

**Spectroscopic Analysis of Proton Exchange during the Photocatalytic  
Decomposition of Aqueous Acetic Acid: An Isotopic Study on Product  
Distribution and Reaction Rate**

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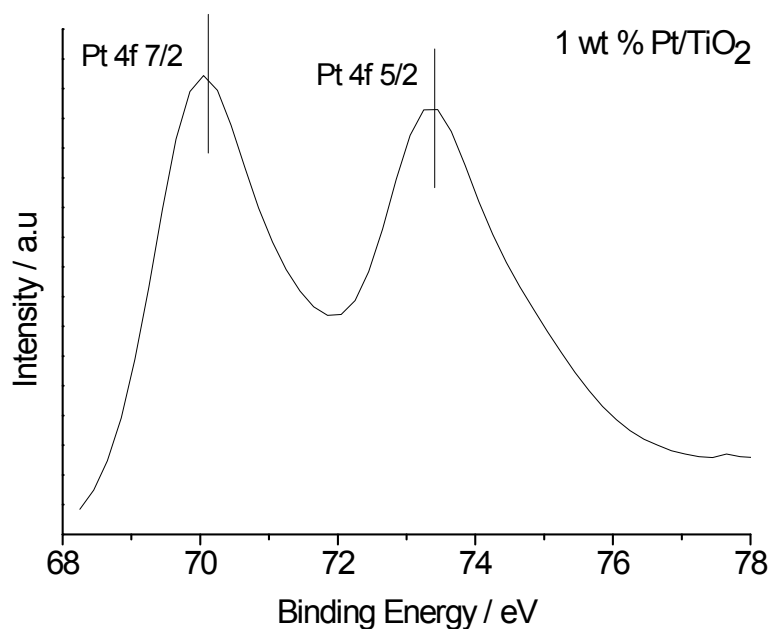
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## SI-1. Material Characterization

### SI-1.1 XPS Spectrum

X-ray photoelectron spectroscopy (XPS) measurements were conducted in a PHI Versaprobe II Scanning ESCA Microprobe (Physical Electronics) equipped with a monochromatized Al K $\alpha$  X-ray source (100 W) and an Ar ion gun. Data was evaluated with CasaXPS software.

