Supplementary information

Grafting titanate nanotubes with 3-aminopropyltriethoxysilane for enhanced CO_2 adsorption

Cynthia Barreto[1]; Edisson Morgado Jr.[1]; Khrissy Medeiros[1]; Marianne Diniz[1]; Marcelo Maia[2]; Aryandson da Silva[3]; Sibele B. C. Pergher[3], Deane Mesquita Roehl[4] and Bojan A. Marinkovic[1*]

[1]*Department of Chemical and Materials Engineering, Pontifical Catholic University of Rio de Janeiro (PUC-Rio), 22453-900, Rio de Janeiro, RJ, Brazil*

[2] *Department of Physics, Pontifical Catholic University of Rio de Janeiro (PUC-Rio), 22453-900, Rio de Janeiro, RJ, Brazil*

[3]*Department of Chemistry, Federal University of Rio de Grande do Norte (UFRN), 59072-970, Natal, RN, Brazil*

[4]*Department of Civil Engineering, Pontifical Catholic University of Rio de Janeiro (PUC-Rio), 22453-900, Rio de Janeiro, RJ, Brazil*

**e-mail: bojan@puc-rio.br*

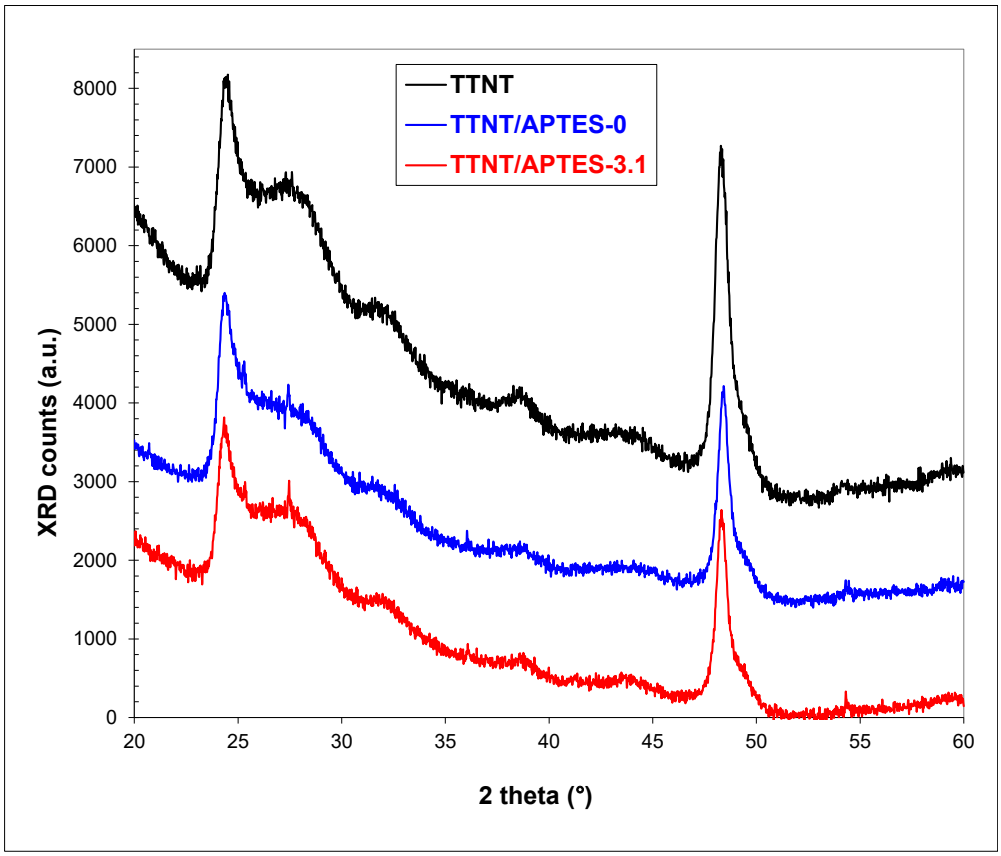
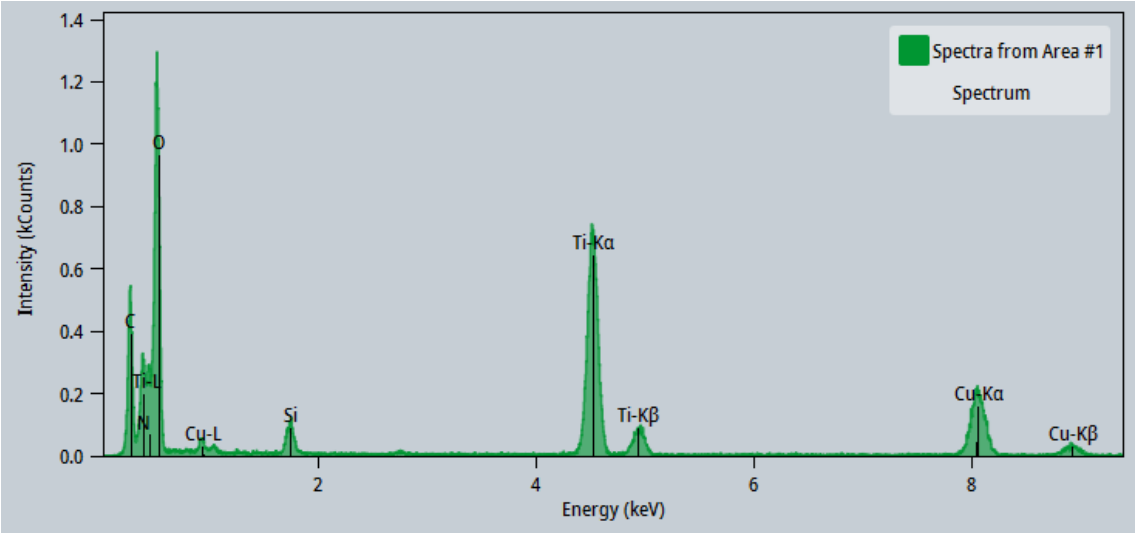


Figure S1 – XRD patterns of pristine TTNT and after treatment with and without APTES.



