## **Supporting Information**

## Photocatalytic Carbon Dioxide Reduction by Copper Oxide Nanocluster-Grafted Niobate Nanosheets

Ge Yin, <sup>†,</sup> Masami Nishikawa, <sup>‡</sup> Yoshio Nosaka, <sup>‡</sup> Srinivasan Nagarajan, <sup>†,</sup> Daiki Atarashi, <sup>†,</sup> Etsuo Sakai, <sup>†,</sup> Masahiro Miyauchi <sup>†,§,\*</sup>

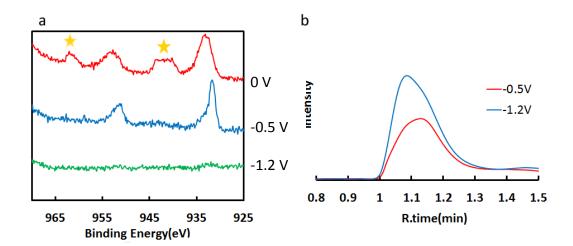
† Department of Metallurgy and Ceramics Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

‡ Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1, Kamitomioka-machi, Nagaoka, Niigata 940-2188, Japan

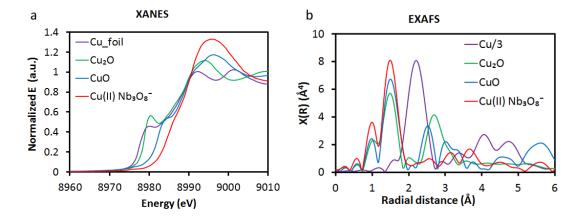
§ Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

Email: mmiyauchi@ceram.titech.ac.jp

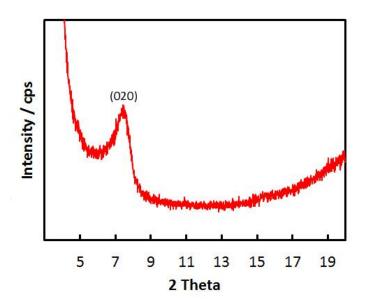
\*To whom correspondence should be addressed.



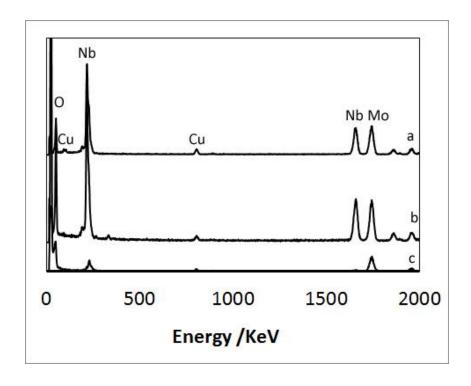
**Figure S1.** (a) XPS spectra of Cu in copper oxide nanoclusters grafted Ti metal electrode after applied the bias-potential of 0 V, -0.5 V and -1.2 V(vs. Ag/AgCl) respectively. Shape-up satellites of Cu(II) are marked with yellow stars. The intensity was the integrated value. Measurement condition: 10 cycles, 3 repeats, one step = 0.15 eV, 40 ms. (b) the gas chromatograph of the headspace gas under bias-potential of -0.5 V and -1.2 V.



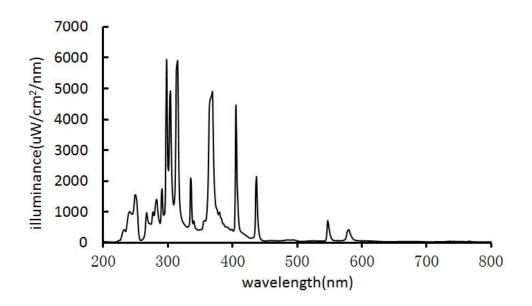
**Figure S2.** Cu K-edge XANES spectra (a) and EXAFS (b) of 0.5%wt copper oxide nanoclusters-grafted Nb<sub>3</sub>O<sub>8</sub> nanosheets. For comparison, the spectra of Cu metal,  $Cu_2O$  and CuO were also included.



