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## Electrochemical redox-based tuning of near infrared localized plasmons of CuS nanoplates<sup>†</sup>

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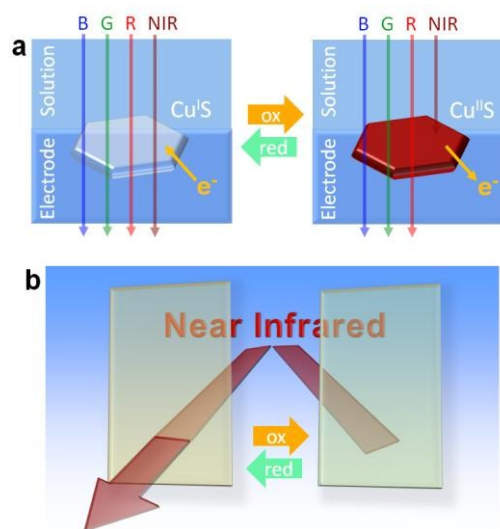
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**Fast and reversible control of plasmonic properties of compound nanoparticles (*i.e.* CuS nanoplates) was achieved through electrochemical redox reactions. Their electrochemical tunability can be applied to fast-switching near infrared electrochromic devices, whose visible appearance is not changed by switching.**

Metal nanoparticles (NPs) are known to absorb and scatter light strongly on the basis of resonance of free electron oscillation with electric field oscillation of incident light. This phenomenon, localized surface plasmon resonance (LSPR), attracts much attention because it can be applied to chemical sensors and biosensors,<sup>1</sup> photovoltaic cells,<sup>2–4</sup> photocatalysts,<sup>2,5,6</sup> photochromic materials<sup>7,8</sup> and electrochromic devices.<sup>9</sup> If LSPR properties of the NPs could be controlled reversibly, those functional materials and devices can be sophisticated further. It is known that LSPR properties including resonant wavelength and intensity are sensitive to particle size<sup>10</sup> and shape,<sup>11</sup> interparticle distance<sup>12</sup> and local refractive index around NPs,<sup>1</sup> as well as density and effective mass of free electrons.<sup>11</sup> The electron density of metal NPs is tunable via electrostatic charging and discharging, and Mulvaney *et al.*,<sup>13</sup> Foss *et al.*<sup>14</sup> and some other groups<sup>15,16</sup> controlled LSPR properties of gold NPs to some extent by the electrostatic means. However, disappearance of LSPR is difficult because free electrons cannot be removed completely. Here we report that the LSPR properties of plasmonic compound NPs can be controlled reversibly and completely through electrochemical redox reactions (Fig. 1a) and demonstrate that the electrochemical tuning can be applied to fast-switching NIR electrochromic smart windows, which allow regulation of radiative heat flux through it (Fig. 1b).

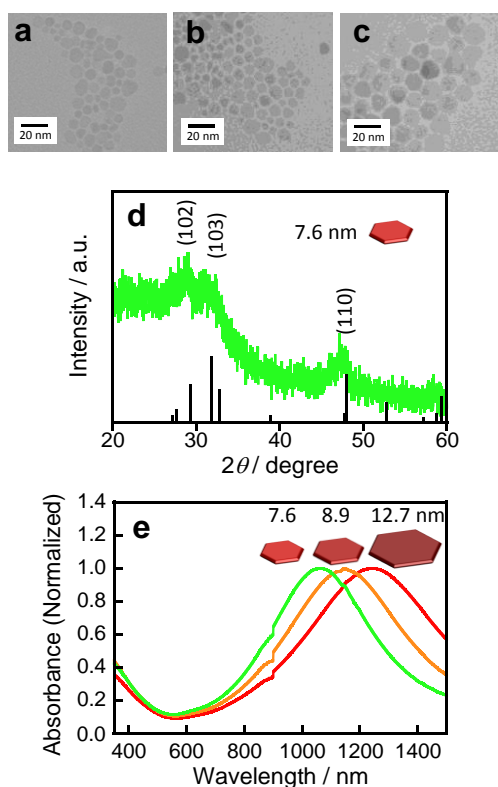


**Fig. 1** Concept of (a) redox-based tuning of near infrared (NIR) localized plasmon and (b) its application to NIR electrochromic smart window.

Recently, it has been reported that NPs of compounds such as tungsten oxide,<sup>17,18</sup> indium tin oxide (ITO)<sup>19</sup> and copper sulfide<sup>20,21</sup> exhibit LSPR in the near-infrared (NIR) region. In the case of ITO NPs, their LSPR intensity and wavelength are regulated by means of chemical control of doping ratio<sup>19,22</sup> and the electrostatic charging.<sup>22,23</sup> Although electrostatic charging is a convenient way of the electrical and reversible control, relatively high voltage (>a few volts) is necessary, and it is basically pushing the plasmonic absorption band aside to longer wavelengths, because complete removal of charge carriers is difficult by electrostatic means.

