Communications

The Surface Nitrate Effect on the Photochromism of Nanocrystalline Hexagonal WO₃ Prepared by Acid Precipitation Method

Jun Young Kwak[†,‡], Young Hee Jung[†,‡], and Yeong Il Kim[†,*]

[†]*Department of Chemistry, Pukyong National University, Busan 48513, Korea.*
[*]*E-mail: ykim@pknu.ac.kr*
[‡]*Research Laboratory, Adchro Inc. Busan 48547, Korea.*
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Photochromism of WO_3 and MoO_3 has been studied for several decades since Deb's report.[1,3] Photochromism is practically a very useful property, if it is reversible, for solar light modulation such as smart windows in energy-saving building.[2] While the electrochromic colorization and bleaching of WO_3 is quite reversible, the photochromic bleaching of WO_3 is so sluggish compared to colorization. This makes the application of WO_3 to the practical photochromic devices not to be feasible. The photochromic (PC) mechanism of WO_3 has been explained in a few different ways. The early explanation was usually done by color center model.[3] In this model oxygen deficient sites play a role of PC colorization. The photogenerated valence band electrons are trapped in these defect sites to form F-like centers. The trapped electrons can absorb photon to develop color. This model, a purely electronic mechanism, has been questioned from several perspectives: there has been no conclusive evidence for the existence of the F band.[4] The very intense coloration in some films is unlikely to be due to a limited number of oxygen defect sites. As the temperature decreases, the PC sensitivity of amorphous films decreases, and the reversibility of photochromism after heat treatment under oxygen cannot be explained. In the small polaron model,[5] photogenerated electrons trapped at lattice defect sites polarize the surrounding lattice, forming small polarons. These polarons absorb photons and hop between adjacent non-equivalent sites, resulting in coloration. It is not clearly revealed that the photogenerated electron actually distorts the lattice and forms a bound polaron. The more widely accepted theory is the intervalence charge transfer (IVCT) model after double charge injection.[6] The bandgap excitation generates electrons and holes in conduction and valence bands, respectively. The holes oxidize the surface absorbed H_2O to produce protons. the electrons are localized in the form of W^{+5} and the protons are inserted into the lattice to compensate charges and hydrogen tungsten bronze (H_xWO_3) is formed. The colorization by visible light absorption is explained by the electron transfer between W^{5+} and adjacent W^{6+} ions (IVCT) in the bronze. IVCT colorization is also doubted in that W^{5+} and W^{6+} sites must be nonequivalent in order to be energetically different and no colorization in WO_3-x (x<0.3) cannot be explained.[7] In addition, for double charge injection there must be an oxidizable cation source like H_2O on surface. This mechanism can be very appropriate to explain the electrochromism of WO_3 because the insertion of cation such as lithium ion from electrolyte solution is easily achieved by an applied electrical field.[8]

Recently we have comparatively studied the photochromism of nanocrystalline WO_3 powders with several crystallite sizes and crystal structures prepared by acid precipitation from paratungstate.[9] In the study the PC effect of nanocrystalline hexagonal WO_3 powders apparently depended on crystallite size rather than crystal structure. The smaller crystallite, the better PC efficiency. But the significantly large difference of the PC effect between the smallest one without thermal treatment and slightly larger one with thermal treatment in air could not be attributed only to surface area difference. The thermal treatment in air, whether it changes crystal structure or not, always decreased the photochromic effect. We also showed that the surface-adsorbed water does not significantly contribute to the PC effect. Therefore, we have come to two conclusions: first, the oxygen deficiency on the surface plays a crucial role in the photochromism of WO_3 because heat treatment in air reduces surface oxygen defect sites. Secondly, the proton injection proposed by the double charge injection model may not be essential since the role of surface adsorbed water in the PC effect was not critical.

In this communication, we would like to briefly report a

very interesting finding on the effect of surface nitrate ion on the photochromism of WO_3 and show that this result supports the critical role of surface defect sites on the oxide's PC behavior and also show that surface oxygen release during colorization may occurs instead of proton injection for charge compensation.

