Near Infrared Electrochromic Smart Window with Plasmonic Compound Nanomaterials

Xiaohuan FU, Seung Hyuk LEE, Yoshinori KUROIWA, and Tetsu TATSUMA *

Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

*Corresponding author: tatsuma@iis.u-tokyo.ac.jp

ABSTRACT

Control of light transmittance is important for optoelectronic devices such as smart windows and switchable photodetectors. In particular, that for infrared light can be used for tuning thermal flows through windows. Plasmonic compound nanomaterials are suitable for those devices because of their electrochemically tunable localized surface plasmon resonance (LSPR). We combined CuS nanoplates with MoO₃ nanosheets for developing complementary near infrared electrochromic cell. CuS loses its plasmonic absorption (peaked at ~1100 nm) when it is reduced, as opposed to MoO₃, whose absorption at >600 nm is suppressed when it is oxidized. An assembled smart window with rocking-chair type lithium ion transport exhibits wide transmittance changes in the near infrared region.

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Keywords : Near Infrared Smart Window, Electrochromism, Localized Surface Plasmon Resonance, Compound Nanoparticle

1. Introduction

The Localized surface plasmon resonance (LSPR) is a resonance phenomenon between collective oscillation of free electrons in nanoparticles and electric field oscillation of incident light.¹ Light absorption and scattering based on LSPR of plasmonic metal nanoparticles occur mainly in the visible region. If optical absorption of plasmonic metal nanoparticles can be controlled by electrostatic charging-discharging^{2–7} or electrochemical redox reactions,⁸ the nanoparticles can be applied to electrochromic smart windows with tunable visible light transparency. The electrostatic method enables fast and reversible responses, but the dynamic range of the transparency is relatively narrow. In contrast, a redox-based method that tunes the plasmonic absorption by electrochemical dissolution and re-deposition of metal nanoparticles is characterized by a large dynamic range, but its reproducibility of the nanoparticle morphology should be lower in principle.

If the metal nanoparticles are replaced with compound nanoparticles having high charge carrier density and mobility, such as slightly reduced WO₃,^{9,10} ITO,¹¹ slightly reduced MoO₃,^{12,13} and CuS,^{14,15} optical transparency in the near infrared (NIR) region could be controlled. Electrochromism of WO₃ and MoO₃ have been well known for long time,¹⁶ and nanoparticle systems have also been reported.¹⁷ ITO nanoparticles were used for NIR electrochromism based on the electrostatic method.^{18,19} We recently developed a NIR electrochromic device based on redox reactions of CuS nanoplates.²⁰

For electrochromic devices, it is necessary to combine the electrochromic electrode with another redox system at the counter electrode. Complementary electrochromic systems are sophisticated because one of the two electrodes is colored when it is oxidized, and

the other one is colored when it is reduced. A typical system is WO₃/Prussian blue complementary device,²¹ in which the WO₃ and Prussian blue^{22,23} are blue-colored upon reduction and oxidation, respectively.

In the present work, we developed a complementary electrochromic system for the CuS nanoplates, which lose plasmonic absorption upon reduction, by combining those with MoO₃ nanosheets, which is colored in a reduction process. It is a rocking chair-type device because Li⁺ intercalation and deintercalation occur for the MoO₃ and CuS electrodes, respectively, when the NIR absorption of the device is activated, and vice versa.

2. Experimental

2.1 Materials

Copper(I) chloride (CuCl), elemental sulfur (S), sodium sulfide (Na₂S), lithium perchlorate (LiClO₄), ethanol, and toluene were purchased from Wako Pure Chemical Industries. Propylene carbonate (PC), oleic acid (OAc), and oleylamine (OAm) were purchased from Sigma-Aldrich.

2.2 Preparation of MoO₃ and CuS electrodes

CuS nanoplates were synthesized by heating CuCl and S (8.33 mmol each) in a mixture of OAm and OAc (OAc : OAm = 45 : 55, 2.5 mL) by stirring under N₂ atmosphere at 140 °C for 5 min.²⁴ After cooling to room temperature, the solution was mixed with ethanol (6 mL) and centrifuged at 5800 g at 5 °C for 5 min. After repeating the washing process for 3 times, the obtained precipitate was re-dispersed in 1 mL toluene followed by filtering through a PTFE syringe filter. Finally, the CuS nanoplates were spin coated on a tin-doped indium oxide (ITO) electrode (160 nm thick on glass, 1.2 × 4.0 cm) at 1000 rpm for 20 s using a 70 μL CuS nanoplate suspension to obtain a CuS electrode.

