

N-Doped TiO₂-Nb₂O₅ Sol–Gel Catalysts: Synthesis, Characterization, Adsorption Capacity, Photocatalytic and Antioxidant Activity

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1. Thermogravimetric analysis

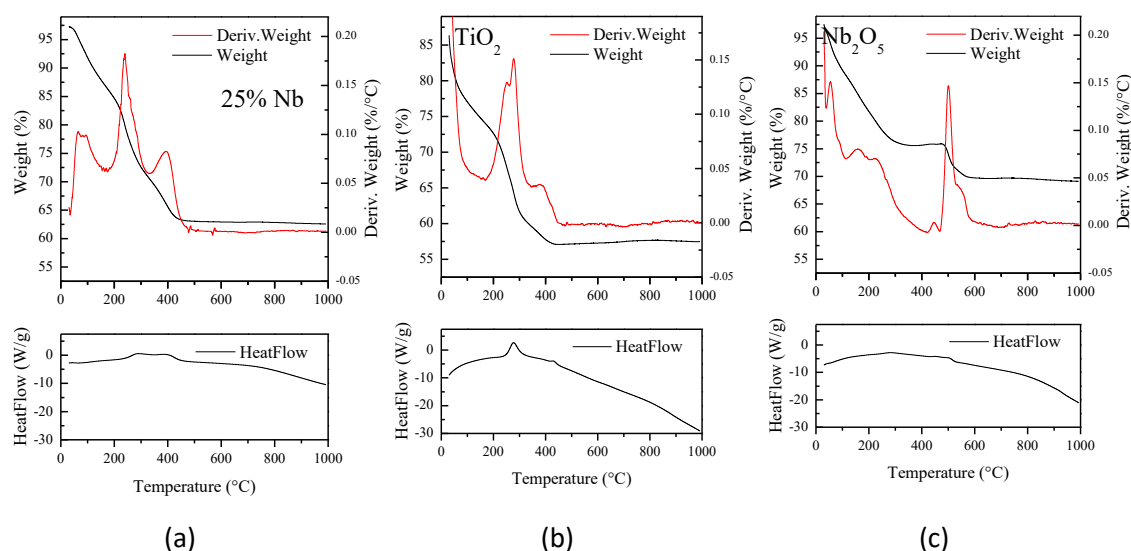


Figure S1 – Thermogravimetric analysis results of samples: (a) 25%Nb catalyst, not calcined; (b) TiO₂ catalyst, not calcined; (c) Nb₂O₅ catalyst, not calcined.

2. Experimental design data

2.1. Four-factors factorial design (2⁴) – SA Photocatalysis

Considering the variables with their real values, and $R^2=0.96405$ e $R^2_{adj}=0.91461$.

Table S1 – Effects estimates and model coefficients of the four-factor experimental design (2⁴). Significant effects are highlighted in bold.

	Effect	Std.Err.	t(3)	p	-95.%	+95.%	Coeff.	Std.Err.	-95.%	+95.%
Mean/Interc.	40.7894	0.950971	42.8924	0.000028	37.7630	43.8158	40.7894	0.950971	37.7630	43.81584
Curvatr.	6.6665	4.252873	1.5675	0.214985	-6.8680	20.2011	3.3333	2.126436	-3.4340	10.10053
(1)T (C)	-20.8075	1.901942	-10.9401	0.001635	-26.8603	-14.7547	-10.4038	0.950971	-13.4302	-7.37734
(2)%Nb	-15.9425	1.901942	-8.3822	0.003561	-21.9953	-9.8897	-7.9713	0.950971	-10.9977	-4.94484
(3)NH ₄ OH	5.5962	1.901942	2.9424	0.060394	-0.4566	11.6491	2.7981	0.950971	-0.2283	5.82453
(4)pH	15.2366	1.901942	8.0111	0.004060	9.1838	21.2894	7.6183	0.950971	4.5919	10.64472
1 by 2	16.9949	1.901942	8.9355	0.002957	10.9420	23.0477	8.4974	0.950971	5.4710	11.52384
1 by 3	-7.0646	1.901942	-3.7144	0.033938	-13.1174	-1.0117	-3.5323	0.950971	-6.5587	-0.50587
1 by 4	9.7367	1.901942	5.1194	0.014427	3.6839	15.7896	4.8684	0.950971	1.8420	7.89479
2 by 3	-4.7499	1.901942	-2.4974	0.087908	-10.8027	1.3029	-2.3750	0.950971	-5.4014	0.65146
2 by 4	3.9528	1.901942	2.0783	0.129214	-2.1000	10.0056	1.9764	0.950971	-1.0500	5.00281
3 by 4	0.5557	1.901942	0.2922	0.789185	-5.4971	6.6086	0.2779	0.950971	-2.7486	3.30428

