. For maximum control of electrochemical synthesis, we developed a scanning electrode probe containing a platinum reference electrode and a platinum counter electrode. After the individual cells were filled with various electrolytes, the electrode could be scanned under computer control to each electrolytic well. Different structures and compositions of the oxides could be electrodeposited in each well by varying the electrolyte composition and voltage across the library.

The library shown in Fig. 1 is a 45-member (5×9 array) WO_3-MoO_3 mixed oxide library, with diversity achieved by variations in deposition voltage and Mo concentration in electrolyte. The library was deposited on titanium foil by using the 63-well parallel reactor block. The concentration of Mo was varied from 0 to 100 mol% and all films were deposited for 10 minutes. After deposition, the

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[‡] This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

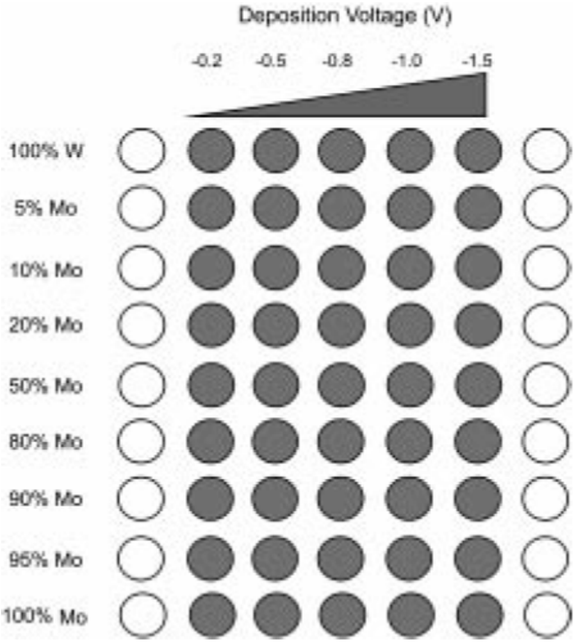

Fig. 1. Library design for WO_3-MoO_3 mixed oxide. The individual electrolyte contained peroxo stabilized tungsten with peroxo stabilized molybdenum at the individual mole percentage for diversity.

library was calcined at 450 °C for 4 hours in air.

Screening of the library for photoelectrochemical activity was performed by measurement of photocurrent at zero and one volt bias. A scanning electrochemical probe, which is described in detail elsewhere, was used [McFarland et al., 2001]. Under computer software control, the probe is moved horizontally to each library location and lowered to the film forming an o-ring seal. The probe contains Pt working and reference electrodes connected to an EG&E 273A potentiostat. Sodium-acetate (0.1 M) electrolyte is pumped automatically into the probe and current-voltage data are obtained while the area is illuminated with a chopped light source. The source was an Oreal Xe 150 W lamp coupled by an optical fiber to the scanning probe with a measured output at the sample of 2.25 mW/cm^2.

Following synthesis, selected library samples underwent more detailed quantitative analysis. Scanning electron microscopy (Philips, XL-30 ESEM-FEG) and electron stimulated energy dispersed x-ray spectroscopy (Princeton Gamma Tech, IMIX) were performed to give surface morphology and composition. X-ray diffraction (Scintag, X2) was used to examine the sample crystal structures.

RESULTS AND DISCUSSION

All as-deposited films were confirmed to be amorphous. After calcinations at 450 °C, all films were crystallized. Fig. 2 shows XRD patterns of WO_3-MoO_3 mixed oxide after calcinations prepared at −1.0 V from 50% W-50% Mo electrolyte. Peaks corresponding tungsten oxide and molybdenum oxide were observed. Electrodeposition of metal oxides, such as WO_3, MoO_3, TiO_2, ZrO_2, and Nb_2O_5 from peroxo precursors has been widely employed [Zhitomirsky, 1997, 1998, 1999]. And electrodeposition is very practical for making mixed metal oxides. It is confirmed from XRD that WO_3-MoO_3 mixed oxide can be synthesized from mixture of peroxo complex.

