

CO₂ Pre-activation in Photo-induced Reduction Via Surface Functionalization of TiO₂ Nanoparticles

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Supporting information

Materials and Methods

Nanoparticle synthesis.

2 nm. 2 nm nanoparticles were obtained via the hydrolysis of titanium isopropoxide (0.540 mL, Sigma Aldrich) in methanol (100 mL MeOH, 0.5 mL H₂O, 63 mg LiOH). The solution was stirred and sonicated, and then rotovapped until a volume of 3 mL was reached. Water was added to bring the final solution volume to 40 mL, which resulted in a solution of 2 nm TiO₂ nanoparticles at pH 11.

5 nm. 5 nm nanoparticles were synthesized via the hydrolysis of 5 mL of titanium tetrachloride (5 mL) in cold water (200 mL). TiCl₄ was added dropwise under an inert atmosphere. The resultant solution was dialyzed twice over a period of 48 hours until a pH of 3.5 was obtained. At this point the solution containing 5 nm TiO₂ nanoparticles at pH 3.5 was collected. (*J. Phys. Chem.* **1996**, *100*, 4538-4545)

Functionalization

Aqueous solutions of 0.1 M 3ASA (or desired ligand) were used to functionalize the nanoparticles. After addition of the appropriate solution, the pH was adjusted with HCl (for 2 nm NPs) or LiOH (5 nm NPs). CO₂ was bubbled through the solution for several minutes.

Optical spectroscopies

UV-vis. UV-vis was carried out in a 100 μ L cell with a Perkin Elmer Lambda 1050 spectrometer in the 300-800 nm range.

Raman. Samples were prepared by depositing the functionalized nanoparticles in a concave slide glass slide and covering it with a coverslip. Raman data was acquired for 60 seconds with 442 nm laser using an InVia Renishaw confocal microscope.

Magnetic resonance

NMR. ¹³C NMR measurements were carried out using a Bruker Avance III 500 MHz spectrometer with a direct cryoprobe. Samples were prepared with ¹³CO₂ (>99% purity) and 200 μ L of D₂O was added to 500 μ L of sample for locking.

EPR. EPR spectra were acquired with a Bruker Elexsys E580 spectrometer equipped with an Oxford CF935 helium flow cryostat with an ITC-5025 temperature controller. The sample was prepared, placed into a quartz EPR tube and degassed with argon for 15 minutes to remove dissolved oxygen. Excitation of the sample in the EPR spectrometer was carried out with a broadband visible Xenon lamp (400 nm cut-off filter). A custom made optical dewar was used for pre-irradiation of the sample at liquid nitrogen temperatures.

Density functional theory

All the DFT calculations were carried out at the B3LYP/6-31G* level. It was shown in our earlier studies (Ref.10 of the MS, and Int. J. Quantum Chem. 111, 2011, 1659) that the Raman spectra evaluated at this level are in good agreement with experiment.

Additional experiments

UV-vis controls

To ascertain whether the amine, CO₂, and the NP were necessary to observe a redshift, we measured the UV-vis of TiO₂-SA with CO₂ (Figure 1), TiO₂-3ASA with N₂.

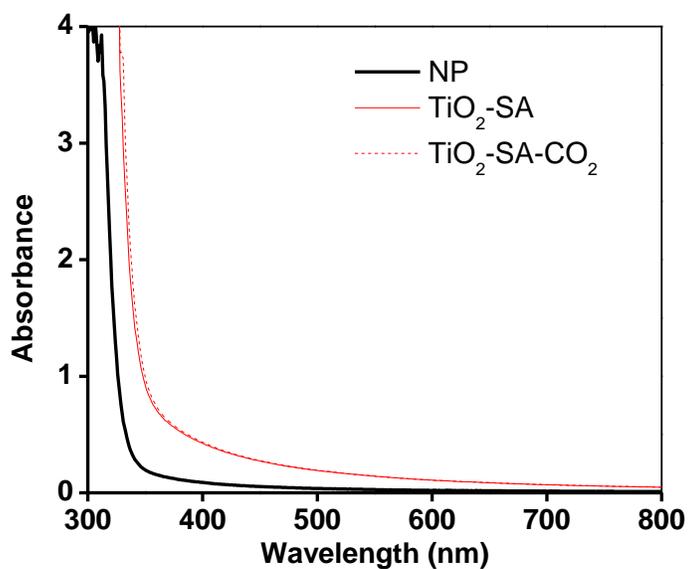


Figure 1. UV-vis of TiO₂-SA before and after bubbling CO₂ at constant pH 7.4.

