SUPPORTING INFORMATION

Trapped State Sensitive Kinetics in $LaTiO_2N$ Solid Photocatalyst with and without Cocatalyst Loading

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1. Effect of variation of excitation intensity on the decay profile

In order to rule out second order recombination it was necessary to confirm that the decay behaviour is independent of the choice of excitation intensity. To confirm this we chose to monitor the decay at 880 nm (though later on we chose to probe at 920 nm but, that does not affect our final conclusion in any way) using several excitation intensities as shown in Figure S1 and found that the decay remains relatively unaffected below 0.3 μJ whereas above it the kinetics was drastically affected. Hence, we chose 0.3 μJ as a reasonable choice to carry out further experiments. Too low an excitation intensity would not have been a good choice as the data quality deteriorates and signal-to-noise ratio becomes high in that case. The transient absorption intensity however was proportional to the excitation intensity indicating absence of any non-linear absorption within the time resolution.

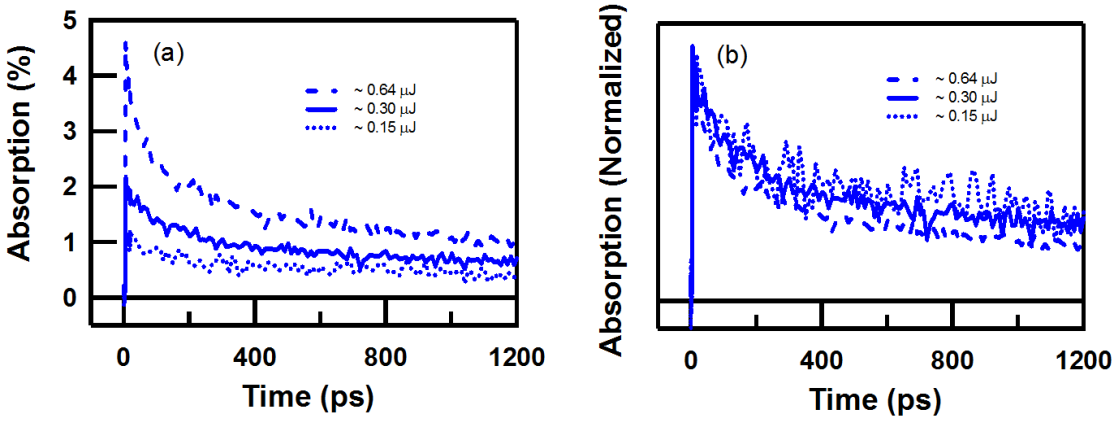

Figure S1: Comparison of femtosecond time profiles (λ_{exc} = 480 nm, pump energy ~ 0.64, ~ 0.3 and ~ 0.15 μJ) for LTON powder monitored at 880 nm.

2. fs-TRDR spectra upto 1300 nm

The fs-TRDR spectrum upto 1300 nm at different delay times is shown in Figure S2. The rising absorption value with increasing wavelength in the near IR region is an attribute of free carriers.[1] This indicates contribution of both trapped and free bulk carriers in the NIR region and beyond.

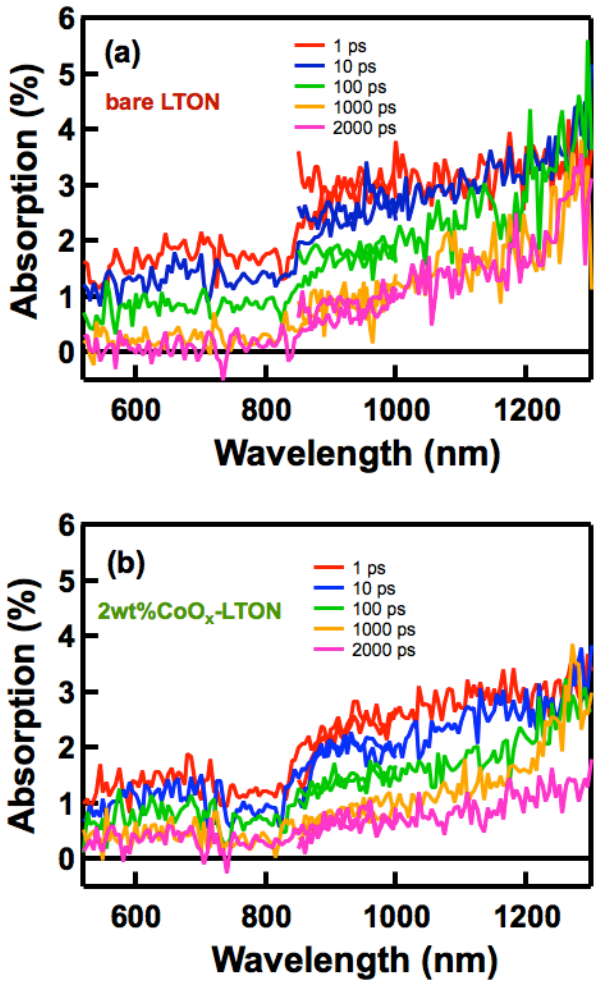

Figure S2: Transient absorption spectrum at different delay times after excitation (λ_{exc} = 480 nm, pump energy = 0.3 µJ) for (a) bare LTON and (b) 2wt%CoO_x-LTON.