Table S2 – Effects estimates and model coefficients of the four-factor experimental design (2⁴). Significant effects are highlighted in bold.

	SS	df	MS	F	p
Curvatr.	35.554	1	35.554	2.4572	0.214985
(1)Temperatura	1731.809	1	1731.809	119.6866	0.001635
(2)%Nb	1016.654	1	1016.654	70.2617	0.003561
(3)NH ₄ OH	125.272	1	125.272	8.6576	0.060394
(4)pH	928.617	1	928.617	64.1773	0.004060
1 by 2	1155.301	1	1155.301	79.8436	0.002957
1 by 3	199.632	1	199.632	13.7967	0.033938
1 by 4	379.217	1	379.217	26.2080	0.014427
2 by 3	90.247	1	90.247	6.2370	0.087908
2 by 4	62.498	1	62.498	4.3193	0.129214
3 by 4	1.235	1	1.235	0.0854	0.789185
Lack of Fit	170.146	5	34.029	2.3518	0.256358
Pure Error	43.409	3	14.470		
Total SS	5939.590	19			

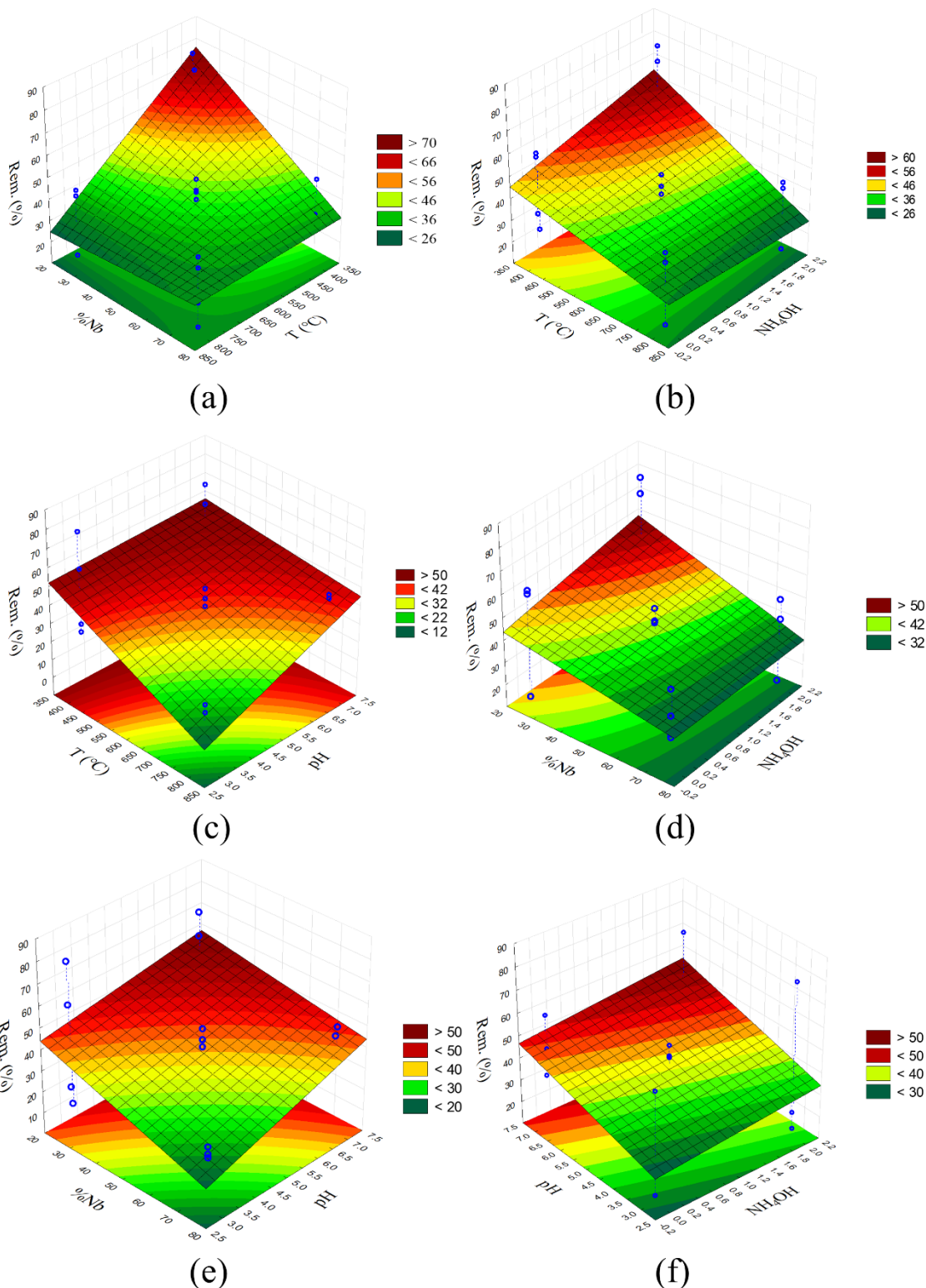


Figure S2 – Response surfaces – linear model - for SA degradation (%) obtained in the four-factor experimental design (2^4), using catalysts containing between 25 and 75% of Nb – molecular basis, in relation to the total number of mols of metals. SA removal (%) in the function of (a) %Nb and T(°C); (b) T(°C) and NH₄OH; (c) T(°C) and pH; (d) %Nb and NH₄OH; (e) %Nb and pH; (f) pH and NH₄OH. Plotted surface $R^2=0.96405$. Variables not indicated in each graph were kept at a fixed value corresponding to their center point value (0 in coded variables).