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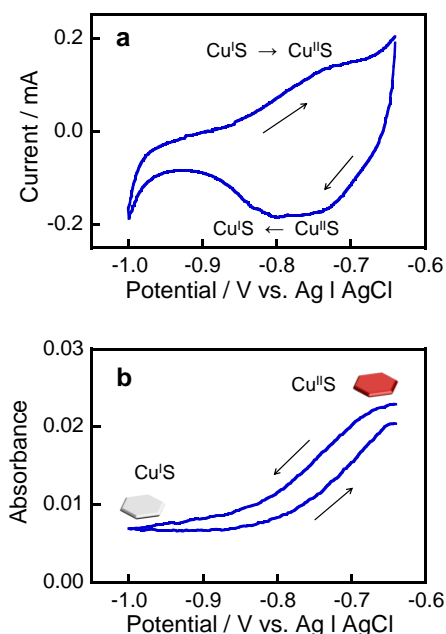
<sup>†</sup> Electronic Supplementary Information (ESI) available: TEM images, absorption spectra and electrochromic response of CuS nanoplates and relationship between relative amount of CuS and absorbance change. See DOI: 10.1039/x0xx00000x



**Fig. 2** (a–c) TEM images, (d) XRD pattern and (e) absorbance spectra in toluene of the synthesized CuS nanoplates with the average width of (a, d) 7.6, (b) 8.9 and (c) 12.7 nm.

Among the plasmonic compound NPs, copper sulfide NPs are intriguing because they consist only of cost-effective and earth-abundant elements, the composition ratios of which can be regulated in a broad range. There are different copper sulfide compounds of wide variety of composition  $\text{Cu}_{2-x}\text{S}$  ( $0 \leq x \leq 1$ ) including chalcocite ( $\text{Cu}_2\text{S}$ ), djurite ( $\text{Cu}_{1.97}\text{S}$ ), digenite ( $\text{Cu}_{1.8}\text{S}$ ), anilite ( $\text{Cu}_{1.75}\text{S}$ ) and covellite ( $\text{CuS}$ ). Many different  $\text{Cu}_{2-x}\text{S}$  NPs can be synthesized and their plasmonic absorption is enhanced and redshifted as the  $x$  value is increased by changing synthesis conditions<sup>20,24</sup> or chemical redox reactions.<sup>25–27</sup> As the  $x$  value is reduced to 0, the plasmonic absorption of the NPs are not only redshifted but also completely suppressed because charge carriers are removed. Nevertheless, electrochemical and reversible tuning of copper valence and composition of  $\text{Cu}_{2-x}\text{S}$  NPs, which would allow development of novel NIR plasmonic materials and devices, has not yet been reported to the best of our knowledge.

We synthesized CuS nanoplates as described elsewhere<sup>28</sup> by heating copper(I) chloride and elemental sulfur (0.125 mmol each) suspended in a mixture of oleylamine (OAm) and oleic acid (OAc) (OAc/OAm = 0.00, 0.33 or 0.82 by vol, 3.75 mL) with stirring under  $\text{N}_2$  atmosphere at 140 °C for 5 min. The nanoplates thus obtained (Fig. 2a–c) have the covellite CuS structure as X-ray diffraction (XRD) data indicate (Fig. 2d). Their width (*i.e.* longest diagonal length for hexagonal and longest diameter for ellipsoidal nanoplates) is  $12.7 \pm 1.8$ ,  $8.9 \pm 1.1$  or  $7.6 \pm 1.2$  nm for the OAc/OAm ratio of 0.00, 0.33 or

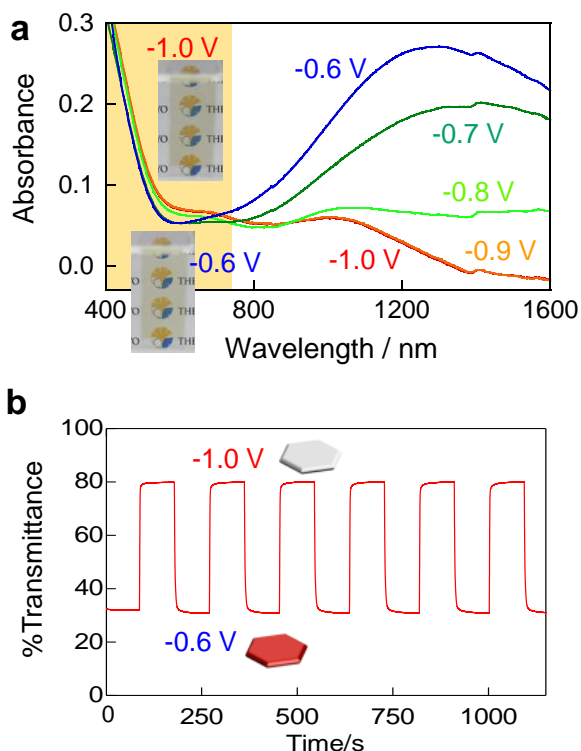


**Fig. 3** Current and absorbance changes of CuS nanoplates on an ITO electrode during potential scanning at 50  $\text{mV s}^{-1}$  in 0.1 M aqueous  $\text{Na}_2\text{S}$  in the range  $-0.63$  to  $-1.0$  V (the 3rd cycle is shown).