Z	Element		Atomic Fraction (%)	% Error	Mass Fraction (%)	%Error
6	C	K	31.62	2.96	18.02	1.79
7	N	K	3.75	0.99	2.49	0.67
8	O	K	42.90	5.17	32.56	5.05
14	Si	K	2.56	0.54	3.42	0.72
22	Ti	K	19.16	3.11	43.51	5.06

Figure S2 – EDS spectra and element analysis of APTES modified sample (TTNT/APTES-3.1)

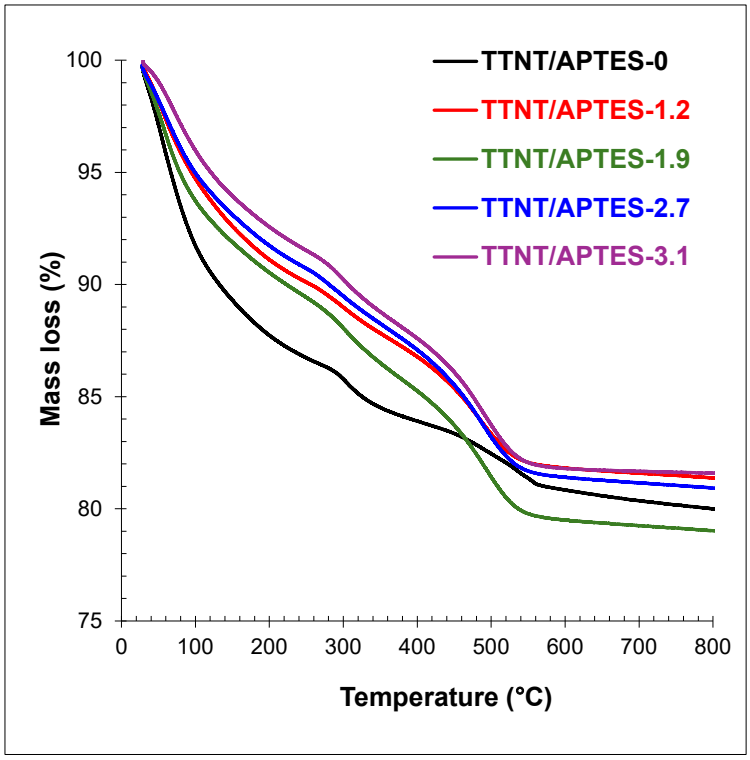


Figure S3 – TGA plots of the studies sample TTNT

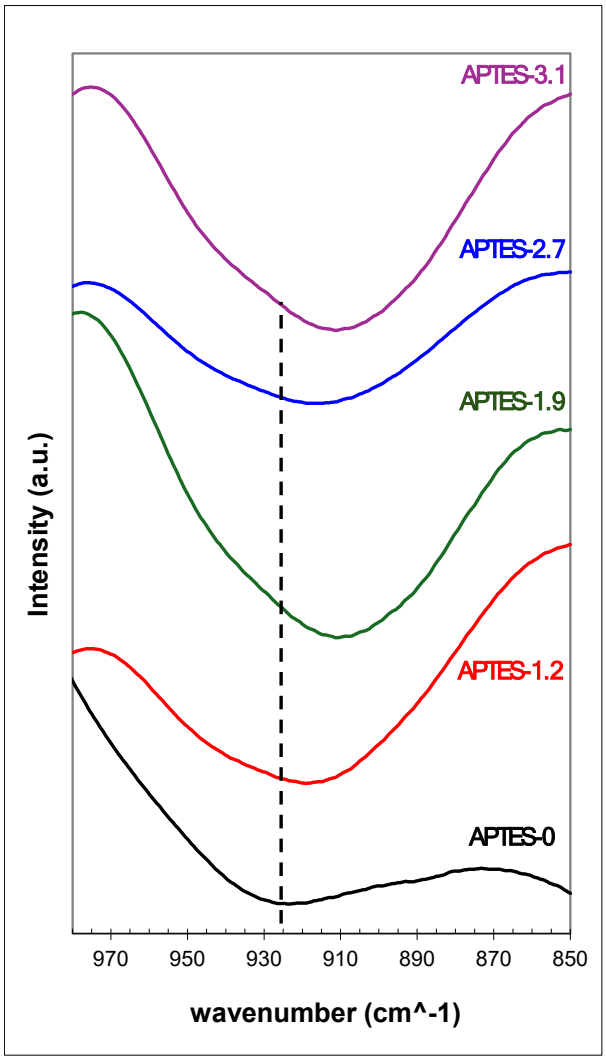


Figure S4: FTIR vibrational spectra, zooming the spectral region 850-1000 cm^{-1}.

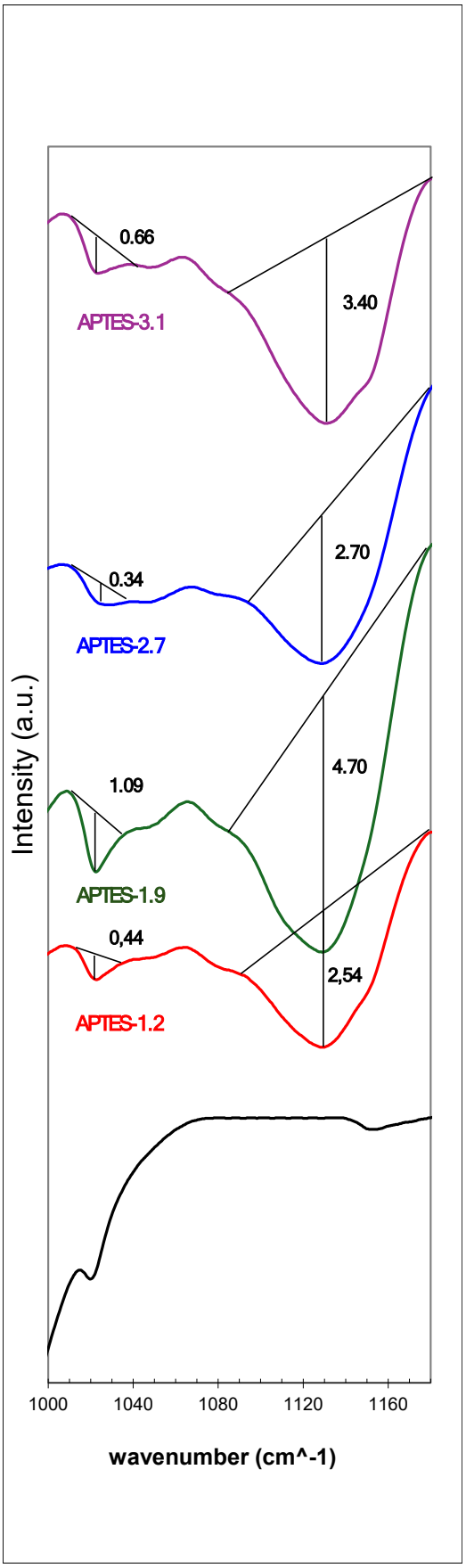


Figure S5: FTIR vibrational spectra, zooming the spectral region of Si-O-Si bond absorptions