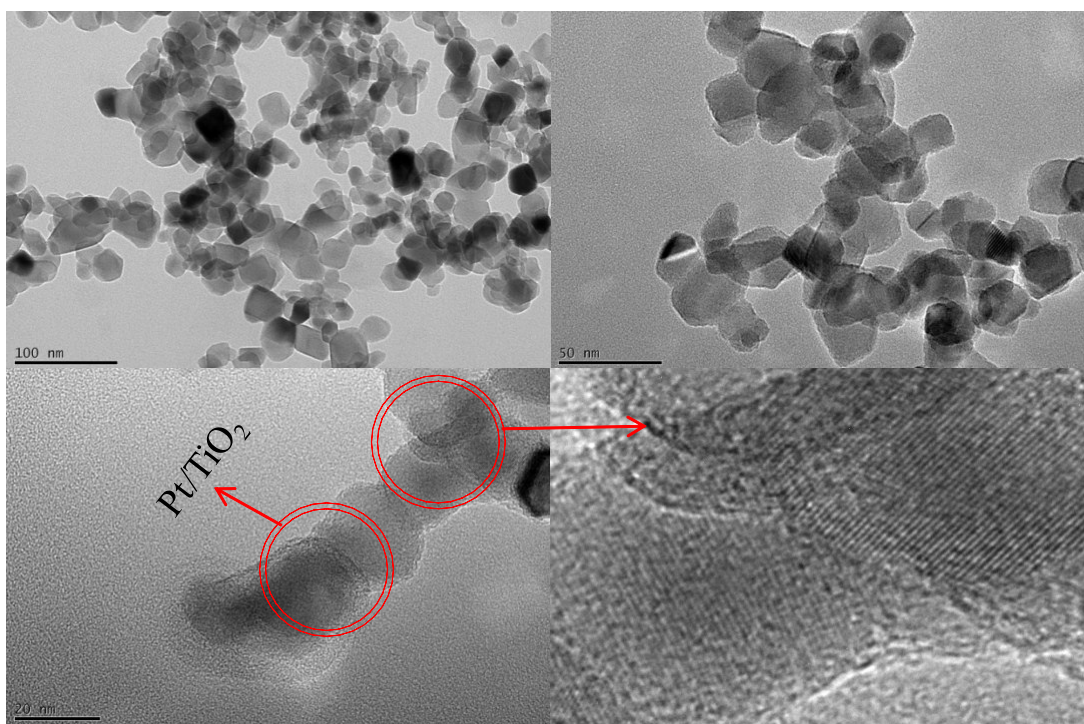


**Figure S1.** XPS spectrum recorded for Pt/TiO<sub>2</sub> prepared by an impregnation method.

XPS spectrum recorded for the Pt/TiO<sub>2</sub> particles exhibited a doublet signal at binding energy 4f 7/2 = 70.1 eV and 5/2 = 73.2 eV corresponding to the metallic Pt (*i.e.*, Pt<sup>0</sup>) (Figure S1). This means that Pt NPs exist on the surface of TiO<sub>2</sub> in their Pt<sup>0</sup> oxidation state<sup>1</sup>.

## SI-1.2 TEM Micrographs

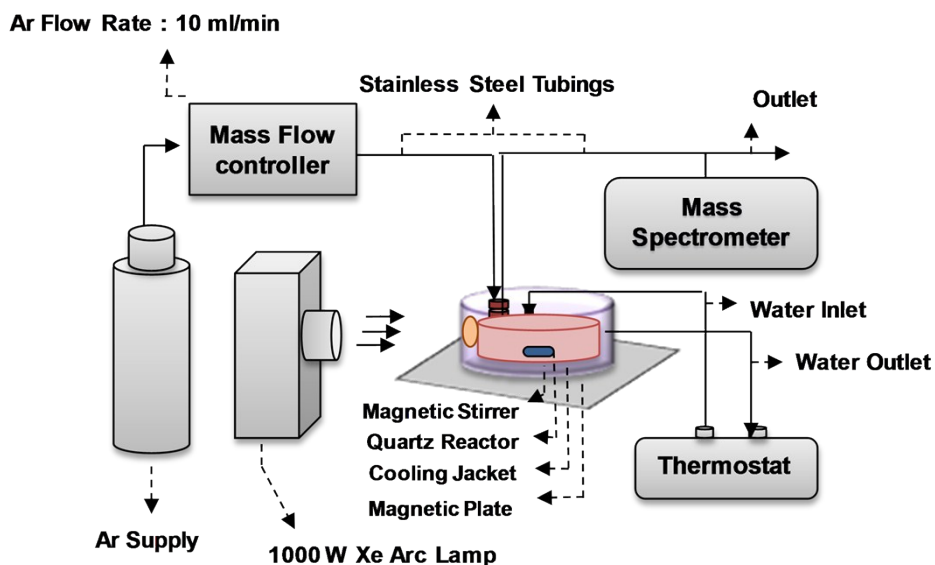
The TEM micrographs were taken by Transmission electron microscopy, model: Tecnai G2 F20 TMP (FEI) with acceleration voltage 200 kV.



**Figure S2.** TEM images of Pt/TiO<sub>2</sub> prepared by an impregnation method.

Figure S2 depicts the TEM micrographs obtained for Pt/TiO<sub>2</sub> photocatalyst. Here, brighter spherical structures represent the TiO<sub>2</sub> particles whereas darker spots correspond to the Pt nanoparticles (NPs) deposited on the surface of TiO<sub>2</sub>. The particle size for TiO<sub>2</sub> was found to be 15 – 25 nm, while Pt NPs were observed in between 15 – 20 nm. It can also be seen in the TEM images, that the dispersion of Pt NPs is very uniform over the whole TiO<sub>2</sub> matrix (Figure S2). In high-resolution TEM micrographs, the crystal lattice is also quite visible for both Pt NPs and TiO<sub>2</sub> particles. Also, the interface between Pt NPs and TiO<sub>2</sub> particles is very obvious (marked with red circles) in the high-resolution TEM images.

