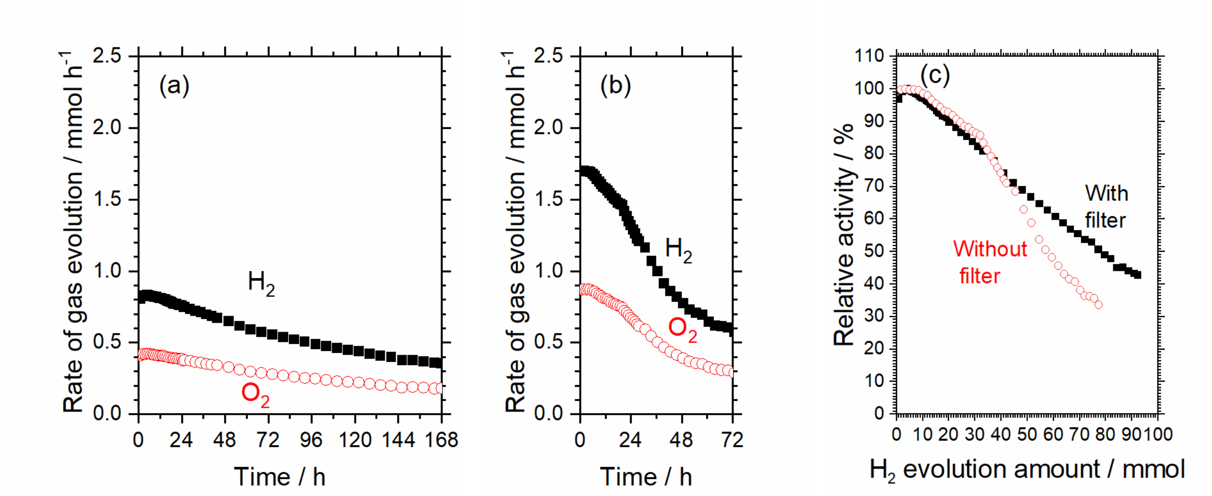

Figure S1. Time courses of water-splitting activity of $SrTiO_3$:Al loaded with $RhCrO_x$ (a) with and (b) without 50% transmission neutral density filter. (c) Relative activities as functions of H_2 evolution amount with and without filter in place. Reaction conditions: photocatalyst, 0.1 g; reaction solution, 100 mL distilled water; reaction temperature, 291 K; light source, 300 W Xe lamp (300 nm < λ < 500 nm).

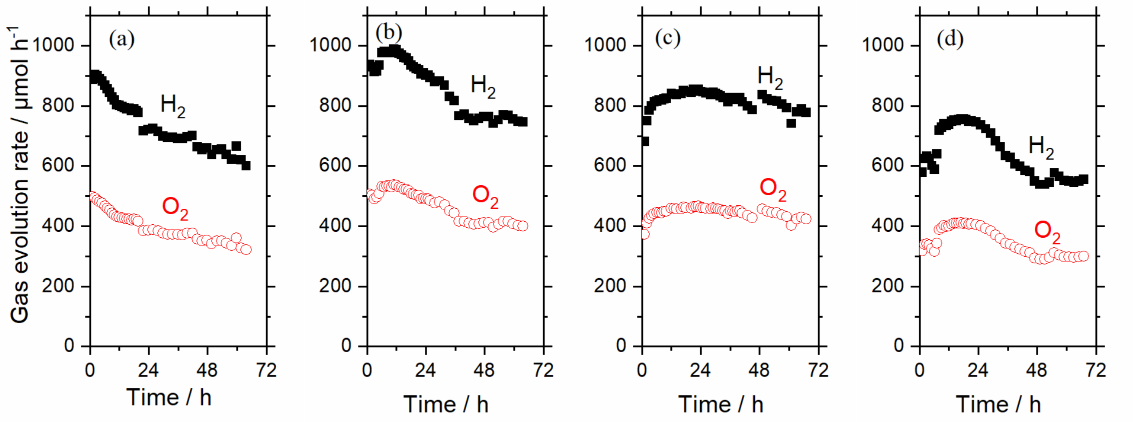

Figure S2. Time courses of water splitting activity of $RhCrO_x/SrTiO_3$:Al coloaded with Co species by *in situ* photodeposition at Co concentrations of (a) 0, (b) 0.1, (c) 0.3 and (d) 0.5 wt%. Reaction conditions: photocatalyst, 0.1 g; reaction solution, 100 mL distilled water; reaction temperature, 291 K; light source, 300 W Xe lamp (300 nm < λ < 500 nm).