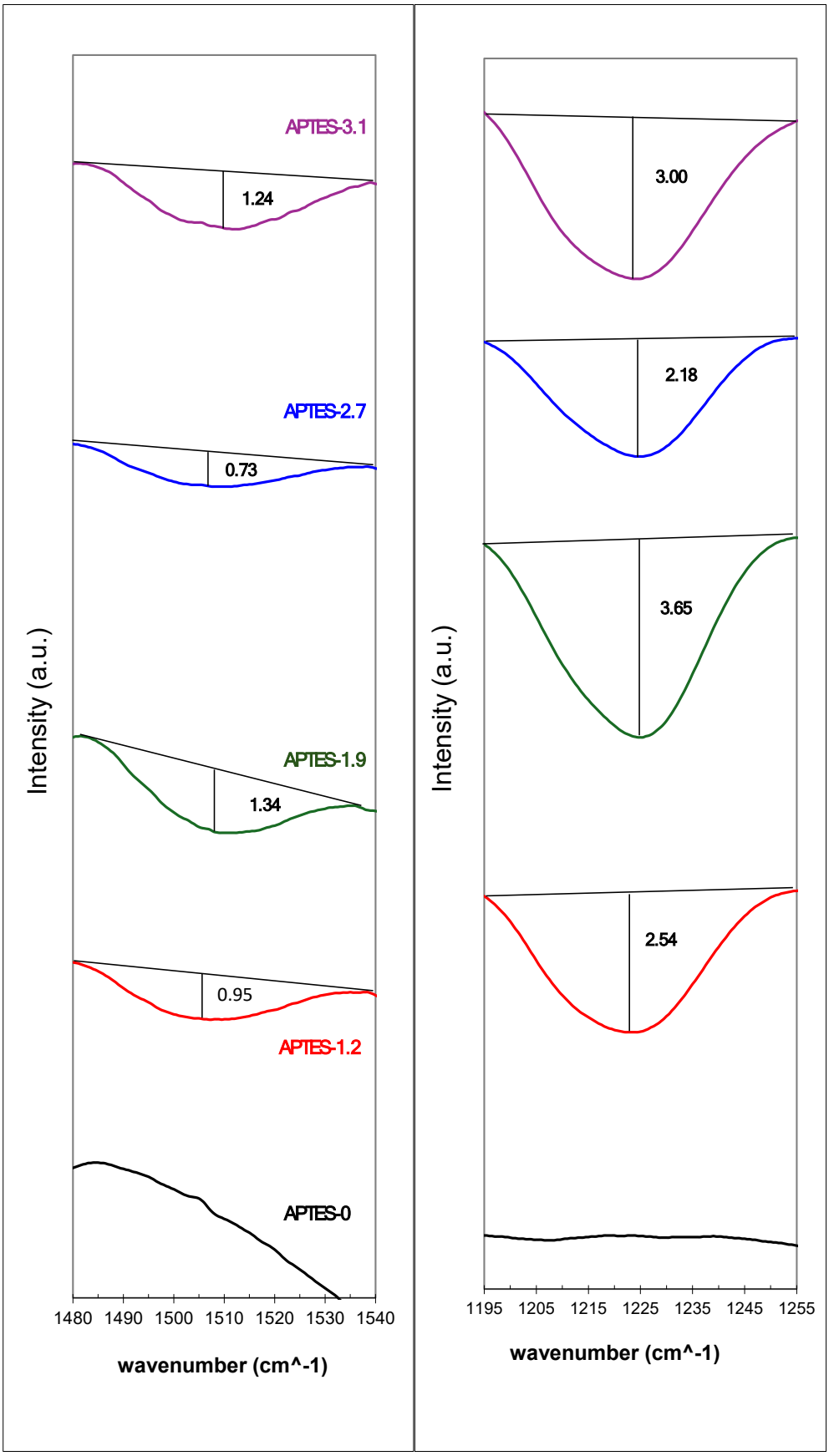


Figure S6: FTIR vibrational spectra, zooming the spectral region of bending vibration H-bonded NH_2 (~1511 cm^{-1}) and of stretching C-N vibration (~1224 cm^{-1})