## SI-2. Photocatalytic Set-up



**Figure S3:** Schematic illustration of Photocatalytic-Set up.

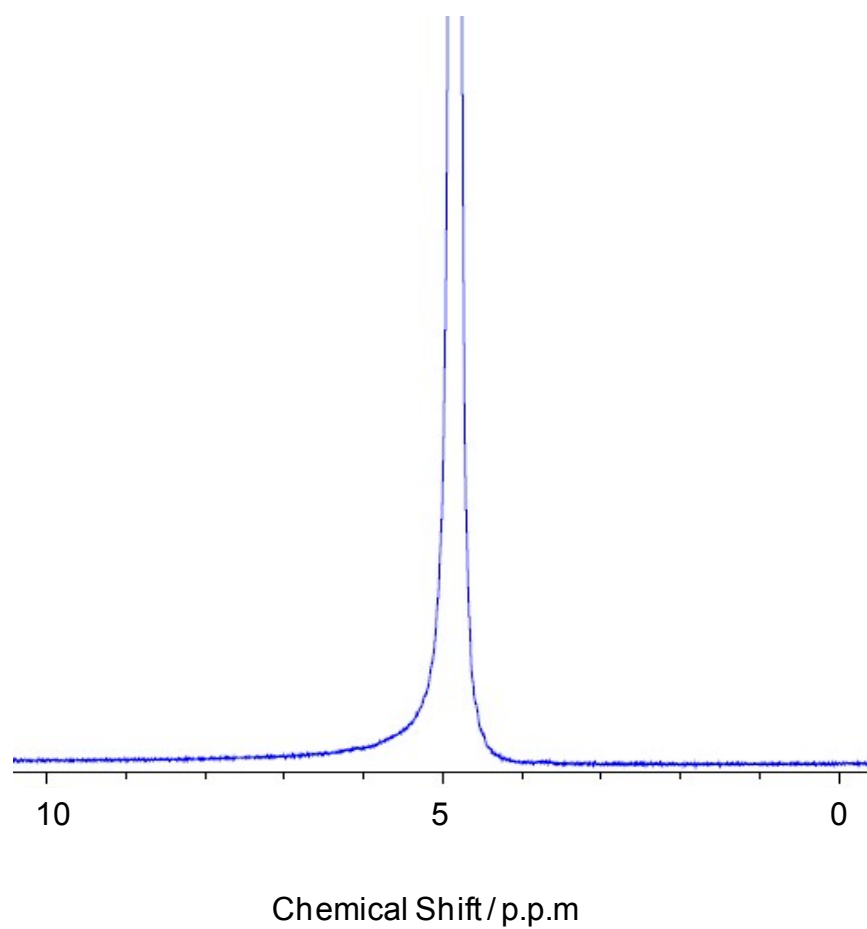
## SI-3. pH Adjustments of Suspension

The same Hg pH electrode was used for the adjustment of pH and pD for both water and deuterated solutions, according to the Gross-Butler-Purlee-theory expressed by the following relation (Eq. S1).<sup>2</sup> The pH value of the suspension was found to play an important role in the overall reaction mechanism. So, pH 2 was found to be the best in a series of experiments for the determination of acetic acid reaction mechanism.