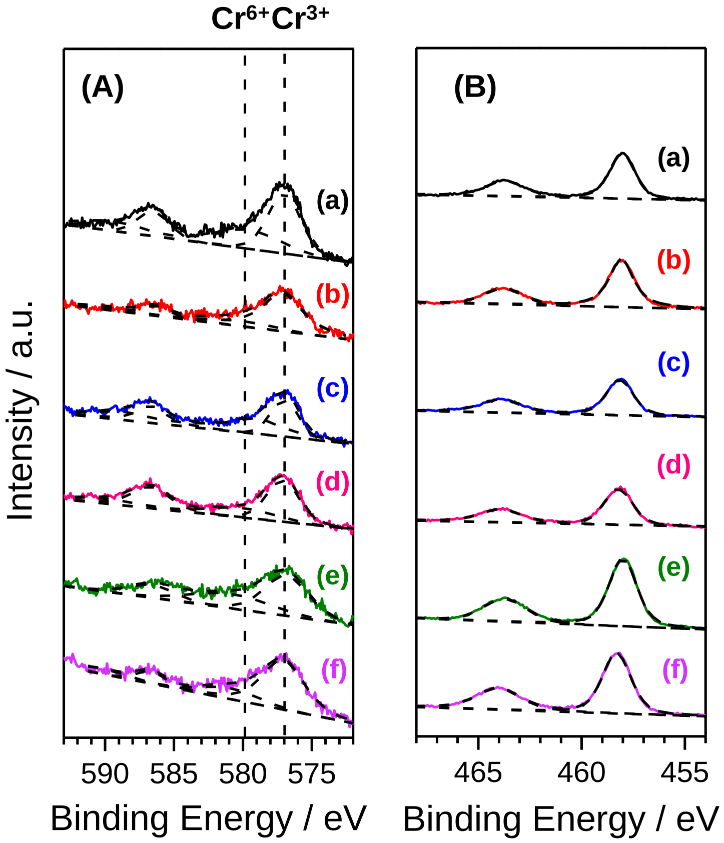

Figure S3. (A) Cr 2*p* and (B) Ti 2*p* XPS spectra for (a,b) $RhCrO_x/SrTiO_3$:Al, (c,d) $RhCrO_x/SrTiO_3$:Al coloaded with 0.3 wt% Co species, and (e,f) $RhCrO_x/SrTiO_3$:Al coloaded with 0.3 wt% Co species and modified with 0.3 wt% TiO_2 (a,c,e) before and (b,d,f) after water splitting reaction over one week time span under irradiation by high-pressure Hg lamp ($\lambda > 300$ nm). The data in (a) were acquired following a 1 h reaction and after the sample was collected to remove water-soluble Cr^{6+} species generated by calcination in air at 623 K.

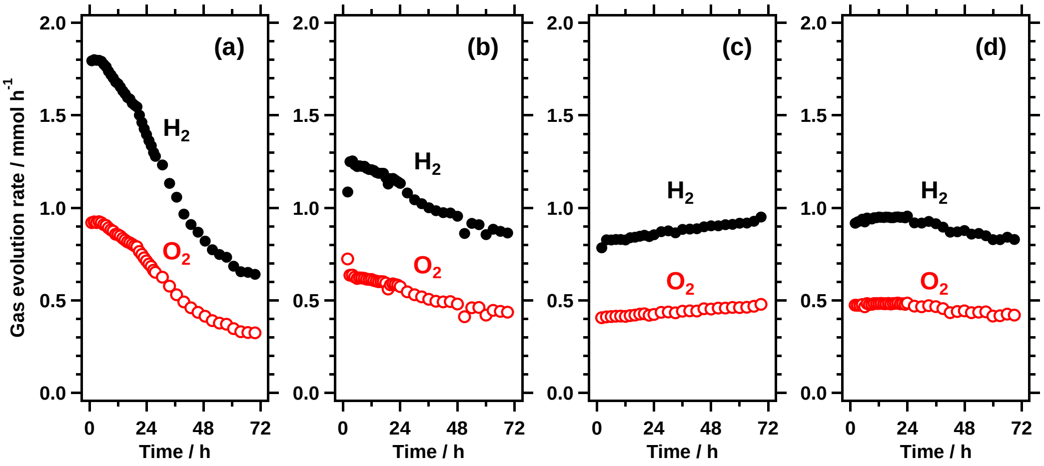

Figure S4. Time courses of water splitting activity of CoOOH/RhCrO$_x$/SrTiO$_3$:Al modified with TiO$_2$ by *in situ* photodeposition at TiO$_2$ amounts of (a) 0, (b) 0.1, (c) 0.3 and (d) 0.5 wt%. Reaction conditions: photocatalyst, 0.1 g; reaction solution, 100 mL distilled water; reaction temperature, 291 K; light source, 300 W Xe lamp (300 nm < λ < 500 nm).

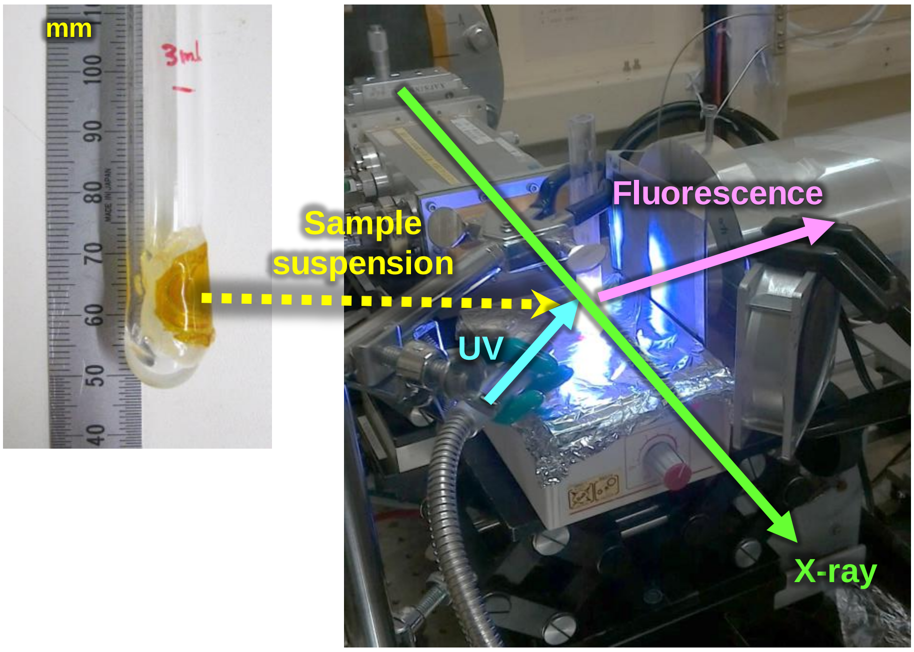

Figure S5. Experimental setup for operando XAFS spectroscopy of CoOOH/RhCrO$_x$/SrTiO$_3$:Al photocatalyst suspension.