3. Time profiles for 650 and 920 nm in bare LTON in presence of MeOH (λ_{exc} = 480 nm)

MeOH is known as a hole scavenger.[2] The decay profiles for 650 and 920 nm in MeOH show comparable kinetics to that of 2wt%CoO_x-LTON thus, establishing the role of CoO_x as an oxidation co-catalyst. The table below shows the values of $t_{1/2}$ and the percentage of surviving carriers at 2 ns for the two cases. Even though MeOH acts as a hole scavenger, CoO_x seems to be more effective as is evident from the $t_{1/2}$ values which indicates faster decay of surface trapped electrons at 650 nm in presence of MeOH. This is due to less effective scavenging of surface holes by MeOH when compared to CoO_x resulting in loss of surface electrons by e-h recombination.

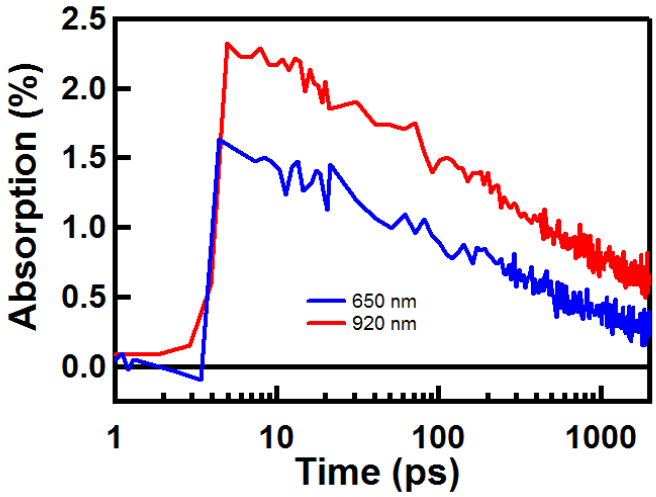

Figure S3: Comparison of femtosecond time profiles (λ_{exc} = 480 nm, pump energy = 0.3 μJ) for MeOH-LTON powder monitored at 650 and 920 nm.

Samples	$t_{1/2}$		%age of surviving carriers (at 2 ns)	
	650 nm	920 nm	650 nm	920 nm
2wt%CoO_x-LTON	320 ps	310 ps	28%	29%
MeOH-LTON	195 ps	330 ps	19%	28%

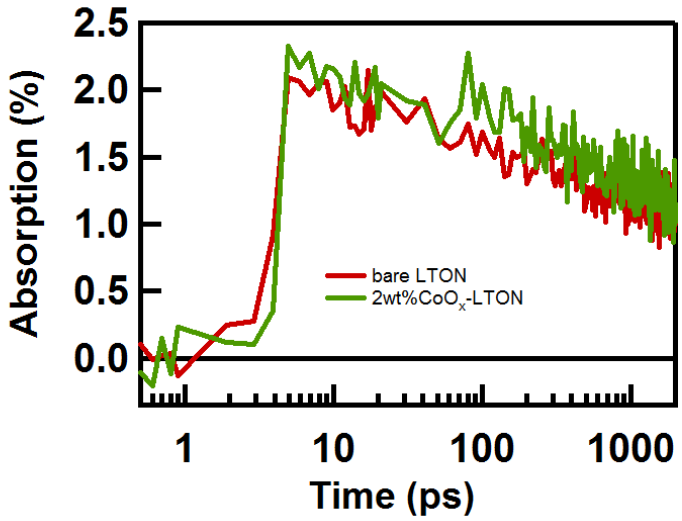

Figure S4: Femtosecond time profiles for bare LTON and 2wt%CoO_x-LTON monitored at 3440 nm for λ_{exc} = 480 nm

References

1) Tamaki, Y.; Hara, K.; Katoh, R.; Tachiya, M.; Furube, A. *J. Phys. Chem. C* **2009**, *113*, 11741–11746.

2) Tamaki, Y.; Furube, A.; Murai, M.; Hara, K.; Katoh, R.; Tachiya, M. *J. Am. Chem. Soc.* **2006**, *128*, 416-417.