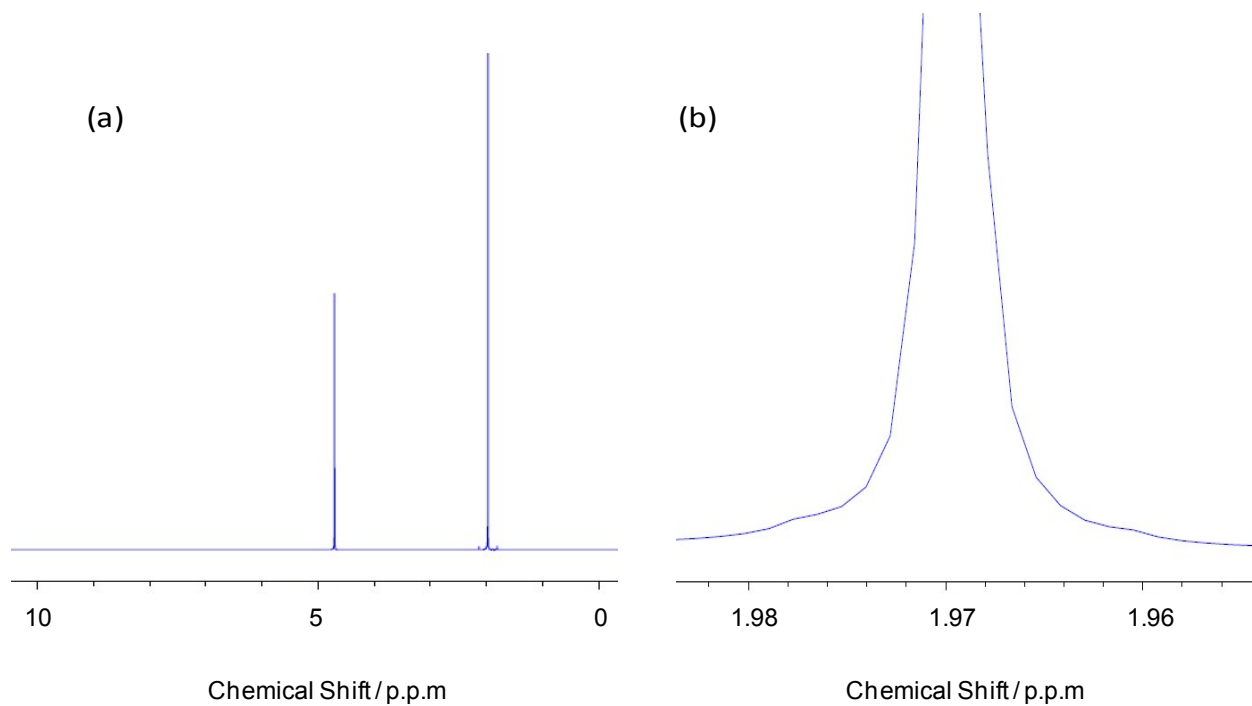
$$pD = pH + 0.44$$

Eq. S1

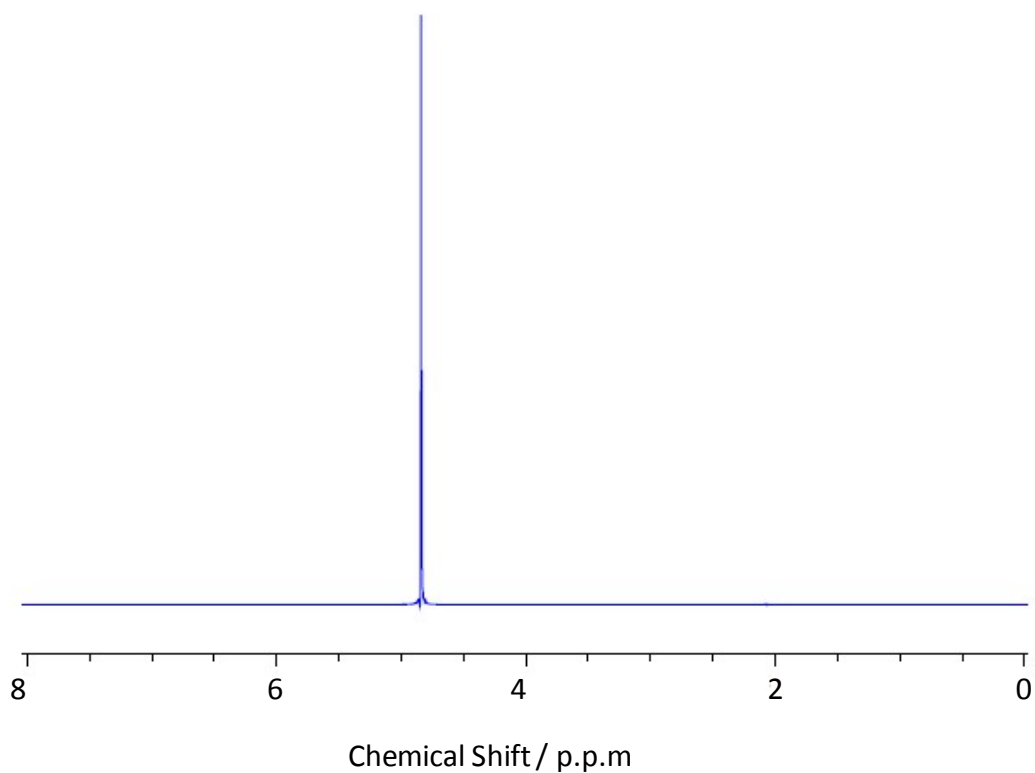
#### SI-4. NMR Spectra



**Figure S4.**  $^1\text{H}$  NMR spectra for reaction system (ii)  $\text{CD}_3\text{COOD-H}_2\text{O}$ , employing 1 wt% Pt  $\text{TiO}_2$ , photocatalyst concentration =  $0.5 \text{ g L}^{-1}$ , acetic acid concentration =  $0.5 \text{ M}$ , before illumination.