Acid titration of 3ASA

The fluorescence of 3ASA is a useful indicator of the binding to TiO₂ nanoparticles. The fluorescence emission around 510 nm is quenched upon adsorption on TiO₂ as the pH is lowered. By performing an acid titration we can determine the pH at which the maximum number of molecules have adsorbed. Measuring the Raman spectra at pH 6.3-6.6 ensures all molecules are adsorbed, separating the effect of CO₂ directly interacting with the adsorbate from the effect of the acidic buffer established.

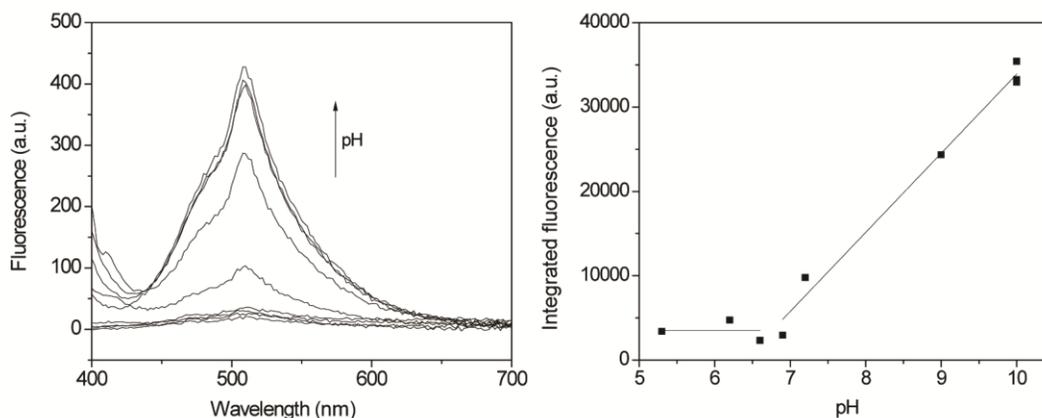


Figure 2. Fluorescence spectrum of 3ASA at 50:1 coverage (left) and integrated area of the fluorescence emission as a function of pH

Effect of substituent position: 3,4 and 5 ASA

We measured the Raman spectrum of 4 and 5ASA. There is no well-defined SERS spectrum for 4ASA, with only very broad features that do not change when CO₂ is bubbled. We note that 4ASA does not make a strong CT complex with TiO₂. The Raman of 5ASA-TiO₂ is better resolved. We see a shift from a peak at 1629 to 1615 upon CO₂ adsorption. Unlike 3ASA-TiO₂ which remains in colloidal suspension, CO₂ causes 5ASA-TiO₂ to precipitate out of solution.