The nanocrystalline WO_3 powders were prepared by the hydrolysis reaction of ammonium paratungstate $((NH_4)_{10}W_{12}O_{41} \cdot 5H_2O)$ in acidic aqueous medium as previously described.[9,10] The formation of WO_3 is done by the simple hydrolysis reaction: $W_{12}O_{41}^{-10}(aq) + 10H^+(aq) \rightarrow 12WO_3(s) + 5H_2O(l)$. The reaction needs an elevated temperature because the hydrolysis of paratungstate barely occurred at ambient temperature. Two different types of acids, i.e., HNO_3 and HCl were used to cross-check the anion effect. The precipitated WO_3 was filtered, washed thoroughly with copious amounts of pure water, and dried at 80 ℃ for 18 h.

The other synthetic conditions such as concentration and temperature were all identical to the previous study.[9]
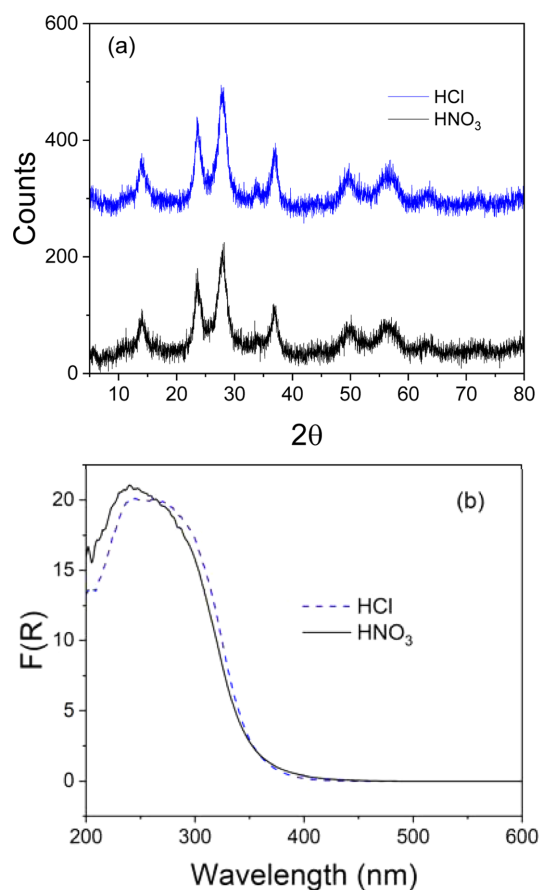
**Figure 1.** (a) XRD patterns and (b) UV-Vis diffuse reflectance spectra of WO_3 samples prepared with HNO_3 and HCl. F(R) is Kubelka-Munk function.

Fig. 1(a) shows XRD patterns of WO_3 prepared with HNO_3 and HCl. Both the patterns are almost same and well matched to the hexagonal crystal structure (JCPDS 33-1387). The crystallite sizes calculated from Scherrer equation were same, approximately 4 nm, for both the samples from HNO_3 and HCl.

UV-Vis diffuse reflectance spectra of both the samples shown in *Fig.* 1(b) showed the similar absorption edges and the bandgap energies (E_g) of WO_3 estimated by Tauc plot[11] were also similar as about 3.3-3.4 eV. The morphologies observed by scanning electron microscopy, not shown here, were not also different. Therefore, all the characteristics of both WO_3 samples prepared with HNO_3 and HCl were not different. That means that if other synthetic conditions are the same, the counter anion has no effect on the structural and morphological characteristics of WO_3 at all.
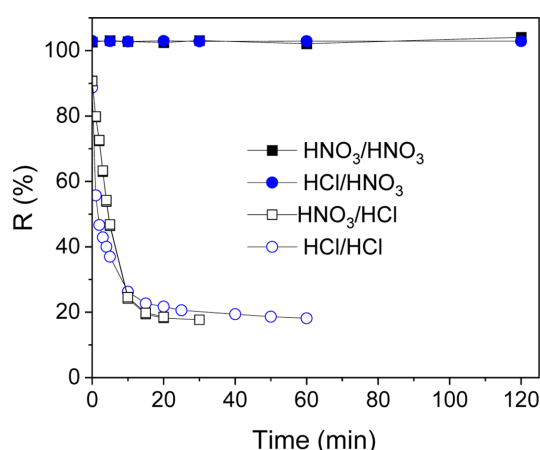
The surface of metal oxide such as WO_3 is positively charged in aqueous solution at pH below the point of zero charge (pzc) and some anions can be adsorbed on the surface. Since the pzc of WO_3 was known to be 2.5 or less,[12] both the samples of WO_3 prepared by the two acids were resuspended in 0.1 M HNO_3 and HCl solution and filtered and dried. In this way, nitrate and chloride ions could be adsorbed on the surface of WO_3.[13] We have shown that the powder of nanocrystalline hexagonal WO_3 prepared by the same method with nitric acid showed an intense PC colorization by ultra violet light in the previous study.[9] When this sample was treated with nitric acid as mentioned above, the PC color change was completely disappeared as shown in *Fig.* 2(a), while the one treated with HCl maintained the PC colorization. In order to confirm this surface-anion effect, the samples prepared with HCl were also checked. *Fig.* 2(b) shows the results. It is exactly the same as the one prepared with HNO_3. Therefore, whether it is prepared with HNO_3 or HCl, if it is well washed, its photochromism is almost same. But if it is subsequently treated with HNO_3 or HCl, the chloride ion has no effect, while nitrate ion completely eliminates the photochromism of WO_3. As far as we know, this nitrate effect on the photochromism of WO_3 is for the first time reported here.