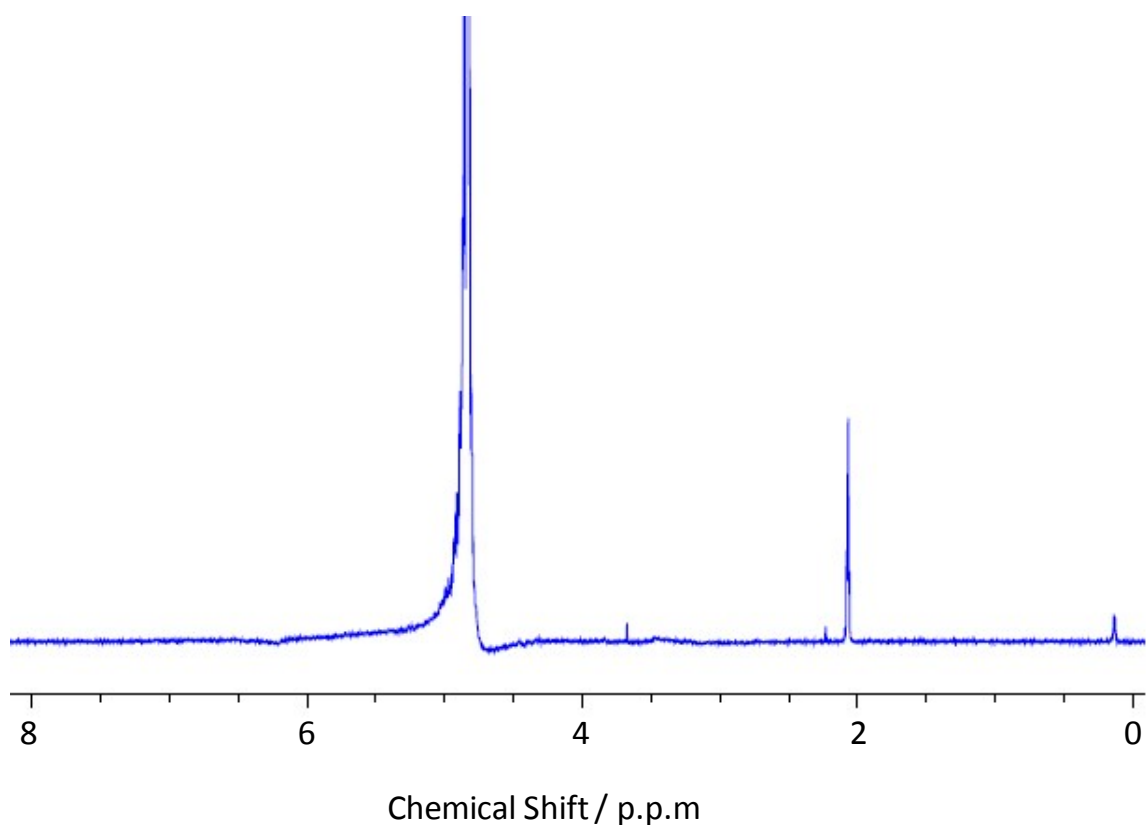


**Figure S5.** <sup>1</sup>H NMR spectra for reaction system (v) CH<sub>3</sub>COOH-D<sub>2</sub>O, employing 1 wt% Pt TiO<sub>2</sub>, photocatalyst concentration = 0.5 g L<sup>-1</sup>, acetic acid concentration = 0.5 M, before illumination (a) Full spectrum, (b) Zoom image representing methyl group.



