Supporting Information

Control of Pore Size in Ordered Mesoporous Carbon-Silica by Hansen Solubility Parameters of Swelling Agent

Meeta Trivedi,[1] Fang Peng,[1†] Xuhui Xia,[1] Pablo I. Sepulveda-Medina,[1] Bryan D. Vogt[2*]

[1]Department of Polymer Engineering, University of Akron, Akron, OH 44325
[2]Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802

[†]Present address: Eastman Chemical, 4210 The Great Road, Fieldale, VA 24089

*To whom correspondence should be addressed: bdv5051@psu.edu

Table S1. Characteristics of the swelling agents examined

Swelling Agent	Log K_{OW}	P^{VAP} @ 25°C (mbar)	Hanson Solubility Parameters[a] $(MPa)^{1/2}$ δ_t	δ_d	δ_p	δ_H
Glyceryl triacetate	0.5	0.00320	19.37	16.5	4.5	9.1
Mesitylene	3.42	2.67	18.01	18.0	0.0	0.6
Dioctyl phthalate	8.1	1.333×10^{-7}	18.28	16.6	7.0	3.1
Triisononyl trimellitate	12.5	0.600	17.69	16.6	5.7	2.2

[a] components include δ_t (total solubility parameter), δ_d (dispersive component), δ_p (polar component), and δ_h (hydrogen bonding component)

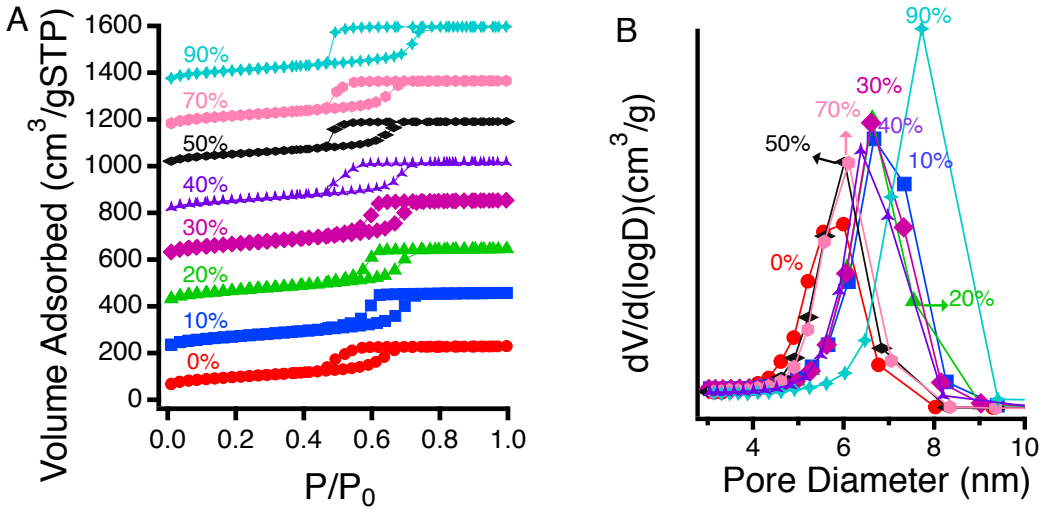

Figure S1. N_2 adsorption-desorption isotherm for mesoporous carbon silica when using TMB as the swelling agent from 0 wt% to 90 wt% (relative to F127). (B) The adsorption isotherms were used to calculate the pore size distribution with the DOP concentrations of (●) 0 wt%, (■) 10 wt%, (▲) 20 wt%, (◆) 30 wt %, (▲)40 wt%, (♦)50 wt %, (⬢) 70 wt %, and (✦) 90 wt %. The isotherms are vertically offset by arbitrary number for clarity