0.82. The nanoplate thickness was determined from the TEM images to be 2–3 nm (Fig. S1 in Supplementary Information). The nanoplates exhibit absorption due to in-plane LSPR mode<sup>29,30</sup> when suspended in toluene and the absorbance peak redshifts as the nanoplate width increases (Fig. 2e).<sup>28</sup> This clearly shows that the nanoplate size is successfully controlled even though the nanoplates are not completely monodisperse. We selected the smallest CuS nanoplates for the following experiments because their absorption is less significantly interfered from NIR absorption in water. The CuS nanoplates were deposited on an ITO-coated glass plate by a spin-coating method at 2500 rpm from the suspension (50  $\mu\text{L}$ ). The LSPR peak observed in air was redshifted to 1150 nm (Fig. S2a) because of high refractive index of ITO (1.8 at 800 nm). Scattering of the electrode was sufficiently low, less than 3% in the range 300–1600 nm.

Spectroelectrochemical measurements were performed using a cell with the prepared CuS nanoplate-modified ITO electrode as the working electrode, Pt wire as counter electrode, and  $\text{Ag|AgCl|KCl}(\text{saturated})$  as reference electrode. The electrolyte was aqueous 0.1 M  $\text{Na}_2\text{S}$ , which prevents deterioration of CuS nanoplates.<sup>31</sup> Potential of the working electrode was scanned between  $-0.63$  V, which is close to the open circuit potential, and  $-1.0$  V at 50  $\text{mV s}^{-1}$ . Changes in absorbance were also monitored *in situ* at 1150 nm.

In the first negative scanning, a large cathodic current and an absorbance decrease were observed, but almost perfectly stable voltammograms with reversible absorbance changes were observed in the following potential cycles (Fig. 3). Although the redox peaks are not very obvious, the voltammogram is quite similar to that of redox-active solids such as  $\text{WO}_3$ ,<sup>33</sup> and is explained in terms of virtually multi-step



**Fig. 4** (a) Absorbance spectra of CuS nanoplates on an ITO electrode at different potentials (vs. Ag|AgCl) in deuterated water containing 0.1 M Na<sub>2</sub>S. The inset shows photographs of the electrode at  $-0.6$  and  $-1.0$  V (focused on the background image), which show the visual transparency is retained during the redox reactions. (b) Transmittance changes of the CuS nanoplates on ITO during the redox switching.

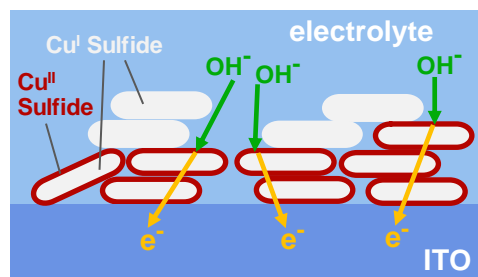
redox processes. The colouration is not due to electrostatic process, because it is observed only at around  $-0.75$  V, which is close to the standard potential of Cu<sub>2</sub>S/CuS couple ( $-0.87$  V).<sup>34</sup>

During electrochemical redox cycles of a solid material, ion exchange occurs between the solid and electrolyte for charge compensation. When a solid is oxidized (from Red to Ox) and loses electrons, anion An<sup>x-</sup> is injected and/or cation Ct<sup>y+</sup> is ejected, as expressed by eq. 1. We therefore discuss the processes on the basis of the corresponding Nernst equation (eq. 2), which correlates the redox potential  $E$  (in V) with the standard electrode potential  $E^\circ$  and activities of Red and Ox.



$$E = E^\circ + (0.059/n)\log(a_{\text{Ox}}(\text{Ct}^{y+})^{t_+/y})/(a_{\text{Red}}(\text{An}^{x-})^{t_-/x}) \quad (2)$$

Since the solution pH is 12.7, exchangeable ions in the electrolyte are Na<sup>+</sup>, S<sup>2-</sup> and OH<sup>-</sup>. When the concentration of Na<sub>2</sub>S in the electrolyte was increased, the redox potential evaluated as the potential giving 50% absorbance change shifted by  $-48$  mV decade<sup>-1</sup>. Therefore, the possibility of Na<sup>+</sup> exchange was excluded by eq. 2. The pH value also increased with the Na<sub>2</sub>S concentration, and the dependence of the redox



**Fig. 5** Schematic illustration of fast NIR electrochromism of CuS nanoplates.

potential on pH was  $-68$  mV pH<sup>-1</sup>. When the pH value was changed by using NaOH at a constant Na<sub>2</sub>S concentration of 0.1 M, the potential change was  $-57$  mV pH<sup>-1</sup>. We therefore conclude that almost selective exchange of OH<sup>-</sup> accompanies the redox processes for charge compensation.