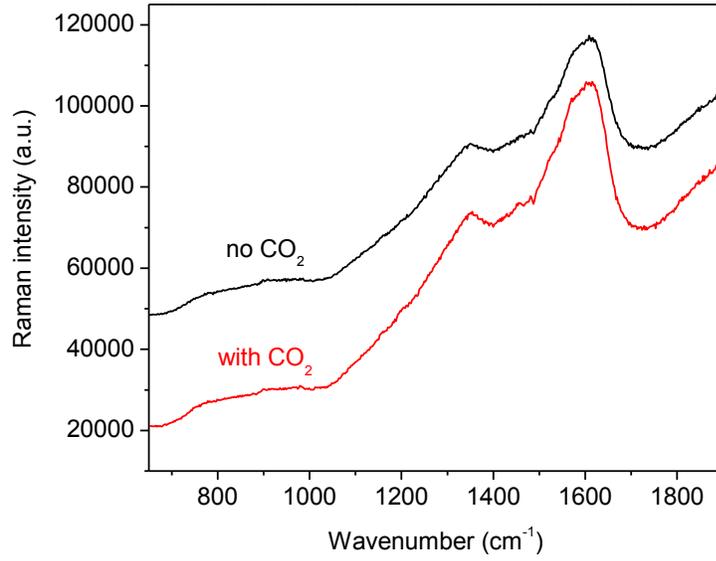


Figure 3. SERS of TiO₂-4ASA

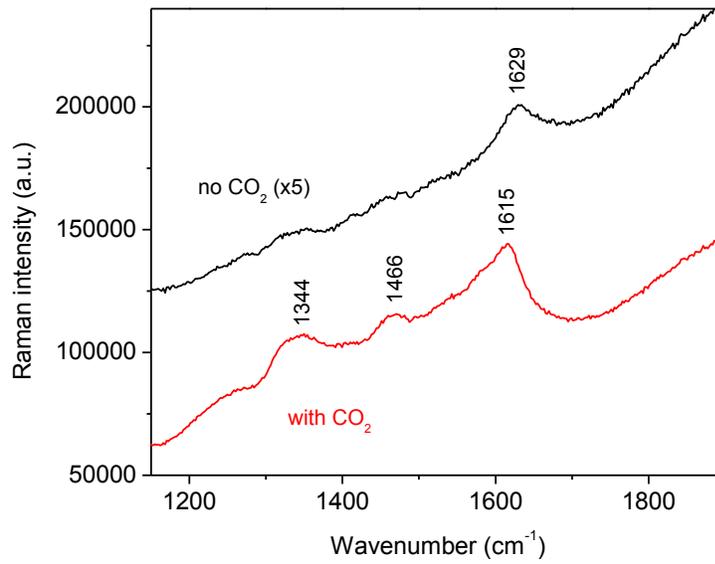


Figure 4. SERS of TiO₂-5ASA

pH effects:

At low pH CO_2 the Raman spectrum remains unchanged when CO_2 is bubbled (Figure 5). If the pH is corrected to pH=9 before bubbling CO_2 , Raman changes in the vibrations reveal CO_2 adsorption.

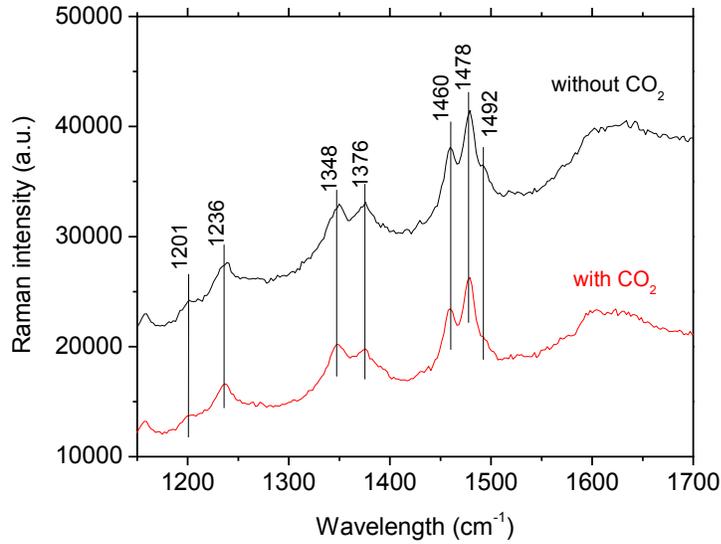


Figure 5. Raman Spectrum of TiO_2 -3ASA at 1:110 coverage for CO_2 bubbled at pH=6