2.2. Three-factors and three levels experimental design (3³) – SA Photocatalysis

Table S3 – Photocatalytic results of the 3³ experimental design.

Real Variables				Coded Variables				Response
%Nb	T	NH ₄ OH	pH	%Nb	T	NH ₄ OH	pH	Rem(%) 30 min
TiO ₂	400	0	3	-1	0	-1	-1	42.77%
TiO ₂	400	0	5	-1	0	-1	0	72.86%
TiO ₂	400	0	7	-1	0	-1	1	68.56%
TiO ₂	400	1	3	-1	0	0	-1	43.86%
TiO ₂	400	1	5	-1	0	0	0	61.95%
TiO ₂	400	1	7	-1	0	0	1	62.66%
TiO ₂	400	2	3	-1	0	1	-1	37.15%
TiO ₂	400	2	5	-1	0	1	0	69.66%
TiO ₂	400	2	7	-1	0	1	1	57.84%
12.5	400	0	3	0	0	-1	-1	43.92%
12.5	400	0	5	0	0	-1	0	51.65%
12.5	400	0	7	0	0	-1	1	48.87%
12.5	400	1	3	0	0	0	-1	50.02%
12.5	400	1	5	0	0	0	0	57.18%
12.5	400	1	5	0	0	0	0	54.73%
12.5	400	1	5	0	0	0	0	57.25%
12.5	400	1	5	0	0	0	0	52.63%
12.5	400	1	7	0	0	0	1	50.02%
12.5	400	2	3	0	0	1	-1	45.12%
12.5	400	2	5	0	0	1	0	48.59%
12.5	400	2	7	0	0	1	1	44.35%
25	400	0	3	1	0	-1	-1	49.75%
25	400	0	5	1	0	-1	0	45.41%
25	400	0	7	1	0	-1	1	45.03%
25	400	1	3	1	0	0	-1	59.88%
25	400	1	5	1	0	0	0	49.03%
25	400	1	7	1	0	0	1	52.45%
25	400	2	3	1	0	1	-1	41.81%
25	400	2	5	1	0	1	0	54.18%
25	400	2	7	1	0	1	1	47.65%

