Fabrication and characterization of a p-type Cu3Nb2O8 photocathode toward photoelectrochemical reduction of carbon dioxide

Fabrication and characterization of new p-type $Cu_3Nb_2O_8$ photocathode for photoelectrochemical reduction of carbon dioxide

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Supporting information

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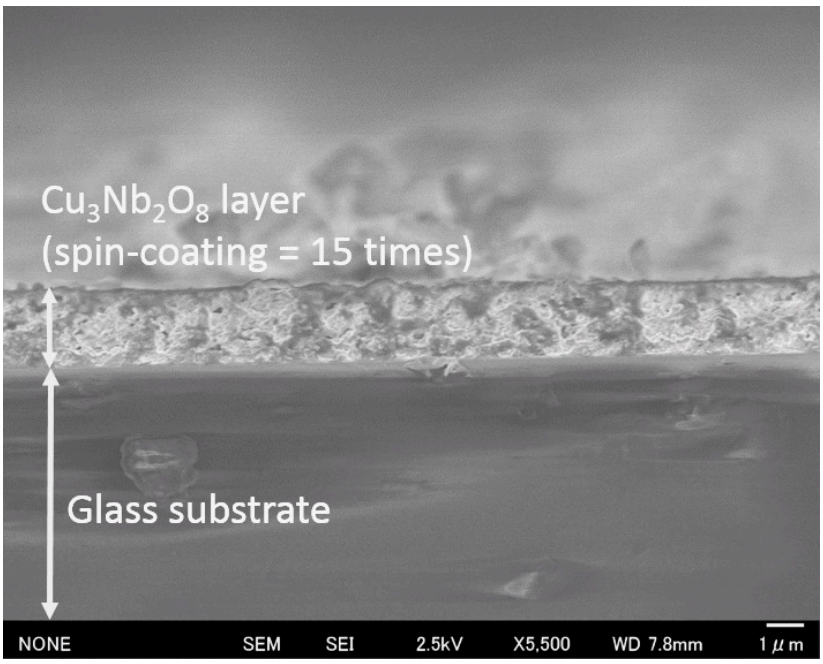

Figure S1. The cross-section SEM image of p-type $Cu_3Nb_2O_8$ polycrystalline on the glass substrate, which was calcined at 873 K in air. To estimate the thickness of $Cu_3Nb_2O_8$ polycrystalline layer, we fabricated the $Cu_3Nb_2O_8$ polycrystalline on the glass substrate with 15 time spin-coat, because 1 time spin-coat $Cu_3Nb_2O_8$ polycrystalline on the Ti substrate was too thin to evaluate its thickness. It should be noted that spin-coating condition to fabricate the $Cu_3Nb_2O_8$ polycrystalline on the glass substrate was same as that on the Ti substrate. As shown this figure, the thickness of 15 time spin-coat $Cu_3Nb_2O_8$ polycrystalline layer was evaluated at 2.18 μm. Therefore, in the case of 1 time spin-coat, the thickness of $Cu_3Nb_2O_8$ polycrystalline was estimated about 145 nm.