Considering the standard reduction potentials of chloride ($E^o = -1.36$) and nitrate ($E^o = +0.934$) ions,[14] chloride ion can be served as electron donor, while nitrate ion can be done as electron acceptor. In this case chloride can enhance the photochromism of WO_3 by serving hole scavenger and blocking the recombination path, while nitrate can block the photochromism by removing photoexcited electrons as electron scavenger. However, our results seem
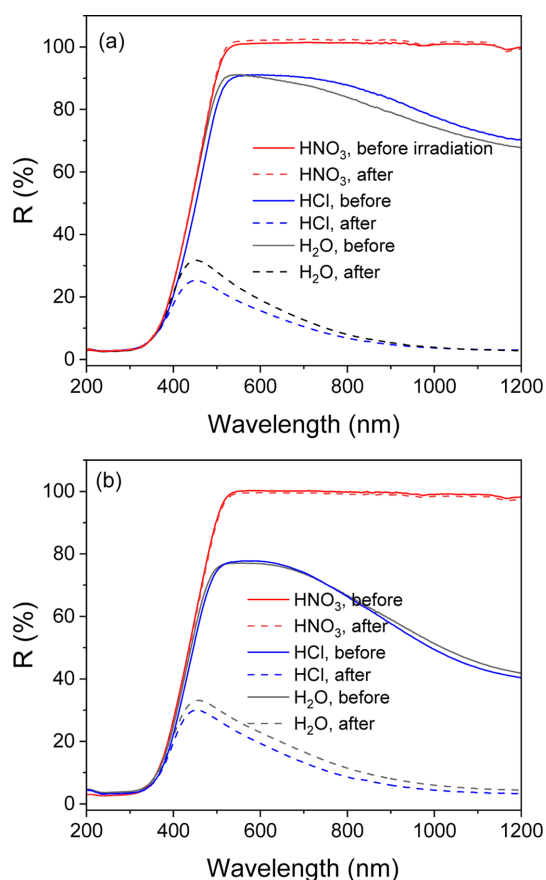
Figure 2. Photochromic diffuse reflectance spectral changes of WO₃ samples prepared with (a) HNO₃ and (b) HCl and treated with HCl, HNO₃ and H₂O (untreated). UV irradiation (Xe-arc lamp, 300 mW/cm²) was done for 30 min. (Black, blue and red lines represent the untreated sample and the samples treated with HCl and HNO₃, respectively. The solid and dashed lines represent before and after irradiation, respectively.)

Figure 3. Time dependence of diffuse reflectance changes at 555 nm for the samples prepared with HNO₃ and HCl after UV irradiation (HNO₃/HCl in legend means that the sample was prepared with HNO₃ and treated with HCl.)

not to be the case. First, chloride did not enhance the PC effect noticeably. If chloride and nitrate serve as hole and electron scavengers, respectively, since they can be served only sacrificially and their amounts on surface are limited, the effect cannot be persisted under continuous illumination. When the samples treated with HNO₃ were tested for more than two hours, they never showed photochromic color changes, while the samples treated with HCl were colorized and saturated in about 30 min as shown in *Fig.* 3. This means that nitrate ion does not act as an electron acceptor. Despite the nitrate ion on surface do not act as electron acceptor, the fact that it makes the PC effect of the oxide completely disappear indicates that the photoexcited electrons in conduction band could not remain somewhere due to the surface nitrate ions and are immediately recombined with the holes created in valence band. This also means that the nitrate ions remove the surface trap sites

where the photoexcited electrons can be abided. Therefore, the PC effect of WO₃ must be critically related to the surface electron trap sites which is usually considered to be defect sites like oxygen deficient sites.