Table S4 – ANOVA table of the 3³ experimental design. Significant effects are highlighted in bold

	SS	df	MS	F	p
Regression	0.205368	18	0.011409333	8.736697993	0.000386
(1)% Nb(L)	0.028905	1	0.028905	58.97732	0.004587
% Nb(Q)	0.012698	1	0.012698	25.90843	0.014656
(2)NH ₄ OH(L)	0.002807	1	0.002807	5.72772	0.096457
NH₄OH(Q)	0.007715	1	0.007715	15.74110	0.028612
(3)pH(L)	0.022149	1	0.022149	45.19211	0.006719
pH(Q)	0.035076	1	0.035076	71.56830	0.003467
1L by 2L	0.004405	1	0.004405	8.98720	0.057767
1L by 2Q	0.007163	1	0.007163	14.61524	0.031510
1Q by 2L	0.000031	1	0.000031	0.06253	0.818682
1Q by 2Q	0.002043	1	0.002043	4.16771	0.133854
1L by 3L	0.042717	1	0.042717	87.15880	0.002602
1L by 3Q	0.025294	1	0.025294	51.61040	0.005557
1Q by 3L	0.007121	1	0.007121	14.53040	0.031748
1Q by 3Q	0.000683	1	0.000683	1.39454	0.322737
2L by 3L	0.000001	1	0.000001	0.00123	0.974245
2L by 3Q	0.002503	1	0.002503	5.10626	0.108956
2Q by 3L	0.002349	1	0.002349	4.79310	0.116329
2Q by 3Q	0.005363	1	0.005363	10.94359	0.045456
Lack of Fit	0.012895	8	0.001612	3.28874	0.178122
Pure Error	0.001470	3	0.000490		
Total SS	0.219733	29			

Table S5 – Effects Estimate. Variables as coded variables of the 3³ experimental design. Significant effects are highlighted in bold

	Effect	Std.Err.	t(3)	p	-95.%	+95.%	Coeff.	Std.Err.	-95.%	+95.%
Mean/Interc.	0.519943	0.004184	124.2769	0.000001	0.506628	0.533257	0.519943	0.004184	0.506628	0.533257
(1)% Nb(L)	-0.080146	0.010436	-7.6797	0.004587	-0.113358	-0.046933	-0.040073	0.005218	-0.056679	-0.023467
% Nb(Q)	-0.044330	0.008709	-5.0900	0.014656	-0.072046	-0.016613	-0.022165	0.004355	-0.036023	-0.008307
(2)NH ₄ OH(L)	-0.024976	0.010436	-2.3933	0.096457	-0.058189	0.008236	-0.012488	0.005218	-0.029094	0.004118
NH₄OH(Q)	0.034554	0.008709	3.9675	0.028612	0.006837	0.062270	0.017277	0.004355	0.003419	0.031135
(3)pH(L)	0.070157	0.010436	6.7225	0.006719	0.036944	0.103369	0.035078	0.005218	0.018472	0.051684
pH(Q)	0.073678	0.008709	8.4598	0.003467	0.045961	0.101394	0.036839	0.004355	0.022981	0.050697
1L by 2L	0.038317	0.012782	2.9979	0.057767	-0.002359	0.078994	0.019159	0.006391	-0.001180	0.039497
1L by 2Q	0.042317	0.011069	3.8230	0.031510	0.007090	0.077544	0.021159	0.005535	0.003545	0.038772
1Q by 2L	0.002768	0.011069	0.2501	0.818682	-0.032459	0.037995	0.001384	0.005535	-0.016229	0.018997
1Q by 2Q	0.018118	0.008875	2.0415	0.133854	-0.010126	0.046363	0.009059	0.004438	-0.005063	0.023181
1L by 3L	-0.119327	0.012782	-9.3359	0.002602	-0.160004	-0.078650	-0.059664	0.006391	-0.080002	-0.039325
1L by 3Q	-0.079521	0.011069	-7.1840	0.005557	-0.114748	-0.044294	-0.039761	0.005535	-0.057374	-0.022147
1Q by 3L	-0.042194	0.011069	-3.8119	0.031748	-0.077421	-0.006967	-0.021097	0.005535	-0.038711	-0.003484
1Q by 3Q	-0.010481	0.008875	-1.1809	0.322737	-0.038725	0.017764	-0.005240	0.004438	-0.019362	0.008882
2L by 3L	-0.000448	0.012782	-0.0350	0.974245	-0.041124	0.040229	-0.000224	0.006391	-0.020562	0.020114
2L by 3Q	0.025013	0.011069	2.2597	0.108956	-0.010214	0.060240	0.012506	0.005535	-0.005107	0.030120
2Q by 3L	-0.024234	0.011069	-2.1893	0.116329	-0.059461	0.010993	-0.012117	0.005535	-0.029730	0.005497
2Q by 3Q	-0.029360	0.008875	-3.3081	0.045456	-0.057604	-0.001115	-0.014680	0.004438	-0.028802	-0.000558