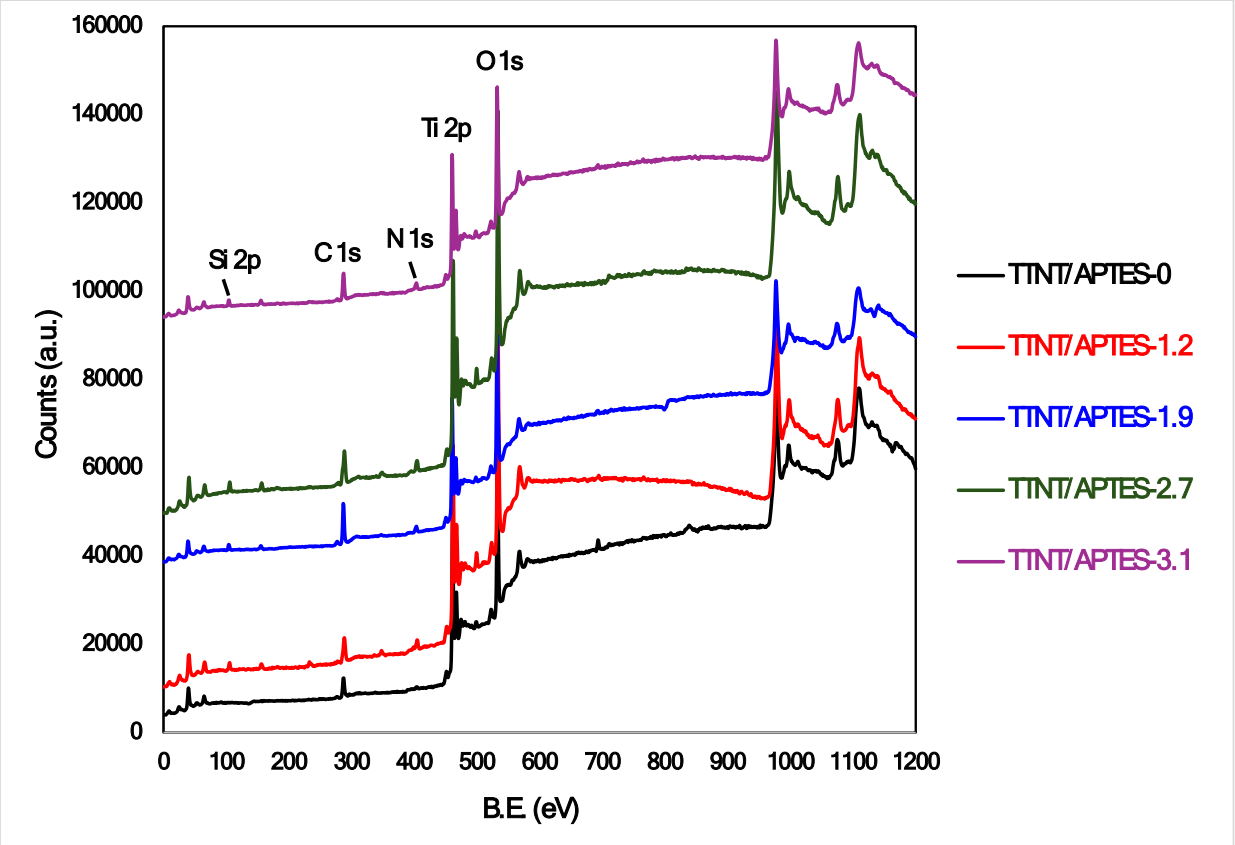


Figure S7: XPS spectra of the samples studied

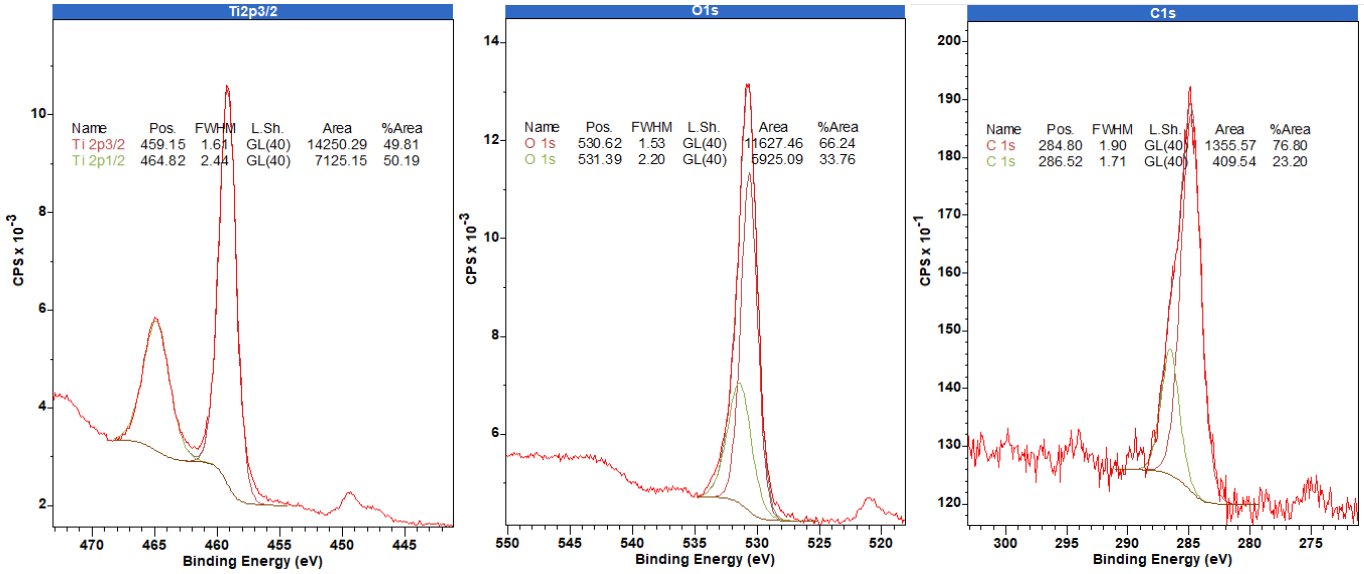


Figure S8(A) - XPS spectra with deconvoluted peaks of sample TTNT/APTES-0

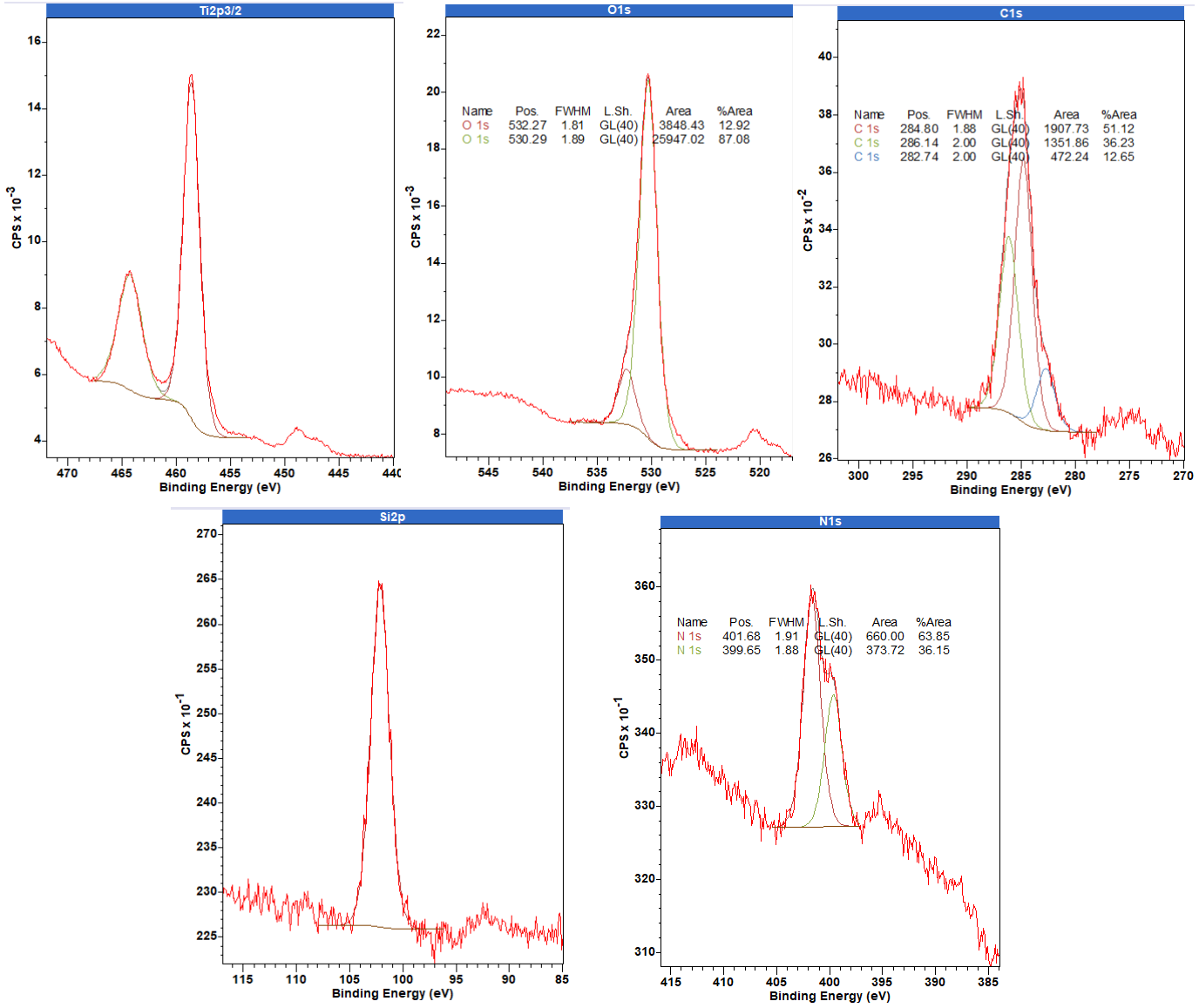


Figure S8(B) - XPS spectra with deconvoluted peaks of sample TTNT/APTES-1.2

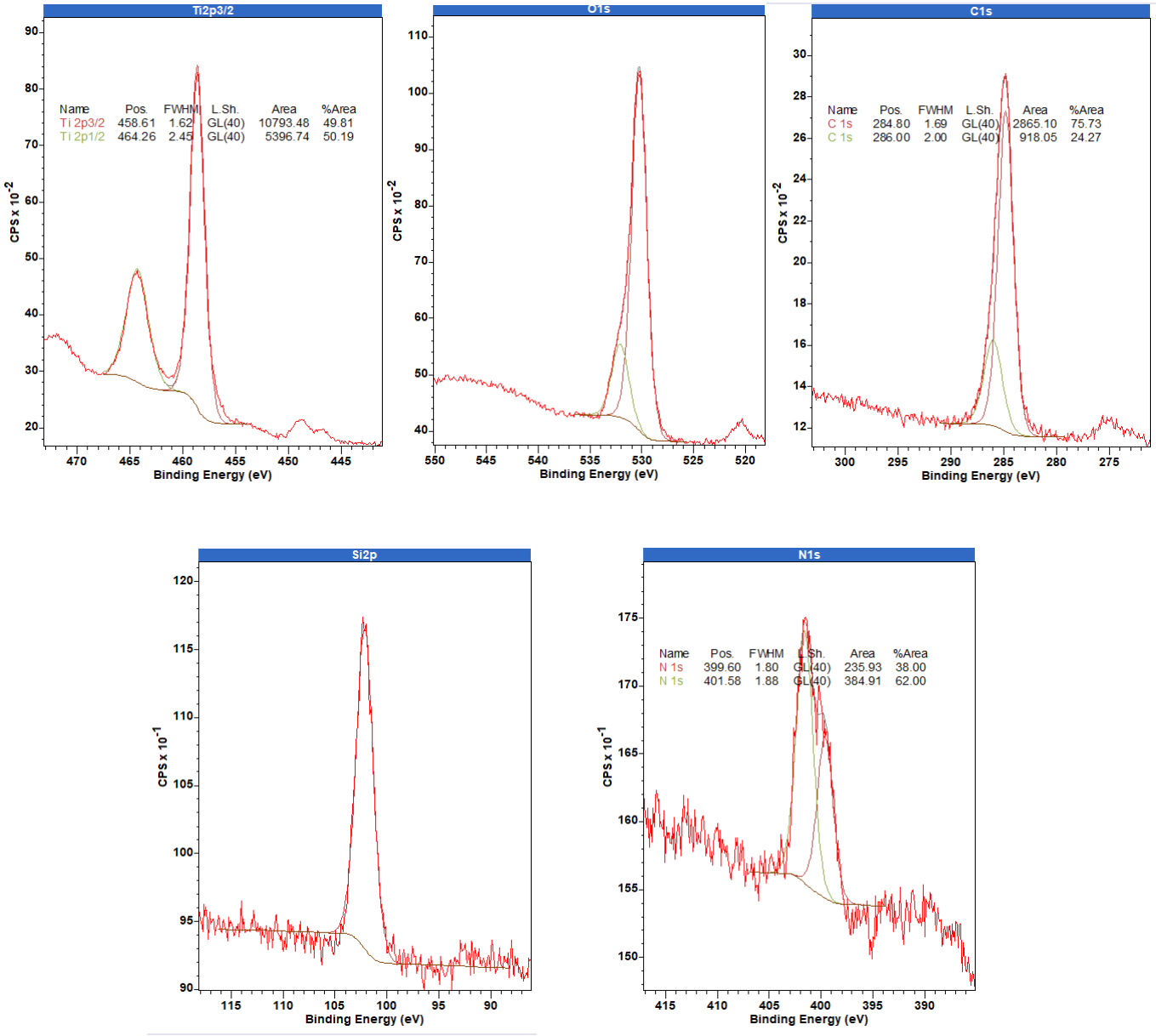


Figure S8(C) - XPS spectra with deconvoluted peaks of sample TTNT/APTES-1.9

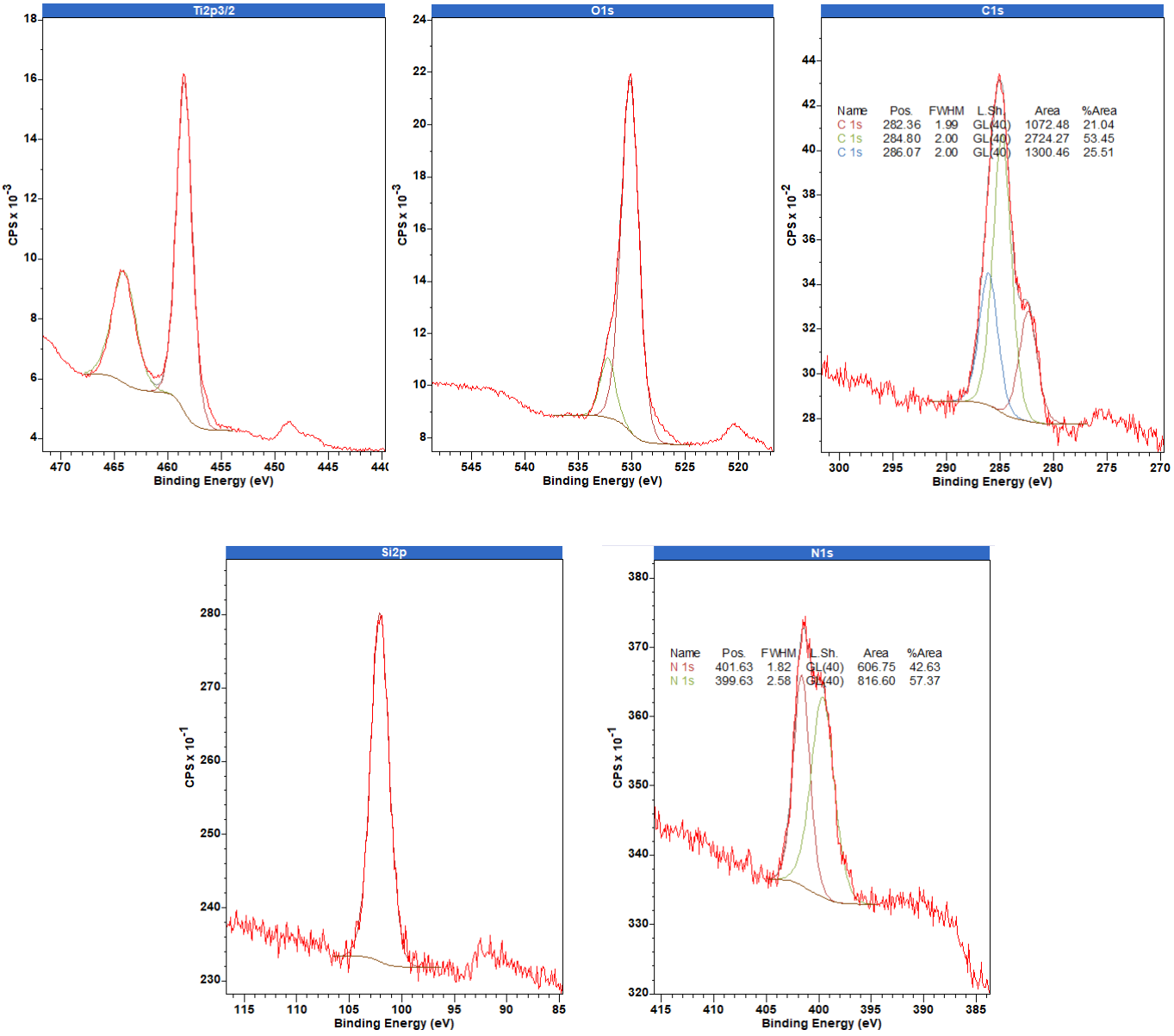


Figure S8(D) - XPS spectra with deconvoluted peaks of sample TTNT/APTES-2.7