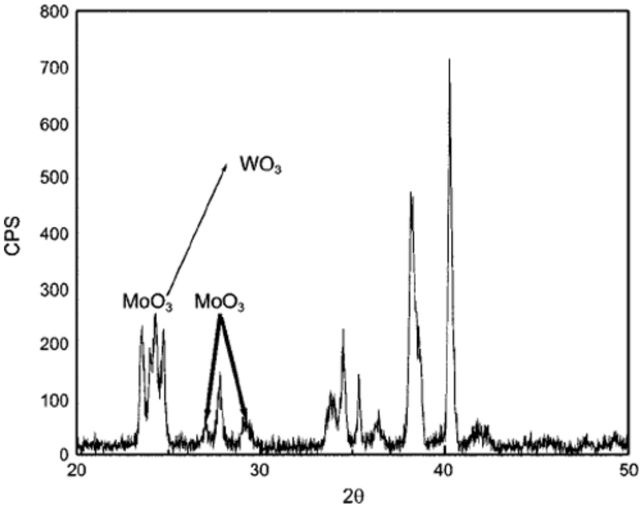

Fig. 2. X-ray diffraction patterns of WO_3-MoO_3 mixed oxide on Ti foil; after being thermally treated at 450 °C.

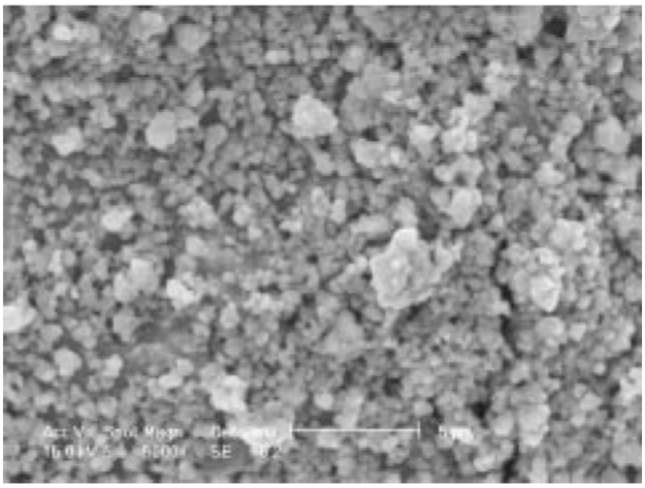

Fig. 3. Scanning electron micrograph of electrodeposited WO_3-MoO_3 mixed oxide synthesized from 50% W-50% Mo electrolyte at −1.0 V.

SEM image of mixed oxide prepared from 50%W-50% Mo electrolyte is shown in Fig. 3. There are no discrete features observed which might suggest phase separation. The film compositions were determined by EDX for fifth row (prepared from 50% W- 50% Mo mixture) and 4th column (electrodeposited at −1.0 V). As expected, with increasing concentration of molybdenum in solution, the atomic fraction of molybdenum in the film increased (Fig. 4). However, the atomic ratio was independent of deposition voltage (−0.2~−1.5 V, not shown).

From the structural and morphological evaluation, electrocodeposition of WO_3 and MoO_3 using peroxo complex gave rise to the synthesis of well mixed oxide of WO_3 and MoO_3, and the use of peroxo complex for the mixed oxide synthesis of tungsten oxide and molybdenum oxide allowed us to obtain deposits with desired composition.