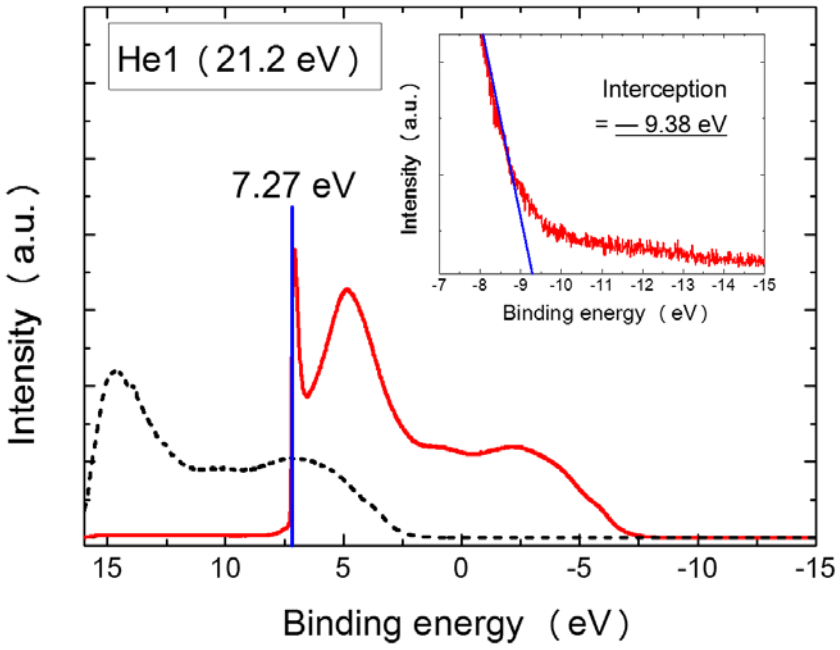

Figure S2. The ultraviolet photoelectron spectroscopy (UPS) spectra of p-type $Cu_3Nb_2O_8$, in which dotted line spectrum was obtained at non-electrical bias potential of 0 V, and solid line spectrum was obtained with applying electrical bias potential at -9.5 V. The figure shows the scale of binding energy with the Fermi level of Au set at 0 V. The work functions of p-type $Cu_3Nb_2O_8$ are estimated to be 4.55 eV. Based on above UPS results, the valence band and conduction band potential of $Cu_3Nb_2O_8$ is considered to be approximately +0.58 V and –2.09 V versus normal hydrogen electrode (NHE) at pH= 7, respectively.

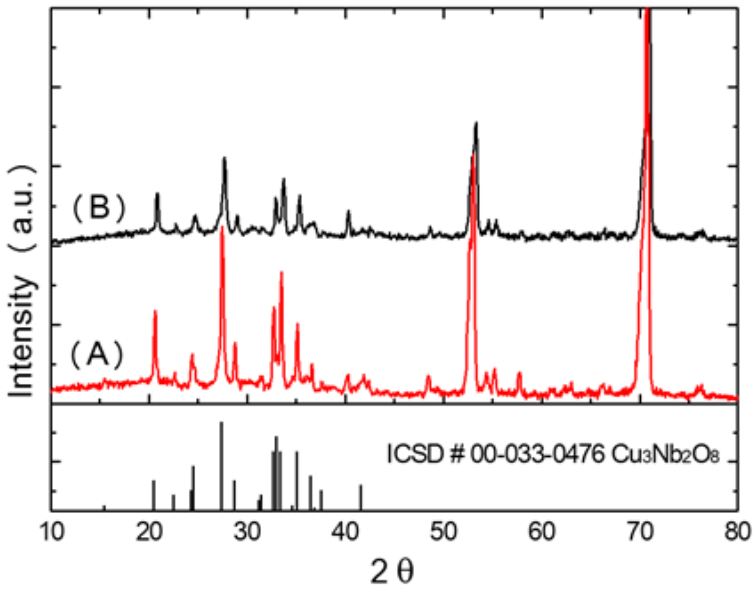

Figure S3. The XRD pattern of p-type $Cu_3Nb_2O_8$ photocathode, in which (A) is as fabricated at 873 K in air, and (B) is after the chronoamperometry measurement. It should be noted that chronoamperometry measurement was carried out with applied bias potential at –0.2 V versus Ag/AgCl for 20 min in CO_2 bubbled aqueous $NaHCO_3$ solution (pH = 7.3).