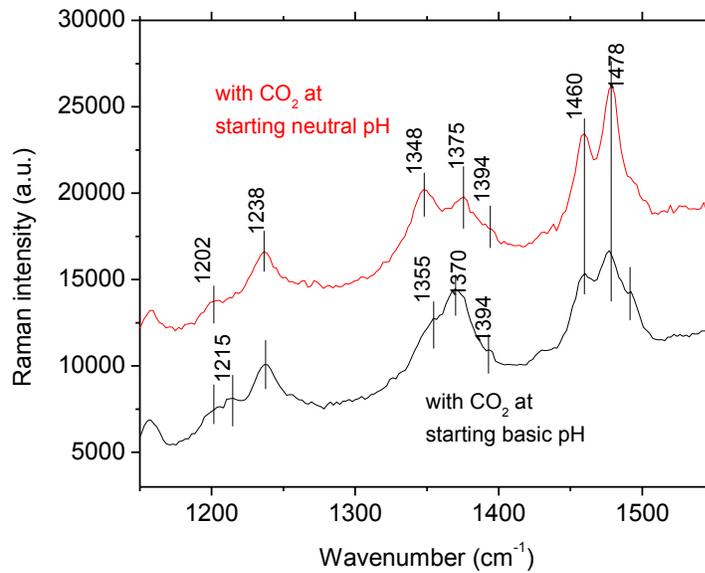


Figure 6. Raman spectrum of TiO₂-3ASA at 1:110 coverage for starting pH neutral (top) and basic (bottom) before bubbling CO₂. Final pH for both solutions is 6.6

Isotopic labeling:

Figure 7 shows the Raman of TiO₂:3ASA at 1:50 coverage with ¹²CO₂ and ¹³CO₂. The lack of shifts between both spectrums indicate an indirect binding between the carbon of CO₂ and the 3ASA linker.

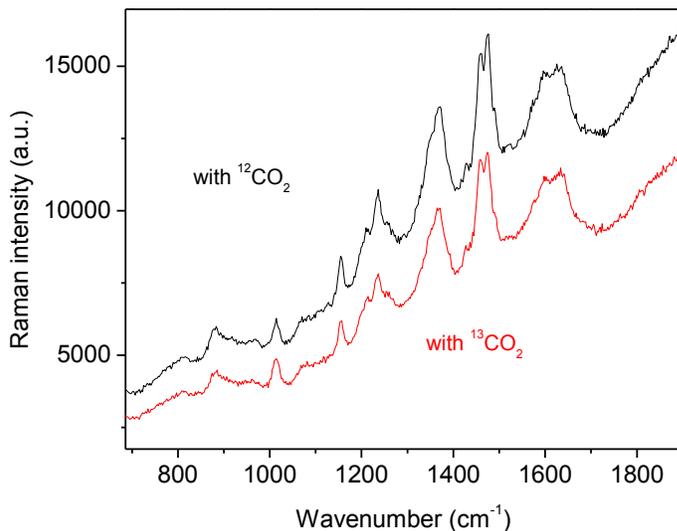


Figure 7. Raman spectrum of TiO₂-3ASA at 1:50 with ¹²CO₂ (black) and ¹³CO₂ (red)

Deuterated amine

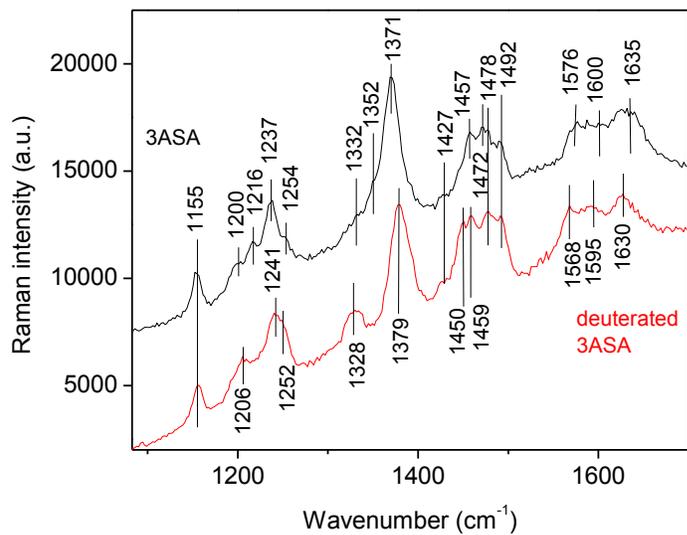


Figure 8. Raman spectrum of TiO₂-3ASA at 1:50 (black) and with a deuterated amine (red)