The photoelectrochemical response of WO_3-MoO_3 mixed oxide was investigated. The scan range was selected such that the surface

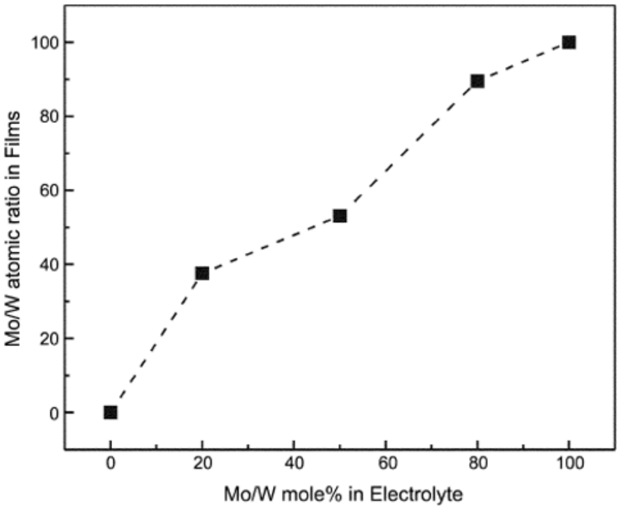

Fig. 4. EDS measured atomic ratio of Mo to W in films as a function of Mo concentration in electrolyte.

would not be chemically altered by the applied bias. The bias voltage was swept between −0.5 and 1.0 V while the current between the sample (working electrode) and the Pt counter electrode in a 0.1 M sodium acetate solution was monitored. The as-synthesized WO_3 was amorphous and showed no photoresponse; however, with calcination there was an increase in photoactivity, presumably as the crystallinity increased and defect density decreased. This result was shown in previous work [Miyauchi et al., 2000], which also reported that bandgaps of tungsten oxide could be decreased by crystallization from 3.1 to 2.8 eV.

The first row and last row were for electrodeposition of pure tungsten oxide and pure molybdenum oxide, respectively. After calcinations at 450 °C, both of pure tungsten oxide and molybdenum oxide showed n-type semiconductor behavior under illumination and zero bias photocurrent of 1.86 $\mu A/cm^2$ and 1.75 $\mu A/cm^2$, respectively, as shown in Fig. 5.

Automated photo-electrochemical screening of the library was performed. A trend in photoresponse as a function of molybdenum concentration in electrolyte was clearly observed. Fig. 6 shows photocurrent at 0 and 1 V bias for WO_3-MoO_3 mixed oxide. Photoactivity of the mixed oxides was strongly dependent on the film composition. The photoresponse increased and reached a maximum when 50% Mo and 50% W concentration in electrolyte was used, and then decreased as concentration of Mo in electrolyte increased. In the cases where MoO_3 concentration was below 10% or above 90%, there was no enhancement of photoactivity compared to either pure WO_3 or pure MoO_3. Interestingly, in the range of 20-80% MoO_3, an increase of photoactivity was observed.

Shiyanovskaya and Hepel [Shiyanovskaya and Hepel, 1999] reported increased photocatalytic activity of WO_3/TiO_2 bicomponent films. In this system, Electrons photogenerated at the conduction band of TiO_2 transfer into the lower lying WO_3 conduction band, while the holes photoexcited at the valence band of WO_3 transfer into TiO_2 valence band. Therefore, the relative locations of the band energies of TiO_2 and WO_3 can promote efficient separation of photogenerated charges, whereas the surface and bulk recombination processes result in a photocurrent decrease. By the same principle, WO_3-MoO_3 mixed oxide might show higher photocatalytic activ-