2.3. Two-factors and three levels experimental design (3²) – MB adsorption

Table S6 – ANOVA table of the 3² experimental design. Significant effects are highlighted in bold

	SS	df	MS	F	p
(1) %Nb(L)	9063.69	1	9063.689	16482.85	0.000061
%Nb(Q)	2822.22	1	2822.215	5132.37	0.000195
(2) NH₄OH (L)	117.84	1	117.844	214.31	0.004634
NH₄OH (Q)	13.04	1	13.035	23.71	0.039690
1L by 2L	53.02	1	53.017	96.41	0.010213
1L by 2Q	109.15	1	109.152	198.50	0.005000
1Q by 2L	13.30	1	13.302	24.19	0.038940
1Q by 2Q	35.20	1	35.200	64.01	0.015265
Pure Error	1.10	2	0.550		
Total SS	13081.23	10			

Table S7 – Effects Estimate. Variables as coded variables of the 3³ experimental design. Significant effects are highlighted in bold

	Effect	Std.Err.	t(2)	p	-95.%	+95.%	Coeff.	Std.Err.	-95.%	+95.%
Mean/Interc.	57.23761	0.237850	240.6458	0.000017	56.21423	58.26100	57.23761	0.237850	56.21423	58.26100
(1) %Nb (L)	77.73326	0.605467	128.3856	0.000061	75.12814	80.33837	38.86663	0.302734	37.56407	40.16919
%Nb(Q)	34.67066	0.483953	71.6405	0.000195	32.58838	36.75294	17.33533	0.241977	16.29419	18.37647
(2) NH₄OH (L)	8.86355	0.605467	14.6392	0.004634	6.25843	11.46866	4.43177	0.302734	3.12922	5.73433
NH₄OH (Q)	2.35626	0.483953	4.8688	0.039690	0.27398	4.43855	1.17813	0.241977	0.13699	2.21927
1L by 2L	7.28129	0.741543	9.8191	0.010213	4.09069	10.47189	3.64064	0.370771	2.04534	5.23595
1L by 2Q	9.04786	0.642195	14.0890	0.005000	6.28472	11.81101	4.52393	0.321098	3.14236	5.90550
1Q by 2L	3.15854	0.642195	4.9184	0.038940	0.39540	5.92169	1.57927	0.321098	0.19770	2.96084
1Q by 2Q	3.73272	0.466544	8.0008	0.015265	1.72535	5.74010	1.86636	0.233272	0.86267	2.87005

