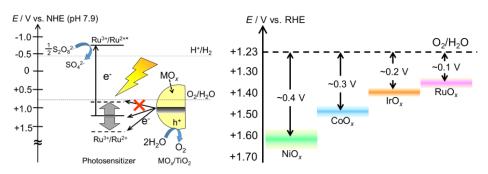
## Measurement of the pseudo overpotential for water oxidation by nano-sized heterogeneous metal oxide catalyst

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Metal oxide (MO<sub>x</sub>) nanoparticles loaded onto a semiconductor photocatalyst are known as water oxidation cocatalysts, which improve charge separation ability to enhance the photocatalytic activity.<sup>1</sup> It is considered that the water oxidation ability of  $MO_x$  – that is, pseudo-overpotential for water oxidation – is strongly related to electrochemical potential of electrons in the  $MO_x$ . However, the quantitative discussion of those potentials in heterogeneous  $MO_x$  nanoparticles has hardly been done due to the difficulty in directly estimating those potentials for highly dispersed nanoparticle catalysts on the semiconductor surface.

In this work, we have established the estimation method of electrochemical potentials of electron by applying a photochemical water oxidation system to measure the pseudo-overpotentials for nano-sized water oxidation catalyst.<sup>2</sup> The potentials of electrons in  $MO_x$  nanoparticle (M = Co, Ni, Ru and Ir) were quantitatively estimated using Ru(II) tris-diimine type photosensitizers. In this reaction system, the photochemical water oxidation proceeds or not reflects whether the electron transition from  $MO_x$  to  $Ru^{3+/2+}$ . The potentials of  $MO_x$  and  $Ru^{3+/2+}$  were adjusted by changing pH conditions in reactant solution and substituent in their ligands, respectively. As a result, we succeeded in estimating not only the potentials of  $MO_x$  but also the pseudo-overpotentials from the calculation of energy gaps between  $O_2/H_2O$  and  $MO_x$  potentials. The order of estimated pseudo-overpotentials were almost same with the results originally obtained from electrochemical catalysts.<sup>3</sup>



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