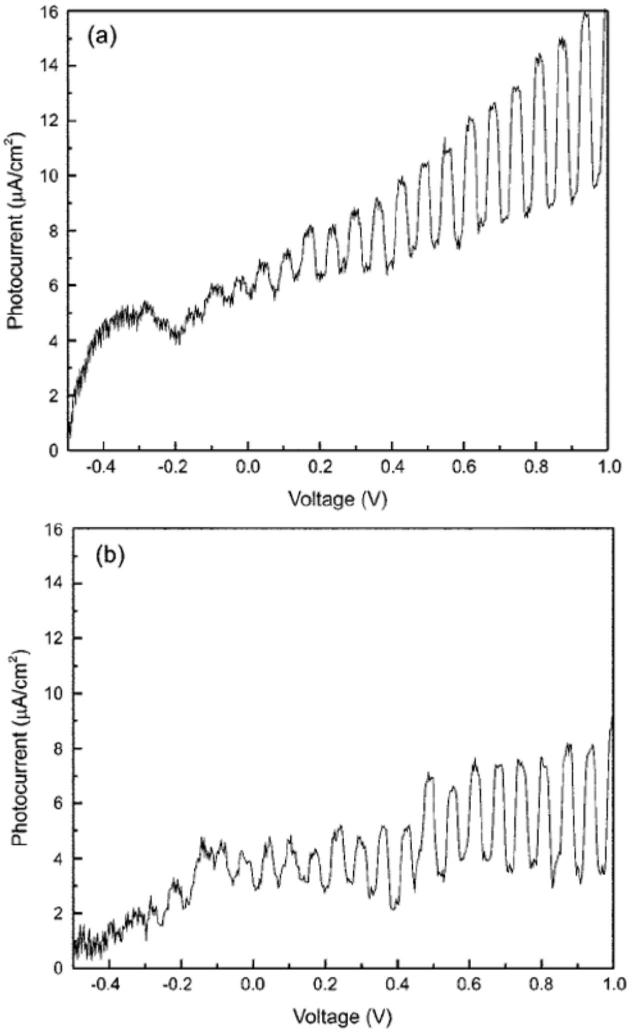

Fig. 5. Potentiodynamic scans under chopped illumination (2.25 mW/cm^2) for (a) tungsten oxide deposited at −1.0 V and (b) molybdenum oxide deposited at −1.0 V.

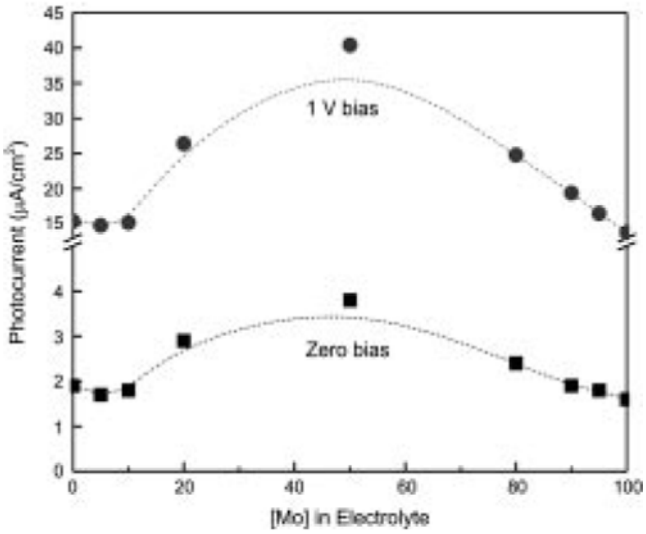

Fig. 6. Photocurrents in 0.1 M sodium acetate solution at zero bias and 1 V bias for WO_3-MoO_3 mixed oxides as a function of Mo concentration in electrolyte (4th column in library).

ity than either pure tungsten oxide or pure molybdenum oxide. Photoexcited electrons at WO_3 conduction band can transfer into MoO_3 conduction band due to the relative location of band energies of the two materials, while the holes from MoO_3 valence band can move in an opposite direction. So, the recombination of photogenerated electron-hole pair might be suppressed, resulting in higher photocatalytic activity.

CONCLUSION

Combinatorial library of WO_3-MoO_3 mixed oxide was rapidly synthesized and screened with a high throughput photoelectrochemical system. By using peroxo precursors, mixed oxide of WO_3 and MoO_3 was successfully prepared and the composition between the two materials could be controlled by the concentration of each component in electrolyte.

Photoactivity of the mixed oxides were strongly dependent on the film composition. Maximum photoresponse was achieved when 50% Mo and 50% W concentration in electrolyte was used. In the cases where MoO_3 concentration was below 10% or above 90%, there was no enhancement of photoactivity compared to either pure WO_3 or pure MoO_3. Interestingly, in the range of 20-80% MoO_3, an increase of photoactivity was observed.

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