**Figure S6.** <sup>1</sup>H NMR spectra for reaction system (vii) CD<sub>3</sub>COOD-H<sub>2</sub>O, employing bare TiO<sub>2</sub>, photocatalyst concentration = 0.5 g L<sup>-1</sup>, acetic acid concentration = 0.5 M, after 15 h illumination.

It can be seen in Figure S6 that NMR spectrum depicted only a peak corresponding to the H<sub>2</sub>O signal. No other peak can be seen in the spectrum recorded from NMR spectroscopy for reaction system (vii) TiO<sub>2</sub>-CD<sub>3</sub>COOD-H<sub>2</sub>O.

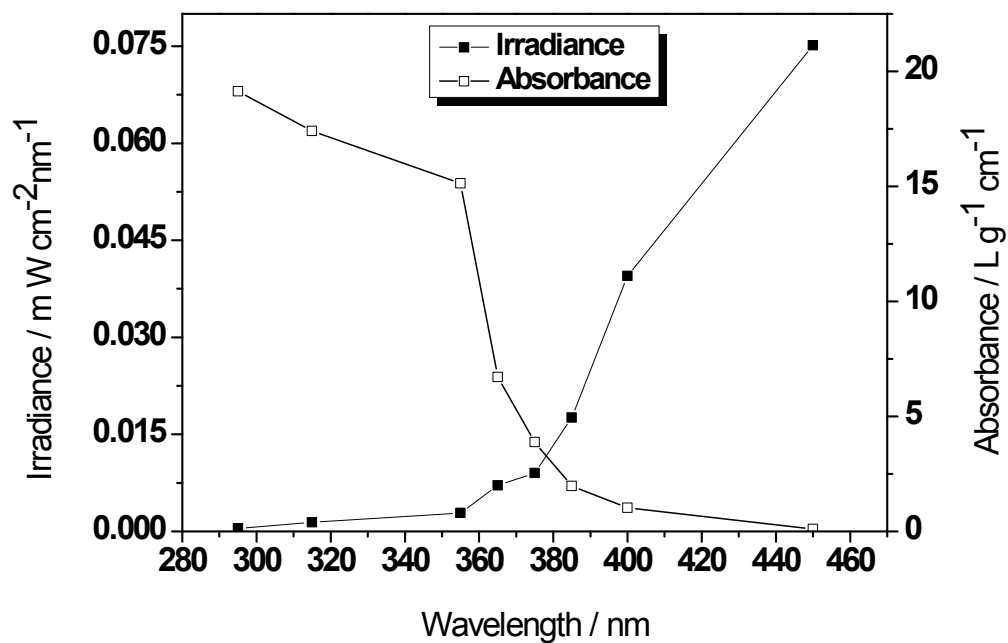


**Figure S7.** <sup>1</sup>H NMR spectra for reaction system (viii) CH<sub>3</sub>COOH-D<sub>2</sub>O, employing bare TiO<sub>2</sub>, photocatalyst concentration = 0.5 g L<sup>-1</sup>, acetic acid concentration = 0.5 M, after 15 h illumination.

Figure S7 demonstrates the NMR spectrum obtained for reaction system (viii) TiO<sub>2</sub>-CH<sub>3</sub>COOH-D<sub>2</sub>O. Here, a peak corresponding to the methyl (CH<sub>3</sub>) group of acetic acid at the chemical shift 2 p.p.m is obvious. Other than this, a peak related to water (H<sub>2</sub>O) signals can also be seen at about chemical shift 5 p.p.m. This peak might come from the residual protons of D<sub>2</sub>O.



## SI-5. Xenon Lamp Spectrum



**Figure S8.** Absorption spectrum of suspended TiO<sub>2</sub> particles in water and irradiance of 30 mWcm<sup>-2</sup> Xenon lamp in the range of 295-450 nm.

## References

1. Hamid, S.; Dillert, R.; Bahnemann, D. W. Photocatalytic Reforming of Aqueous Acetic Acid into Molecular Hydrogen and Hydrocarbons over Cocatalyst-Loaded TiO<sub>2</sub>: Shifting the Product Distribution. *J. Phys. Chem. C* **2018**.
2. Purlee, E. L. On the solvent isotope effect of deuterium in aqueous acid solutions. *J. Am. Chem. Soc.* **1959**, *81*, 263-272.