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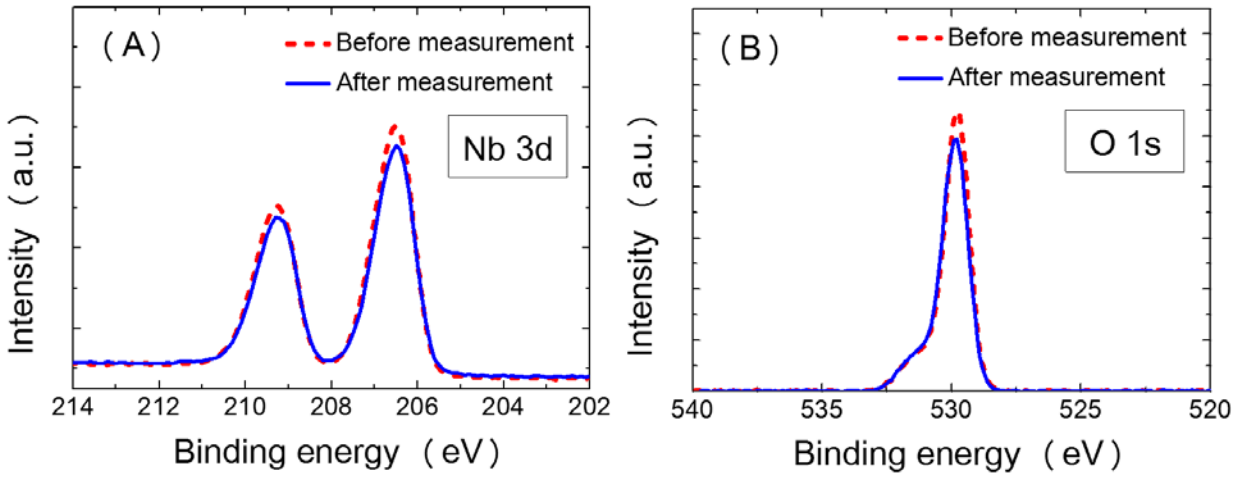

Figure S4. XPS spectra of (A) Nb *3d* and (B) O *1s* of p-type $Cu_3Nb_2O_8$ photocathode, which obtained before and after chronoamperometry measurement.

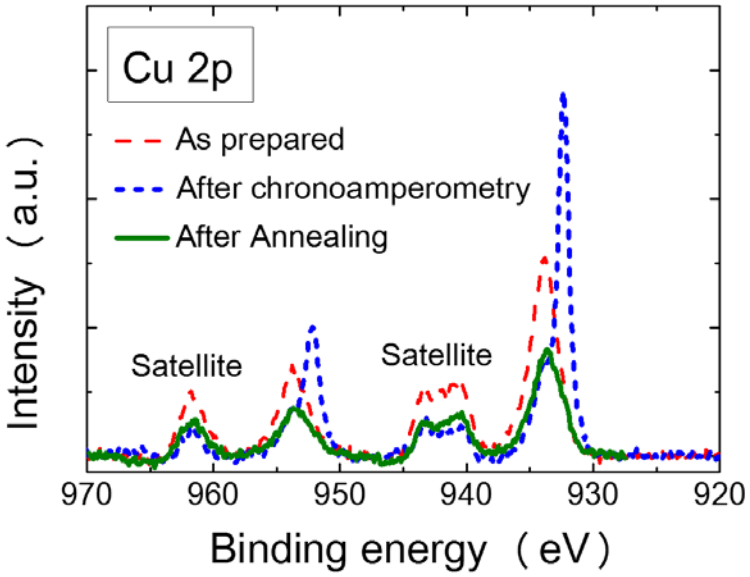

Figure S5. XPS spectra of Cu *2p* of p-type $Cu_3Nb_2O_8$ photocathode, which obtained as prepared (dashed line) and after chronoamperometry measurement at -0.2 V versus Ag/AgCl in CO_2 bubbled aqueous $NaHCO_3$ solution (dotted line). This indicating that Cu (II) species in p-type $Cu_3Nb_2O_8$ photocathode was reduced to Cu (I) and/or Cu (0) species by the chronoamperometry measurement. After that measurement, p-type $Cu_3Nb_2O_8$ photocathode was thermal annealed at 873 K for 15 minutes and resulting XPS spectra of Cu *2p* are shown in Fig.S5 (solid line). The XPS spectra revealed that Cu (I) and/or Cu (0) species was oxidized to Cu (II) species by thermal annealing.