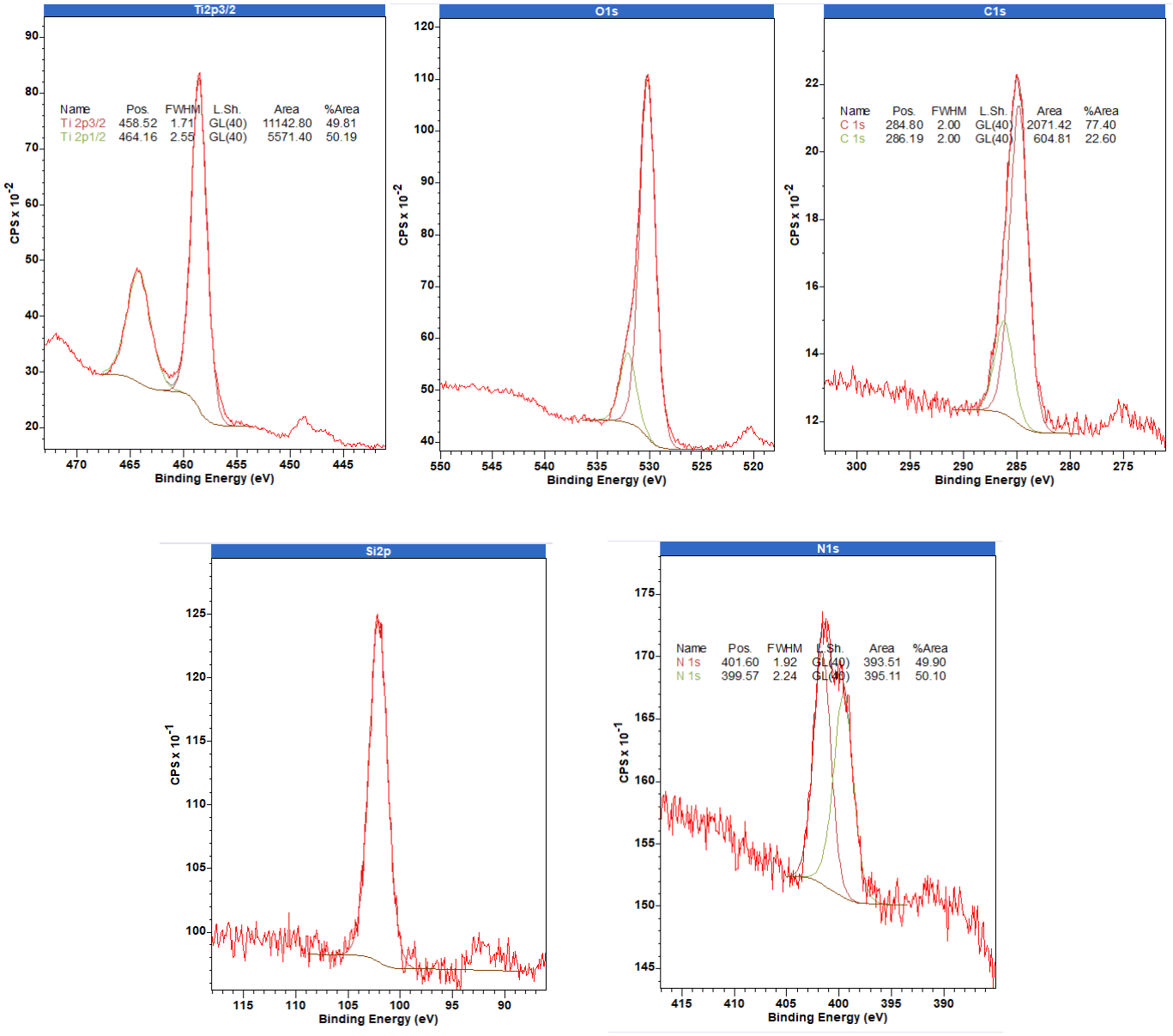


Figure S8(E) - XPS spectra with deconvoluted peaks of sample TTNT/APTES-3.1

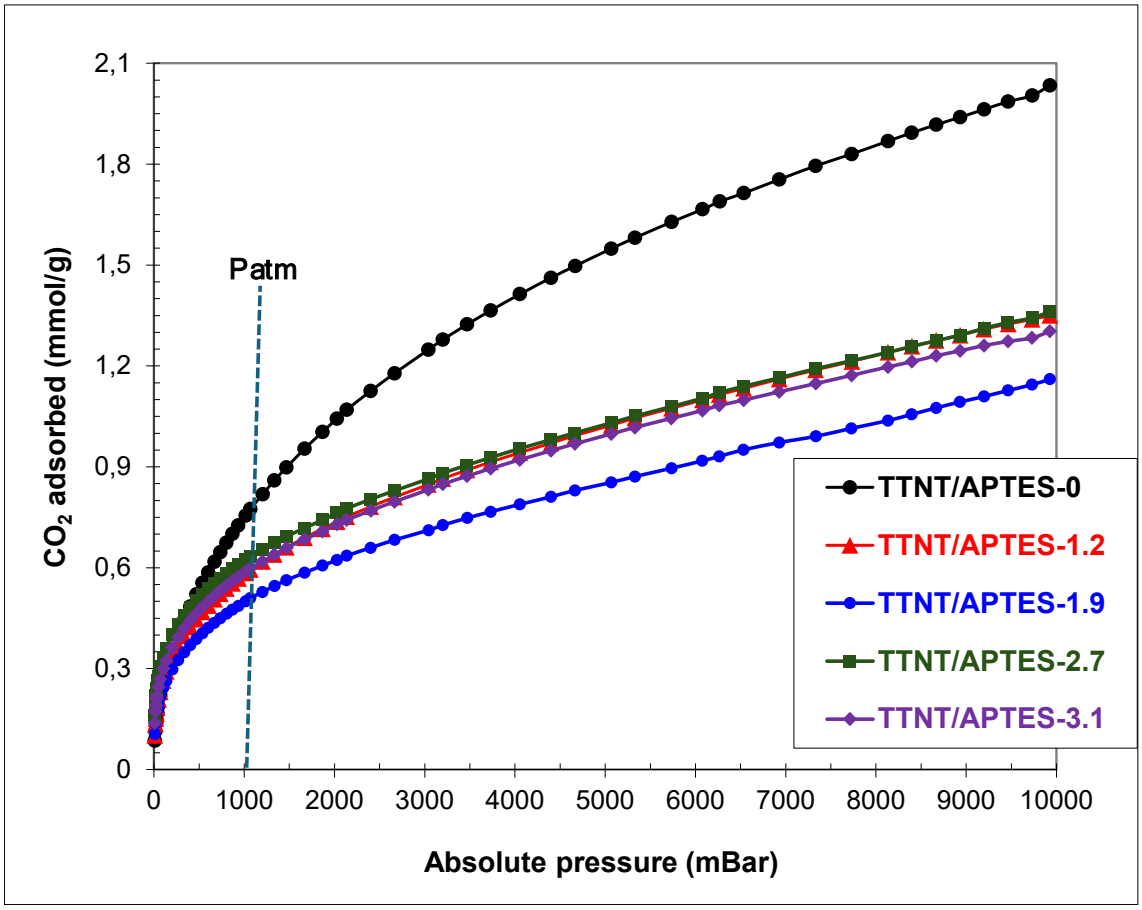


Figure S9 – Wide pressure range CO_2 adsorption isotherms (23°C) of the samples studied

Table S1: CO_2 adsorption capacities of the samples ($mmol \cdot g^{-1}$) at constant low pressures

Pressão Parcial (mBar)	**0.456 ***	**1**	**10**
TTNT/APTES-0	0.013	0.021	0.086
TTNT/APTES-1.2	0.026	0.038	0.111
TTNT/APTES-1.9	0.036	0.048	0.115
TTNT/APTES-2.7	0.054	0.073	0.176
