Multiple modification of $CuW_xMo_{1-x}O_4$ photoanode for photoelectrochemical water oxidation

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Abstract: Photoelectrochemical cell has been issued because it can convert unlimited solar energy to produce hydrogen from water. $CuWO_4$ is interesting material, low bandgap around 2.3eV. Although $CuWO_4$ retains advantages related to visible light absorption, notorious drawbacks so called poor bulk and surface charge transportation still exist. Suitable treatments have been studied for solving these matters, but their effects were still insignificant. Molybdenum can be readily substituted to tungsten site owing to its analogous radius thereby electronic structure can be changed. In this work, several treatments such as hydrogen treatment, co-catalyst attachment were adjusted to CuWxMo1-xO_4 photoanode for the better reaction.
Keywords: water splitting, hydrogen treatment, co-catalyst.

1. Introduction (11-point boldface)

To solve energy crisis-related problems, studies of clean and sustainable energies, in particular solar energy, have been explosively researched from several decades ago thanks to its unlimited amounts as well as the nontoxicity for utilization.[1] $CuWO_4$ (CWO) is one of the approaches as a purpose to utilize more visible light rather than WO_3.[2] Even though a number of researchers have tried to improve bulk and surface treatment of this materials, CWO still retains improvement points we have to resolve.[3] James C. Hill et al. reported n-type $CuW_xMo_{1-x}O_4$ (CWMO) electrodes which was attained more enhanced visible light absorption.[4] However, not only bulk but also surface properties have to be improved. Hydrogen treatment can generate oxygen vacancies which play key roles to generate much charge carrier densities thereby bulk properties can be improved.[5] In addition, sluggish surface kinetics can be relieved by the aid of co-catalysts.[6] In this presentation, multiple modification including hydrogen treatment and Co-pi deposition was adjusted to CWMO for improving bulk and surface properties.

2. Experimental

CWMO thin film was fabricated on conductive FTO glass as notated in **Figure 1**. Spin coating method was used for material synthesis. Furthermore, hydrogen treatment and co-catalyst deposition was carried out for main modification.

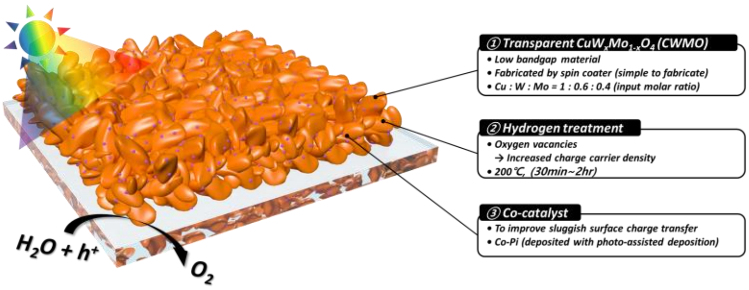

Figure 1 The Scheme of CWMO photoanode and experimental information

3. Results and discussion

Even though there are no other specific changes between CWMO and hydrogen treated CWMO (H:CWMO) in most characterization part (such as XRD, UV-vis, SEM, TEM), main difference was observed by x-ray photoelectron spectroscopy (XPS) as shown in **Figure 2**. All peaks of each elements were matched with their own binding energy positions. However, shoulder-like peak which is accordance to Cu^+

take place after hydrogen treatment. In **Table 1**, O_V (oxygen vacancy related peak) of H:CWMO was increased comparing to the XPS result of CWMO O element. Those Cu+ as well as oxygen vacancies would contribute to transport charge carriers inside the bulk.

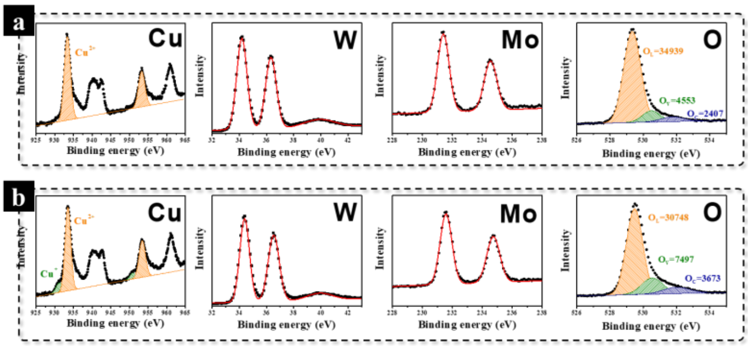

Figure 2 XPS analysis of (a) CWMO and (b) H:CWMO

	Relative ratio of O 1s peak areas		
Samples	Lattice(O_L)	Vacancy(O_V)	Chemisorb(O_C)
CWMO	0.834	0.109	0.057
H:CWMO	0.734	0.179	0.087

Table 1 Peak area ratio of oxygen elements deconvoluted from XPS

As you can see in **Figure 3**, photoactivity (here, photocurrent) was gradually enhanced as we modified with hydrogen gas and co-catalysts. In particular, the main effect of hydrogen treatment was the improvement of bulk property according to the comparison of photocurrent densities between CWMO and H:CWMO measured under hydrogen peroxide (sacrificial reagent) because we can assume that all surface holes are consumed and be regarded as perfect surface reaction.

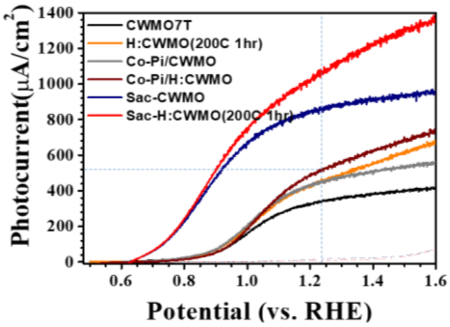

Figure 3 Photocurrent density of bare CWMO (black), H:CWMO (orange), Co-Pi/CWMO (gray), Co-Pi/H:CWMO (brown) under KPi electrolyte (pH 7) and Sac-CWMO (blue), Sac-H:CWMO (red) under sacrificial reagent.

4. Conclusions

Low band gap material, CWMO, was well synthesized and modified by not only hydrogen treatment but also co-catalyst deposition. Hydrogen treatment did not change any kind of physical properties like morphology, crystal structure, and absorbance. However, oxygen vacancies were occurred, and it afford photoanode contains much charge carrier density which induces to improve bulk properties. Although the effect of co-catalyst seemed to be slight, synergetic effect caused by both of successive modifications improved this anode material.

References

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