Bicarbonate

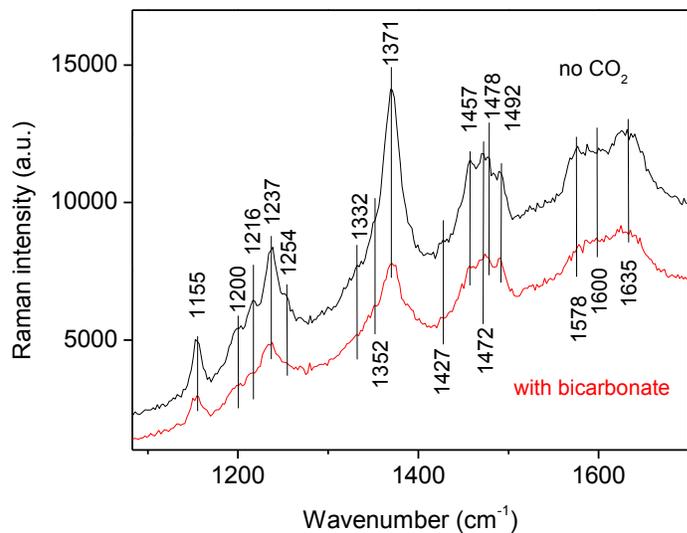


Figure 9. Raman spectrum of TiO₂-3ASA at 1:50 (black) and with bicarbonate (red)

Raman assignments

without CO ₂ (cm ⁻¹)	with CO ₂ (cm ⁻¹)	deuterated (cm ⁻¹)	deuterated with CO ₂ (cm ⁻¹)	theory (without CO ₂) (cm ⁻¹)	assignment
1200	1200	1200	1200	1182	vCC; A'(8b)
1216	1212	1206	1210	1217	v _{as} CH; A'(13)
1237	1237	1241	1241	1251	δCH; A'(3)
1254	1258	1252	1252	-	vCC; A'(14)
1332	-	1328	1330	1331	
1352	1352	-			
1371	1371	1379	1374	1386	vCOO ⁻
1427	1427	1427			
		1450	1450		
1457	1459	1459	1467		vCC; A'(19b)
1472	-	-			-
1478	1475	1478	1478	1496	vCC; A'(19a)
1492	1492	1492		1515	
		1568			
1576	1576	1585	1574		vCC;A'(8b)
1600	1600				
1635	1635	1630	1635/1622	1640	vC=O

Table 1.

EPR simulations

TiO₂ – 3ASA

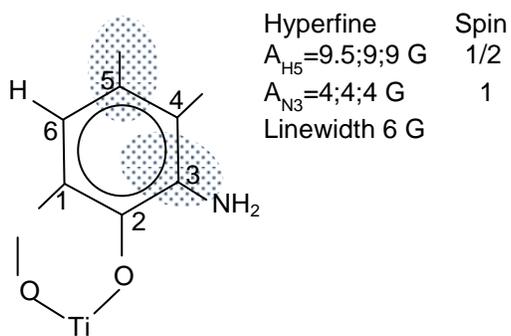
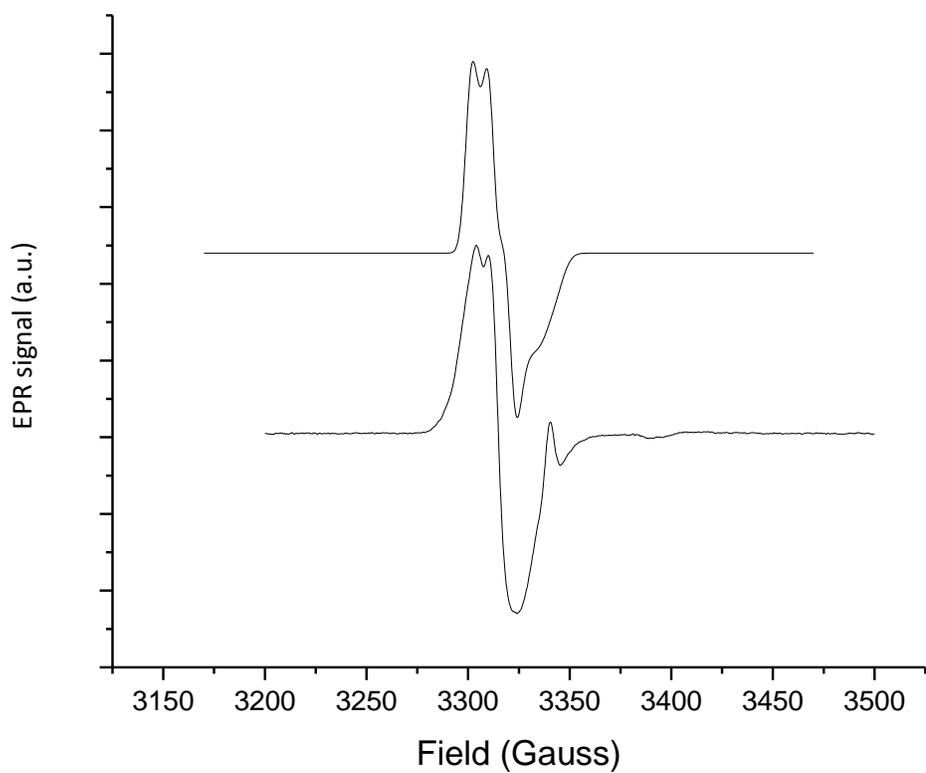


