Electronic Supporting Information (ESI) for

Fabrication of a porous $ZnRh_2O_4$ photocathode for photoelectrochemical water splitting under visible light irradiation and significant effect of surface modification by ZnO necking treatment

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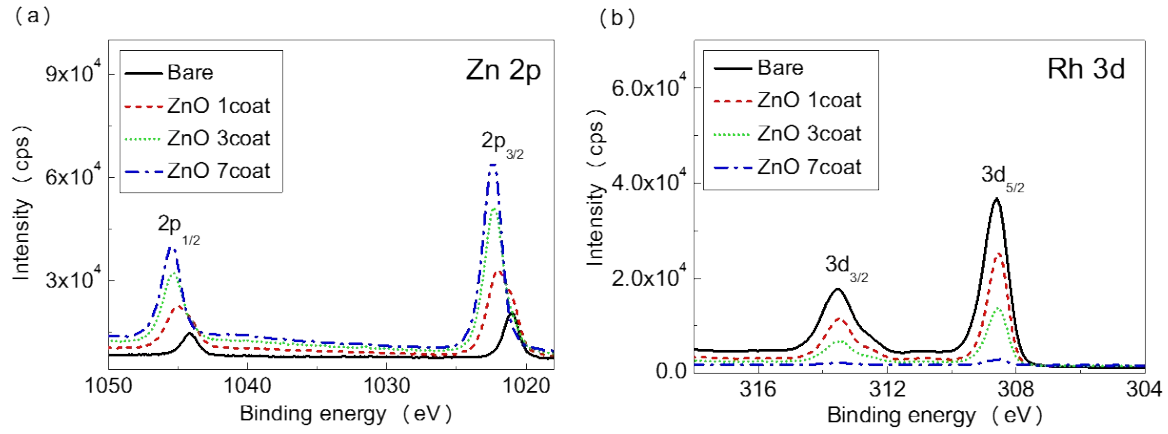

Figure S1. XPS spectra of bare $ZnRh_2O_4$ and $ZnO/ZnRh_2O_4$ electrode.

For the bare $ZnRh_2O_4$ (see **Fig. S1(a)**), major peaks at 1021.0 eV and 1044.1 eV were observed, which peaks were attributed to typical values of Zn $2p_{3/2}$ and $2p_{1/2}$ in $ZnRh_2O_4$, respectively. This our observation was similar to a previous report by Irie *et al.* (refer to *Journal of Materials Chemistry A*, 2016, **4**, 3061 – 3067). These Zn *2p* XPS intensities were increased with an increase in the number of drop−casts of ZnO precursor solution, implying that amount of Zn species was increased by necking treatment. It should be noted that peak shift (~ ca.1 eV) of the Zn *2p* XPS spectrum was observed after necking treatment; major peaks at 1022.4 eV and 1045.5 eV were newly appeared, and these peaks were attributed to typical values of Zn $2p_{3/2}$ and $2p_{1/2}$ in ZnO (refer to *Thin Solid Films* 2005, **491**, 153 – 160). In contrast, the Rh *3d* XPS intensities were decreased with an increase in the number of drop−casts. These results suggest that ZnO amount at $ZnO/ZnRh_2O_4$ surface is increased with an increase in the number of drop−casts, which leads to inhibit of X-ray excitation of $ZnRh_2O_4$, resulting decrease of Rh *3d* XPS intensity.