The reduction process in the first potential scanning is ascribed to reduction of CuS to Cu<sub>2</sub>S accompanied by ejection of S<sup>2-</sup>. Actually, Cu<sub>2</sub>S is known to exhibit no LSPR.<sup>25</sup> In the following redox cycles, OH<sup>-</sup> is exchanged for the charge compensation as described above. Since OH<sup>-</sup> is a rather bulky ion, it is likely that its exchange occurs only in the surface region of the CuS nanoplates in the present potential range (further discussed below). It has been reported that CuS has high electric conductivity based on hole transport,<sup>29,30,35</sup> whereas Cu<sub>2</sub>S is an insulator.<sup>36</sup> It is reasonable that a CuS nanoplate exhibits LSPR even if the conductive area is only in the surface region, because LSPR is based on the surface carrier oscillation. In fact, it is well known that nanoshells exhibit LSPR.<sup>37</sup>

We increased the amount of CuS nanoplates on the electrode by 11.8 times (Fig. S2b) and obtained transmittance spectra at different potentials between  $-1.0$  and  $-0.6$  V, at which the CuS nanoplates were perfectly reduced and re-oxidized, respectively (Fig. 4a). Here we used deuterated water for preparation of the electrolyte in order to observe NIR spectra clearly, although essentially identical behavior was observed in an aqueous solution with non-deuterated water. The spectra were obtained in reference to those of a bare ITO electrode at the same potentials, so that the slightly negative absorbance could be obtained because of insignificantly different ITO thickness. Absorbance of the nanoplate layer at  $\sim 1300$  nm was changed by  $\sim 0.27$  as a result of reductive disappearance and oxidative reappearance of LSPR. On the other hand, the absorbance changes in the visible range were virtually negligible (Fig. 4a). Actually, the electrode at  $-1.0$  V looked almost the same as that at  $-0.6$  V as shown in Fig. 4a (insets). The colour of the nanoplates must be according to their bandgap, and those of CuS and Cu<sub>2</sub>S are different (2.2<sup>38</sup> and 1.2<sup>39</sup> eV, respectively). These facts also support that the redox reactions take place only in the surface region.

Thus we conclude that the CuS nanoplates can be applied to an electrochromic device that regulates its transmittance exclusively in the NIR range. A previously reported NIR electrochromic device is based on electrostatic charging and



discharging of ITO NPs, so that it exhibits gradual absorption change in a wide potential range (2.5 V).<sup>22,23</sup> In contrast, the present device with CuS nanoplates, which exhibits NIR absorbance changes on the basis of redox reactions in a narrow potential range (0.4 V), operates even in an aqueous electrolyte. The narrow potential range is also advantageous for low energy consumption. The present redox reaction allows complete disappearance and reappearance of LSPR, because redox reactions allow complete but reversible removal of charge carriers. Here we employed an ITO-coated glass plate as an electrode and no significant absorbance change was observed for the ITO electrode without CuS nanoplates in the potential range examined.

The amount of the CuS nanoplates on an ITO electrode was increased by a factor of 19.0 in comparison with that in Fig. 3 and potential of  $-1.0$  and  $-0.6$  V were applied alternately for 90 s each. Figure 4b shows the transmittance changes monitored at 1300 nm. Transmittance was changed between  $\sim 80$  and  $\sim 30\%$  reversibly with coloration efficiency of  $30\text{--}40\text{ cm}^2\text{ C}^{-1}$ . The transmittance change reached 90% of the maximum change in 5.3 s and 2.3 s after the alteration of voltage in the oxidation and reduction process, respectively (Fig. S3). The response is very fast considering that switching of the practically used electrochromic devices in the visible range takes several tens of seconds. The fast responses may be explained in terms of the thin nanoplate structure and the superficial redox reactions, which allow facilitated exchange of electrons and ions, in addition to fast transportation of  $\text{OH}^-$  in an aqueous solution (Fig. 5). The transmittance change can be controlled by changing the amount of the nanoplates on the electrode (Fig. S4).

In summary, we achieved fast and reversible control of LSPR properties of compound nanoparticles through electrochemical redox reactions. We used CuS nanoplates and applied their electrochemical tunability to fast-switching NIR electrochromic devices. Further optimization of the reaction conditions and the cell structures would lead to electrochromic devices with higher durability, faster response and greater dynamic range.

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