IVCT-double charge injection model for the photochromism of WO₃ does not need electron trap sites because photogenerated holes are immediately removed by electron donors and electrons in the form of W⁵⁺ are stabilized by simultaneous injection of cations from the oxidized donors. Our results do not support this model at all. On the other hand, the color center model and small polaron model start with electron trap sites although the subsequent light absorption to lead colorization is interpreted differently. Therefore, our result appears to provide more support for these two models, even apart from the subsequent light absorption process to develop color. However, the very slow bleaching process and the fact that bleaching requires at least expose to oxygen[15] are judged to be insufficient to explain the photochromism of WO₃ by a mechanism solely based on surface defect sites, that is deep trap sites, since the electrons in trap sites must be eventually recombined with the generated holes unless other charge compensation processes occur. *Fig.* 4 shows the time dependence of coloring and bleaching processes of our untreated WO₃ sample in air. The average bleaching rate is several thousands of times slower than the coloring rate. The slow bleaching, we believe, may be based on the charge compensation arising from the removal of surface oxygen during UV irradiation rather than proton injection as claimed in the double charge injection model. The surface oxygens near defect sites must be chemically unstable due to incomplete bond-
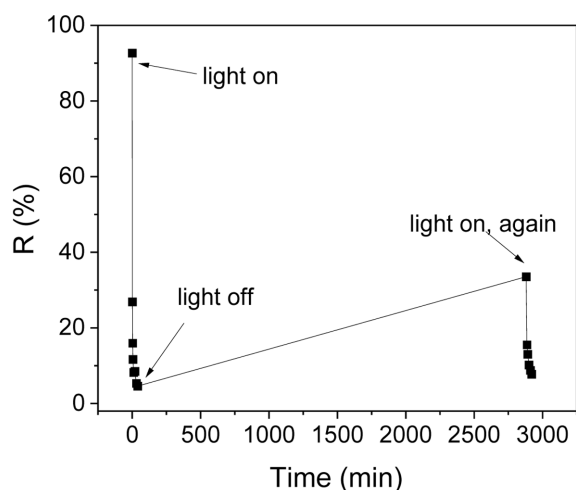
Figure 4. Time dependence of diffuse reflectance changes at 555 nm for the samples prepared with HNO_3 and untreated under UV light irradiation and dark.

ing. As photoexcitation drives electrons from oxygen in valence band to tungsten in conduction band, the oxidized surface oxygen may escape and the surface oxygen deficiency increases and more nonstoichiometric tungsten oxide ($W^{VI}_{1-2x}W^V_{2x}O_{3-x}$, $x < 3$) that is much more stable than the charge separated state in deep traps may form. Since the samples tested here have hexagonal crystal structure that is metastable and very small crystallite size (~4 nm), it may have more the surface defects and more unstable surface oxygen. Therefore, the photoexcitation can give rise to easy oxygen escape from the surface.

In order to test this assumption, we performed semi-quantitative analyses of the ratio of O/W in the untreated WO_3 sample before and after UV-irradiation using scanning electron microscopy/energy dispersive spectrometer (SEM-EDS). When the measurements of EDS were done in 2-3 h after UV-irradiation for 30 min, the ratio of O/W in the colored sample (after irradiation) was consistently lower than that of uncolored sample (before irradiation) by roughly 10% from three repeated measurements. Although the reliability of the analysis is not good due to the low sensitivity to oxygen in EDS, the decrease of the ratio after irradiation was clearly observed. This result definitely explains why oxygen is needed for bleaching.

In summary, we report for the first time that the surface nitrate ions completely eliminated the PC effect of nanocrystalline hexagonal WO_3, while the chloride ions have no effect. The nitrate ions seem to occupy or eliminate all the surface defect sites and the photoexcited electrons cannot be trapped, preventing PC effect from occurring.

This dramatic effect of nitrate ions further supports the critical role of surface defect sites on the PC effect of WO_3, as demonstrated in our previous study. In addition, it is assumed that the surface oxygen radicals, which are hole sites created during photoexcitation, are released to give the charge compensation and the long-lived colored state maintains. Therefore, this result is opposed to double charge injection model that is widely cited. Currently, we are systematically investigating the effect of several surface anions on the PC properties of WO_3 and MoO_3 with different structures and sizes, with the aim of clarifying the mechanism of photochromism of transition metal oxides semiconductors.

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