Figure 10. CW-EPR experiment (bottom trace) and simulation (top trace) along with a diagram of the calculated spin density. Hydrogens at the 4 and 6 positions make a negligible contribution to the hyperfine coupling.

TiO₂ – 3ASA – CO₂

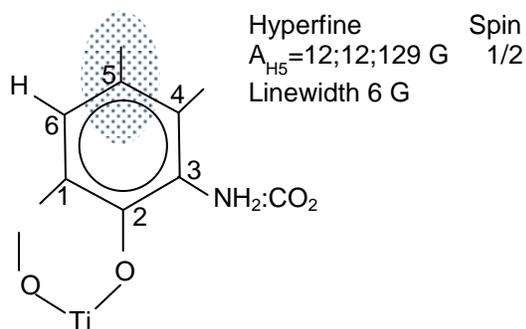
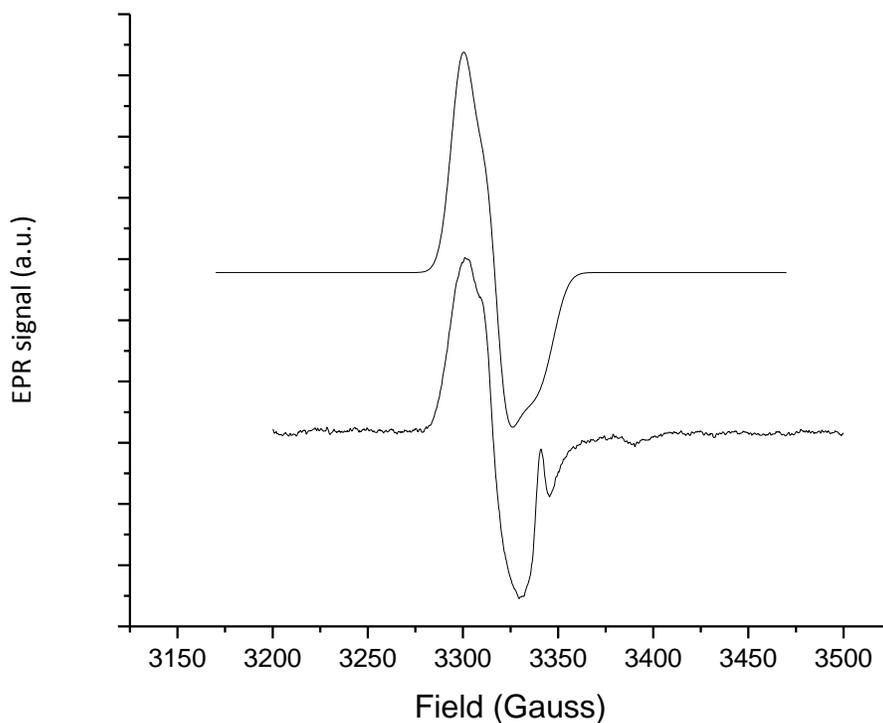


Figure 11. CW-EPR experiment (bottom trace) and simulation (top trace) along with a diagram of the calculated spin density.

The contribution of the hydrogens in position 4 and 6 to hyperfine coupling is much smaller (Borg D.C. Biochem. Pharmacology, 1965, vol 14 (4) pp 627-631, Ayscough P.B., Sergent, Wilson R, J. Chem. Soc. 1966, 903-906).