To prepare a MoO_3 electrode, MoO_3 was evaporated onto an ITO electrode with different thickness of 20, 40, 60, and 100 nm by a thermal vapor deposition system (VPC-260F). Then, the MoO_3 /ITO substrate was heated up at 2°C min^{-1} to 400°C and annealed for 3 h in air. The MoO_3 nanosheets thus prepared was reduced to a colored state at -0.5 V vs. $\text{Ag}|\text{AgCl}$ in a PC solution containing 1.0 M LiClO_4 .

2.3 Characterization

X-ray diffraction (XRD) patterns of the CuS and MoO_3 electrodes were recorded with D/MAX 2500V (Rigaku) equipped with $\text{CuK}\alpha$ radiation. Absorbance spectra were measured with a V-670 (JASCO) spectrophotometer.

2.4 Electrochemical measurements

For investigation of each plasmonic electrode, the CuS or MoO_3 working electrode was immersed in a PC solution containing 1.0 M LiClO_4 together with a Pt wire counter electrode and a Ag quasi-reference electrode. Potential values were converted to those vs. $\text{Ag}|\text{AgCl}$ on the basis of the formal potential of ferrocene in PC. The applied voltage was controlled by a potentiostat model 263A (Princeton Applied Research). Absorbance spectra from 350 to 1350 nm were obtained after applying each potential for 90 s. For investigation of a CuS- MoO_3 cell, a MoO_3 working electrode was combined with a CuS counter electrode and NIR absorption spectra were collected at a constant voltage in the range of -0.9 – $+1.0\text{ V}$. The NIR transmittance of the cell was monitored at 1150 nm during alternate application of -0.9 and $+1.0\text{ V}$.

3. Results and Discussion

3.1 Preparation of MoO_3 and CuS electrodes

CuS nanoplates were synthesized from CuCl and S, and re-dispersed in toluene. The dispersion exhibited LSPR at $\sim 1100\text{ nm}$ (Fig. 1a), suggesting that the average in-plane size of the nanoplate was $7\text{--}8\text{ nm}$.²⁴ The CuS nanoplates were spin coated on an ITO electrode. A red-shift of the absorption peak was observed (Fig. 1a), since the nanoplates were in contact with ITO having high refractive index. The XRD pattern of the electrode (Fig. 1b) indicates the existence of covellite CuS²⁵ on bixbyite ITO. The lateral size calculated from the (110) peak of CuS via Scherrer equation was $\sim 10\text{ nm}$, roughly in agreement with the value estimated from the absorption spectrum.

To obtain a MoO_3 electrode, 20 nm thick MoO_3 was evaporated onto an ITO electrode, followed by annealing at 400°C for 3 h. From an XRD analysis, it was confirmed that orthorhombic MoO_3 nanosheets²⁶ were deposited on the electrode and the thickness of each nanosheet was $20\text{--}25\text{ nm}$ (Fig. 1c). The MoO_3 nanosheets thus obtained were electrochemically reduced, and the reduced MoO_3 nanosheets exhibited a broad absorption in the NIR region (Fig. 1d).²⁶

3.2 Redox behavior of each electrode

Absorption spectra of the prepared CuS and MoO_3 electrodes were collected at different potentials in a PC solution containing 1 M LiClO_4 by using a three-electrode system. As shown in Fig. 2a, the CuS electrode showed a broad peak at $\sim 1100\text{ nm}$ in the oxidized state at $+0.2\text{ V}$ vs. $\text{Ag}|\text{AgCl}$. The absorption was decreased gradually as the potential was shifted negatively, and almost completely suppressed at -0.9 V . The LSPR of CuS nanoplates are due to oscillation of holes in their valance band. The holes are removed from the valance band in the reduction process, and the absorption is suppressed.