3. Adsorption isotherms

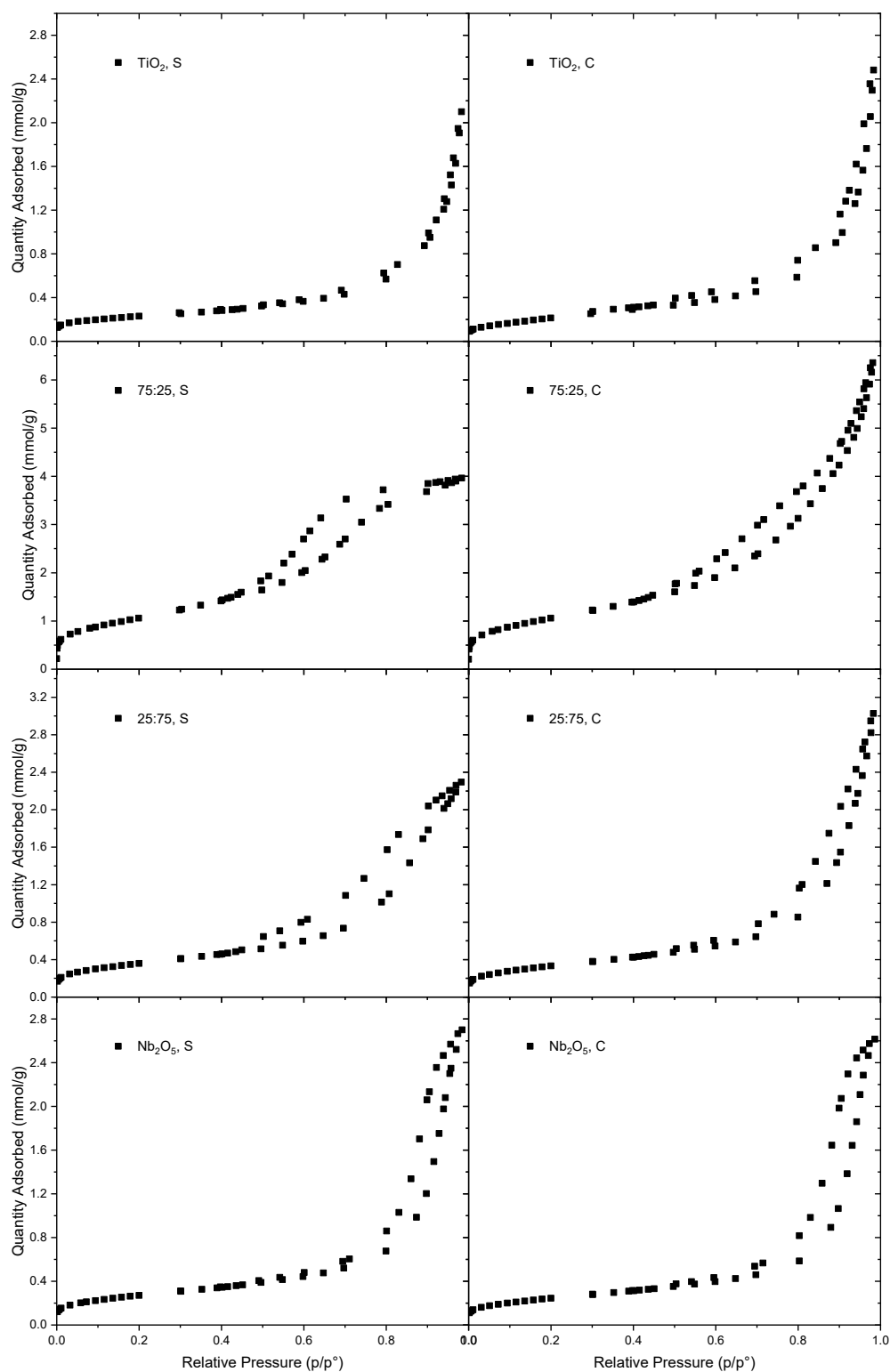


Figure S3 – Adsorption isotherms of the samples calcined at 400°C. Percentages of Ti:Nb. S=0 mol of NH₄OH. C=2 mol of NH₄OH.