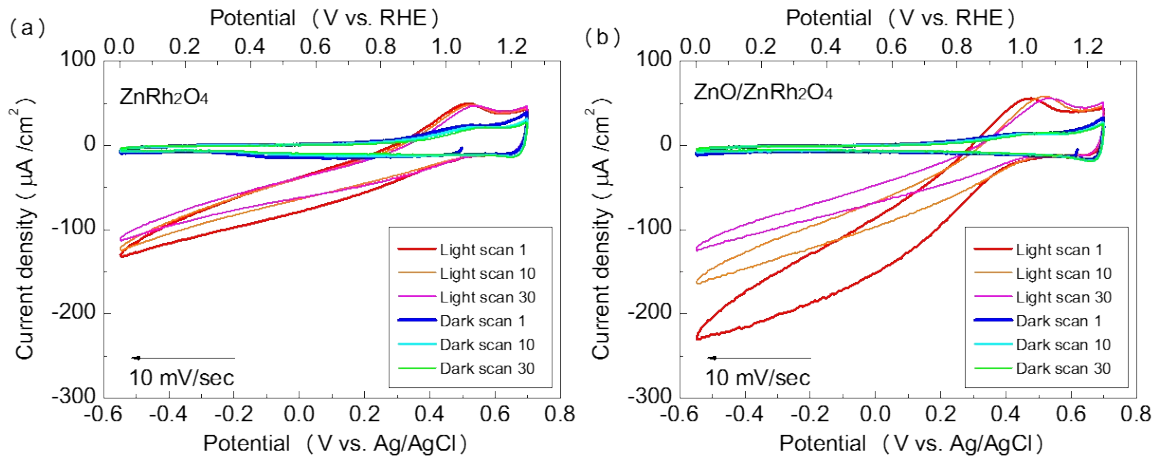

Figure S2. Cyclic voltammetry (CV) for bare and $ZnO/ZnRh_2O_4$ photocathodes.

The CV curves were measured for bare and $ZnO/ZnRh_2O_4$ photocathodes in Ar−purged 0.1 M Na_2SO_4 solution at potential sweep rate 10 mV/sec. Light source was used Xe-lamp equipped with L-42 cut off filter. The potential first to scan from rest potential to −0.6 V vs. Ag/AgCl at which the scan direction was reversed to +0.7 V vs. Ag/AgCl, and then scan back to the initial potential. It should be noted that the rest potential of bare and $ZnO/ZnRh_2O_4$ photocathodes were +0.50 V and +0.62 V vs. Ag/AgCl, respectively. As seen in this figure, the photocurrent response of bare $ZnRh_2O_4$ electrode was a relatively stable under PEC reaction. In contrast, the photocurrent of $ZnO/ZnRh_2O_4$ photocathode was gradually decreased with a number of cycles. This indicating that durability of $ZnO/ZnRh_2O_4$ photocathode is not good.

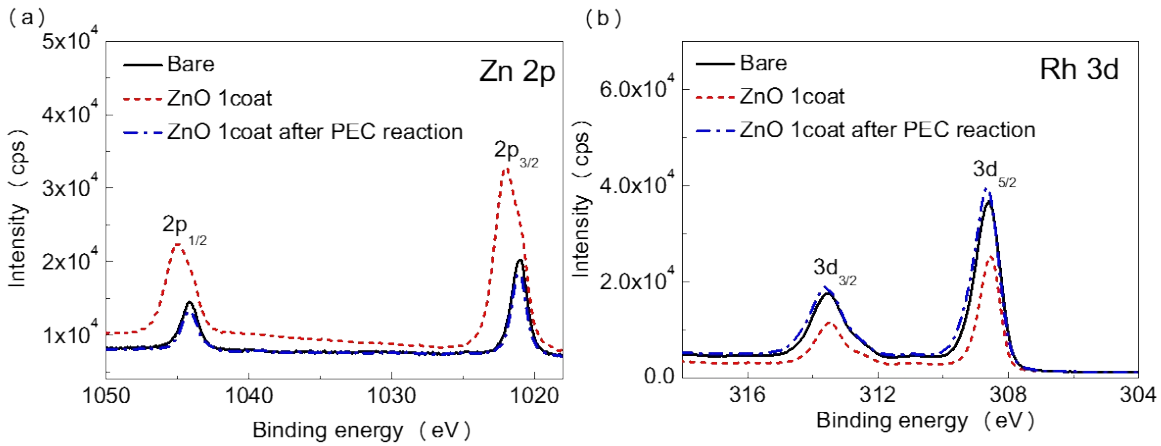

Figure S3. XPS spectra of $ZnO/ZnRh_2O_4$ electrode before and after PEC reaction.