During the redox reactions of CuS in aqueous solutions, charge compensation was achieved by intercalation of OH^- .²⁰ In order to study ion exchange behavior of CuS in the PC solution, we replaced

Figure 1. (a) Absorption spectrum of the toluene solution of CuS nanoplates (vs. toluene) and that of the ITO electrode modified with CuS nanoplates in air (vs. ITO electrode). (b) XRD pattern of the CuS nanoplates on ITO. (c) XRD pattern of the MoO_3 nanosheets on an ITO electrode. (d) Absorption spectrum of the ITO electrode modified with MoO_3 nanosheets in air (vs. ITO electrode).

Li^+ in the solution with more bulky tetrabutylammonium ion (TBA^+), and the CuS electrode lost its electroactivity. We therefore conclude that the charges in CuS are compensated by exchanging Li^+ in the present system, as the system with acetonitrile solution containing LiClO_4 .²⁷

In the case of the MoO_3 electrode, the wide NIR absorption band observed at -0.5 V was suppressed at $+0.3\text{ V}$ (Fig. 2b). The electrochemical control of absorption can be explained in terms of reversible intercalation of Li^+ .^{28,29} because the absorption suppressed at $+0.3\text{ V}$ did not reappear upon applying a negative potential of -0.5 V in a PC solution containing TBAClO_4 .

Figure 2. Visible–NIR absorption spectra of (a) CuS and (b) MoO₃ electrodes at different potentials (vs. ITO electrode). (c) Capacity of the MoO₃ electrode with different MoO₃ precursor film thickness measured by chronoamperometry in the potential range of -0.5 – $+0.3$ V vs. Ag|AgCl.

Since the CuS and MoO₃ electrodes show opposite absorption changes upon redox reactions with Li⁺ exchange, those electrodes are suitable for assembling a rocking chair type complementary electrochromic device (Fig. 3a).

In such a device, it is preferable to match the capacity of one electrode with that of the other electrode. The average charge passed for the redox reactions of CuS in the potential range of -0.5 – $+0.3$ V was 3.6 mC cm^{-2} . We therefore measured capacities of MoO₃ electrode with different MoO₃ precursor film thicknesses before annealing (20–100 nm indicated by a quartz crystal microbalance) (Fig. 2c). It was found that the capacity was almost proportional to the precursor thickness. We conclude that the optimum precursor thickness is ~ 60 nm, which gives the capacity of $\sim 3.0 \text{ mC cm}^{-2}$.

3.3 Behavior of the CuS–MoO₃ complementary device

The optimized MoO₃ electrode prepared from a 60-nm-thick precursor MoO₃ and the CuS electrode were assembled into a two-electrode CuS–MoO₃ cell, and its absorbance spectra were measured at different bias voltages from -0.9 to $+1.0$ V (Fig. 3b). As expected, the highest NIR absorption was achieved at -0.9 V, and the lowest one was observed at $+1.0$ V. The shoulder at ~ 800 nm is ascribed to MoO₃, and the broad peak at ~ 1100 nm is attributed to the absorption peak of CuS and the NIR plateau of MoO₃.

The NIR transmittance of the two-electrode system was monitored at 1150 nm during alternate potential application of

Figure 3. (a) Rocking-chair-type behavior of the CuS–MoO₃ complementary electrochromic cell. (b) Difference absorption spectra of the cell at different bias voltages vs. the spectrum at $+1.0$ V. (c) Transmittance changes of the CuS–MoO₃ cell, CuS–ITO cell, and ITO–MoO₃ cell at 1150 nm during alternate application of -0.9 and $+1.0$ V.

-0.9 V and $+1.0$ V, as shown in Fig. 3c (black curve). Although obvious transmittance changes were observed for the CuS–MoO₃ cell, the changes were almost negligible when one of the two electrodes of the cell was replaced with a bare ITO electrode. Therefore, we conclude that cooperative redox reactions of both CuS and MoO₃ are necessary for operation of the electrochromic cell.

4. Conclusions

In summary, CuS and MoO₃ electrodes were assembled into a two-electrode complementary electrochromic cell by matching the charge density of both electrodes measured in three-electrode systems. By combining these two electrodes, carriers released from either electrode were used for the electrochemical reaction of the opposite electrode on the basis of Li ion exchange at both electrodes.

Acknowledgments

This work was supported in part by a Grant-in-Aid for Scientific Research (A) (JP20H00325) and a Grant-in-Aid for Challenging Exploratory Research (JP20K20560) from the Japan Society for the Promotion of Science (JSPS).

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