

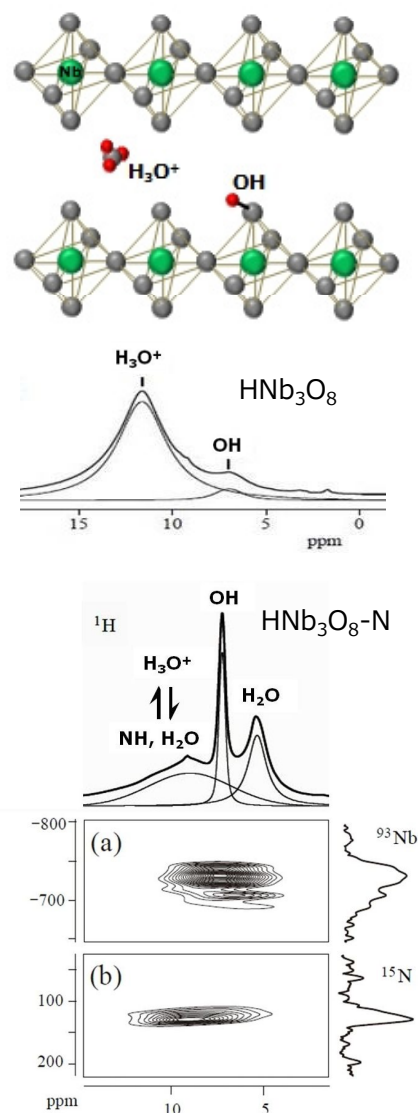
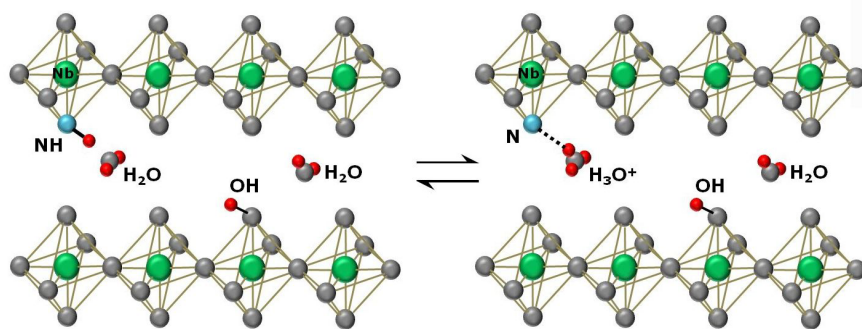
## Microstructures of Visible-light-responsive Photocatalyst $\text{H Nb}_3\text{O}_8\text{-N}$ Studied by $^1\text{H}$ MAS and $^1\text{H}\text{-}^{93}\text{Nb}/^1\text{H}\text{-}^{15}\text{N}$ HETCOR NMR

Much attention has been paid to visible-light-responsive photocatalysts, decomposing carbon dioxide and toxic chemicals under visible-light irradiation. Niobic acid  $\text{H Nb}_3\text{O}_8$  was found to change from ultra-violet-responsive to visible-light-responsive by nitrogen doping. This Note introduces an NMR study clarifying the microstructures of nitrogen-doped niobic acid  $\text{H Nb}_3\text{O}_8\text{-N}$ .

In niobic acid  $\text{H Nb}_3\text{O}_8$ ,  $\text{H}_3\text{O}^+$  ions are intercalated between the layers comprising  $\text{NbO}_6$  octahedra networks, yielding  $^1\text{H}$  signals together with OH protons;  $\text{H}_3\text{O}^+$ : 11.6ppm, OH: 7.0ppm.

In contrast, nitrogen-doped niobic acid  $\text{H Nb}_3\text{O}_8\text{-N}$  exhibits three distinct  $^1\text{H}$  signals. To assist the assignment of the  $^1\text{H}$  signals,  $^1\text{H}\text{-}^{93}\text{Nb}$  and  $^1\text{H}\text{-}^{15}\text{N}$  HETCOR (HETeronuclear CORrelation) spectra, indicating the proximity of H, Nb, and N atoms, were observed.

As a result, the  $^1\text{H}$  signal around 7ppm shows the correlation with  $^{93}\text{Nb}$ , proving that the protons are assigned to OH attaching to  $\text{NbO}_6$ . On the other hand, the  $^1\text{H}$  signal around 9ppm shows the correlation with  $^{15}\text{N}$ . One probable model for the microstructures is that NH (0-2ppm),  $\text{H}_2\text{O}$  (5.3ppm), and  $\text{H}_3\text{O}^+$  (11.6ppm) exchange as shown below.



Ref : T. Shimizu, T. Nakai, K. Deguchi, K. Yamada, B. Yue, and J. Ye, *Chem. Lett.*, 43, 80-82 (2014).