TTNT/APTES-3.1	0.046	0.062	0.149

* *assumed partial pressure of CO_2 in atmosphere (DAC application)*

Calculation Memory (Mass Losses)

Molar Mass Ratio, OH/H_2O

In thermal dehydroxylation, OH groups combine with each other to form water molecules, and the mass loss obtained by TGA is related to this water released as vapor. A stoichiometric ratio must be applied to calculate the mass of OH lost as structural water from both TTNT surface and attached hydrolyzed APTES (if the case).

$$2OH -> H_2O$$

$$MMR_{OH/H2O} = \frac{2 * MM_{OH}}{MM_{H2O}}$$

Total concentration of -OH in pristine TTNT, C_{OH}

The total concentration of OH groups in TTNT before functionalization ($\boldsymbol{C}_{OH}$ in mol.g^{-1}) is estimated from its mass loss percentage (released as structural water) determined by TGA in the range 200-650°C ($ML^{-OH\ TOTAL}$ – see Table 3), according to the following equation, where MM_{H2O} is the molar mass of H_2O.

$$C_{OH} = \frac{ML^{-OH\ TOTAL}}{100 * MM_{H2O}} * MMR_{\frac{OH}{H2O}} = \frac{7.2}{100 * 18.01} * = 0{,}0075\ mol/g = 7.5\ \text{mmol/g}$$