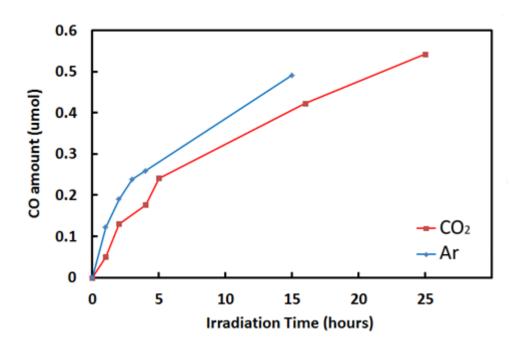
**Figure S3.** The X-ray diffraction pattern of the Nb<sub>3</sub>O<sub>8</sub> nanosheets thin film.



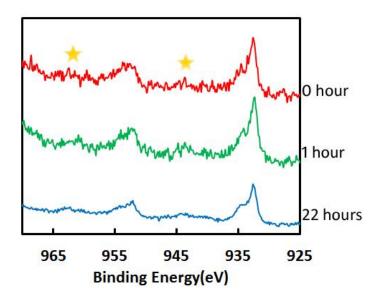
**Figure S4.** The energy dispersive X-ray spectroscopy (EDS) of 2.5% wt copper oxide nanoclusters-grafted Nb<sub>3</sub>O<sub>8</sub> nanosheets (a). For comparison, the spectroscopy of bare Nb<sub>3</sub>O<sub>8</sub> nanosheets (b) and bare sample stage (c).



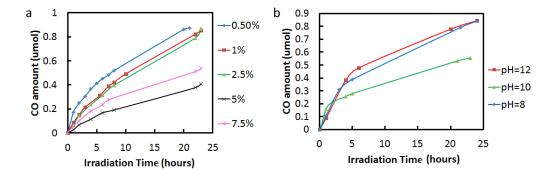
**Figure S5.** The spectrum of the Xe-Hg UV light lamp.



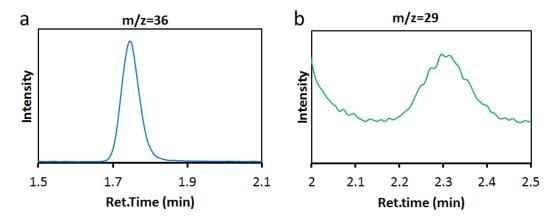
**Figure S6.** Photocatalytic  $CO_2$  reduction evaluation of  $Nb_3O_8$  nanosheets powders without any co-catalysts grafted.



**Figure S7.** XPS spectra of Cu in the 10 wt% copper oxide nanoclusters-grafted niobate nanosheets after the UV irradiation of 0 hour, 1 hour and 22 hours. Shape-up satellites of Cu(II) are marked with yellow stars. The intensity was the integrated value. Measurement condition: 10 cycles, 3 repeats, one step = 0.15 eV, 40 ms.



**Figure S8.** (a) The produced CO amount on terms of copper oxide nanoclusters loading amount. Each group used 900 mg photocatalysts respectively. (b) The produced CO amount on terms of electrolyte pH for 0.5%wt copper oxide nanoclusters grafted niobate nanosheets.



**Figure S9.** (a) The mass chromatography spectra of  $^{18}O_2$  (m/z=36) generated from UV-irradiated Nb<sub>3</sub>O<sub>8</sub> nanosheets grafted with 0.5 wt% copper oxide nanoclusters in 0.5 M KHCO<sub>3</sub>/ $H_2^{18}O$  solution purged with  $^{12}CO_2$ ; (b) the peak of  $^{13}CO$  (m/z=29) generated from UV-irradiated copper oxide nanocluster-grafted Nb<sub>3</sub>O<sub>8</sub> nanosheets in 0.01 M NaOH/ $H_2^{16}O$  solution purged with  $^{13}CO_2$ .