4. Photoacoustic spectroscopy results

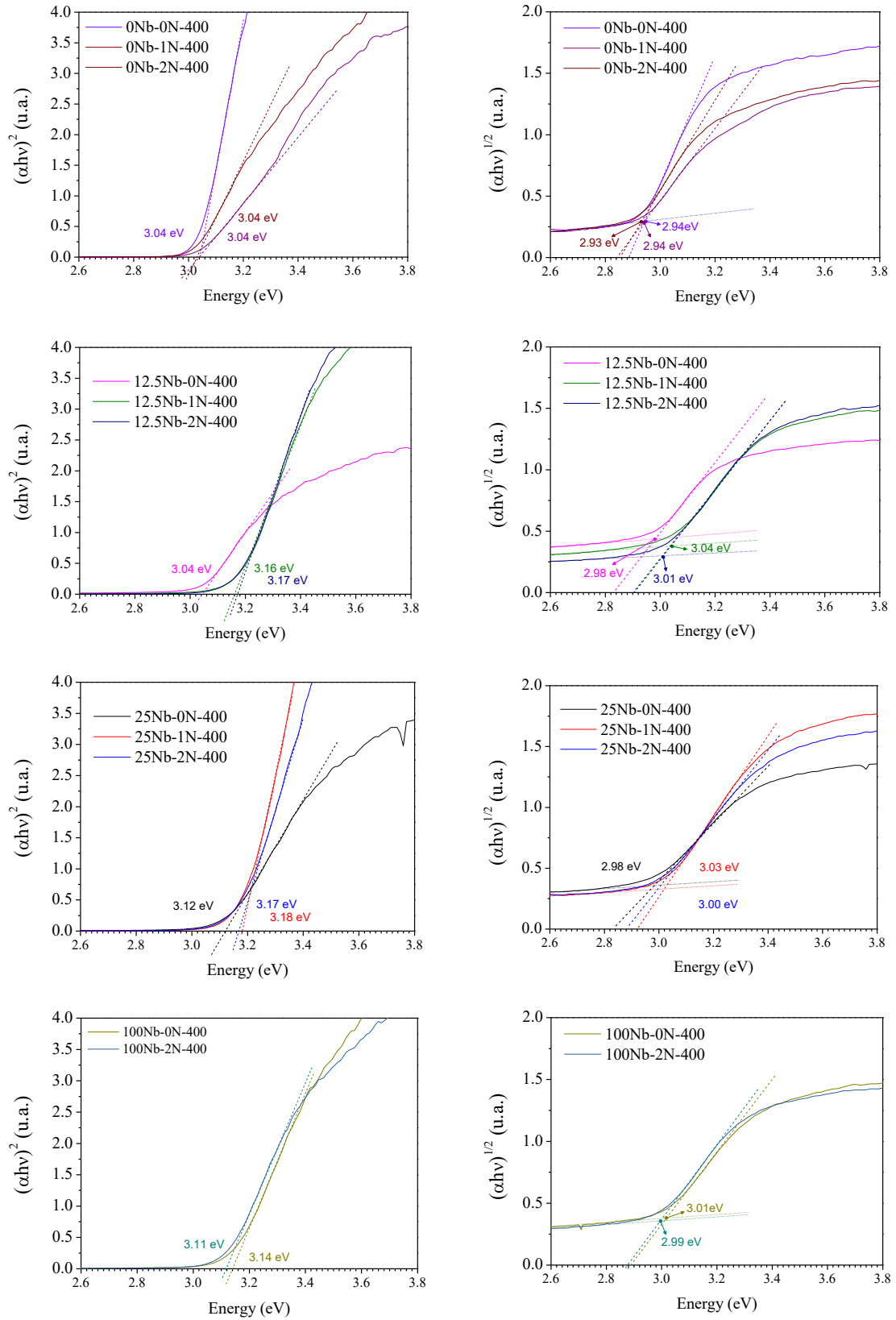


Figure S4 – Tauc plots for direct and indirect band gap estimations. Data obtained from photoacoustic spectroscopy analysis.