OH per nm^2 in pristine TTNT

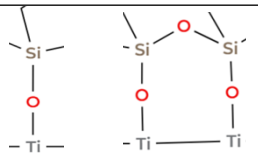
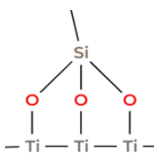
The corresponding amount of OH groups per nm^2 on the TTNT surface is calculated by multiplying the total concentration of OH ($\boldsymbol{C}_{OH}$) by the Avogadro's constant divided by the specific area of the TTNT ($BETSA = 271 m^2.g^{-1}$) converted to nm^2.g^{-1}.

$$\frac{\text{OH}}{\text{n}m^2} = \frac{C_{OH} * N_A}{BETSA_{TTNT}} * 10^{-18} = 16.77$$

Calculated mass loss due to dehydroxylation from non-used Ti-OH in grafted samples (*ML*$^{-OH\ TTNT}$)

The concentration of -OH due to dehydroxylation from remaining Ti-OH in TTNT surface is calculated by subtracting the mole concentration of incorporated APTES combined with surface hydroxyls through n bonds ($\boldsymbol{N}_{bonds}.\boldsymbol{C}_{APTES}$ in mol.g^{-1}) from the total concentration of -OH in the unfunctionalized sample ($\boldsymbol{C}_{OH}$ in mol.g^{-1}). This is multiplied by the Molar Mass of the hydroxyl group (MM_{-OH}) divided by the Molar Mass Ratio $MMR_{OH/H2O}$ to obtain the corresponding relative mass loss of water released due to dehydroxylation of Ti-OH groups ($ML^{-OH\ TTNT}$), which is expressed in percentage after multiplying by 100. $\boldsymbol{C}_{APTES}$ has been determined by chemical analyses (see Table 2) with the value of 1.05*10^{-3} mol.g^{-1} been considered for the calculations.

$$ML^{-OH\ TTNT} = \frac{MM_{-OH} * (C_{OH} - (N_{bonds} * C_{APTES}))}{MMR_{OH/H2O}} * 100$$

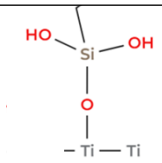
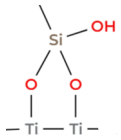
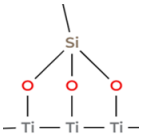
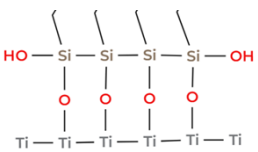
N bonds	Bond configuration	*ML*$^{-OH\ TTNT}$ (%)
1		5.9
2		4.9
3		4.0

Calculated mass loss due to dehydroxylation from Si-OH groups in grafted samples (*ML-OH APTES*)

It refers to the concentration of -OH due to dehydroxylation from remaining uncondensed Si-OH in the attached APTES molecules on grafted TTNT, which is directly related to C_{APTES}, through the following equation, also depending on the binding configuration (Nbonds).

$$ML^{-OH\ APTES} = (3 - N_{bonds}) * \frac{MM_{-OH} * C_{APTES}}{MMR_{OH/H2O}} * 100$$

In the case of non-hydrolyzed APTES and in the case of complete hydrolysis with tridentate configuration (3 bonds), the value is zero. In the crosslinking monodentate configuration the *ML-OH APTES* is certainly lower than the corresponding anchoring configuration since most of the Si-OH groups underwent internal condensation, but terminal hydroxyls may have remained. *ML-OH APTES* may be negligible if polymeric crosslinking (long chains) takes place.

N bonds	Bond configuration	*ML-OH APTES* (%)
1		1.9
2		0.9
3		0.0
1 (crosslinked with terminal -OH)		0.0 – 0.9 *(nearly zero in long crosslinking chain)*

Calculated mass loss due to thermal degradation of attached propylamine group in grafted samples (ML^{-PrNH2})

It refers to the concentration of propylamine groups attached on grafted TTNT, which is directly related to the mole concentration of incorporated APTES (C_{APTES}), through the following equation that includes conversion to a percentage.

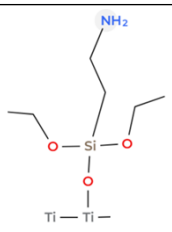
$$ML^{-PrNH2} = MM_{-PrNH2} * C_{APTES} * 100 = 58.102 * (1.0$$

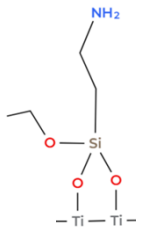
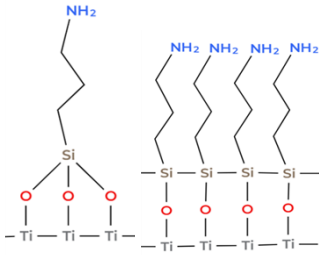
The value was calculated as 6.1% and it is the same for all binding configurations as long as the concentration of incorporated APTES is constant.

Calculated mass loss due to thermal degradation of ethoxy groups from APTES in grafted samples (ML^{-OEt})

The mass loss ascribed to thermal degradation of ethoxy groups in non-hydrolyzed and partially hydrolyzed APTES is also directly related to the mole concentration of incorporated APTES (C_{APTES}), through the following equation that includes conversion to a percentage and also depends on the binding configuration (Nbonds). In cases with complete hydrolysis of APTES the value of ML(-OEt) is null.

$$ML^{-OEt} = (3 - Nbonds) * MM_{-OEt} * C_{APTES} * 100$$

N bonds	Bond configuration	ML^{-OEt} (%)
1		9.5

2		4.9
3 1 (crosslinked)		0.0

Total mass loss

$$ML^{200-650} = ML^{-OH\ TTNT} + ML^{-OH\ APTES} + ML^{-PrNH2} + ML^{-OEt}$$

List of Symbols

$ML^{200-650}$= Total mass loss between 200 ºC and 650 ºC (%)

ML^{X} = Mass loss of species X (%)

MM_X = Molar Mass of species X in grams per mol

$MMR_{OH/H2O}$ = Molar Mass Ratio between OH and H_2O in the water formation, dimensionless

OH/nm^2 = Amount of OH groups per nm^2 on the surface of TTNT

C_0 = Total concentration of OH groups in TTNT before functionalization in mol per gram

C_{APTES} = Concentration of incorporated APTES in mol per gram

N_{bonds} = Number of bonds between APTES and the TT