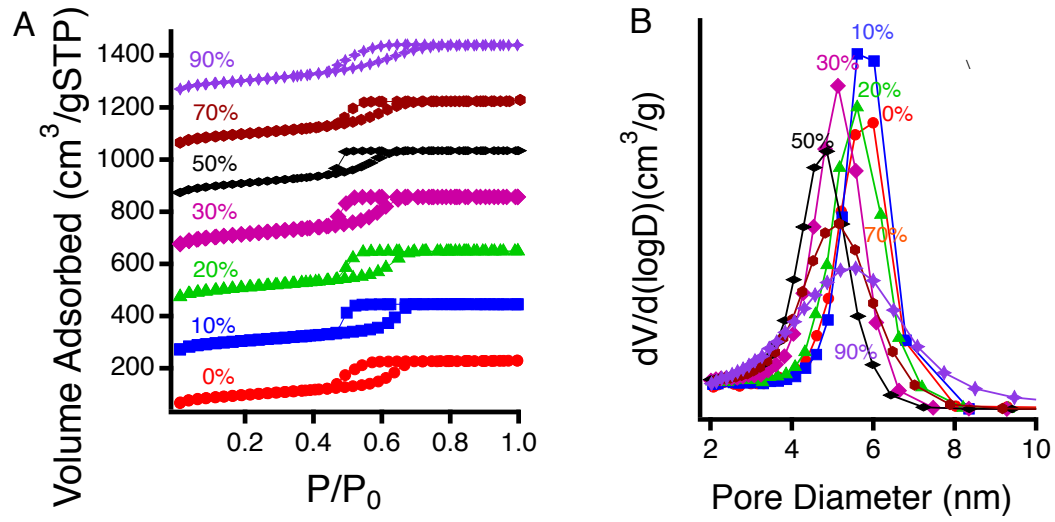

Figure S2. N_2 adsorption-desorption isotherm for mesoporous carbon silica when using GTA as the swelling agent from 0 wt% to 90 wt% (relative to F127). (B) The adsorption isotherms were used to calculate the pore size distribution with the DOP concentrations of (●) 0 wt%, (■) 10 wt%, (▲) 20 wt%, (◆) 30 wt %, (♦) 50 wt %, (⬢) 70 wt %, and (✦) 90 wt %. The isotherms are vertically offset by arbitrary number for clarity

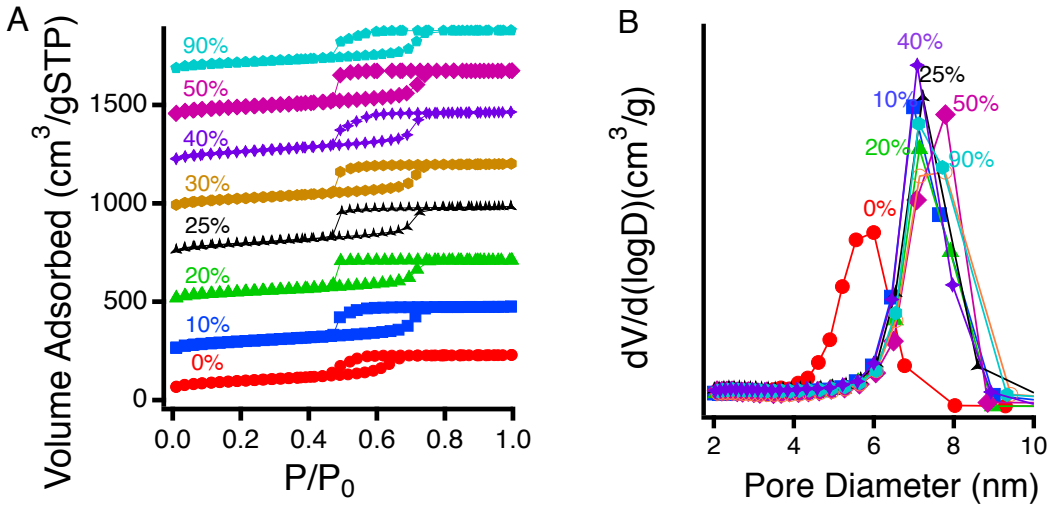

Figure S3. N_2 adsorption-desorption isotherm for mesoporous carbon silica when using TITM as the swelling agent from 0 wt% to 90 wt% (relative to F127). (B) The adsorption isotherms were used to calculate the pore size distribution with the DOP concentrations of (●) 0 wt%, (■) 10 wt%, (▲) 20 wt%, (▲) 25wt%,(⬢) 30 wt %, (✦)40 wt %, (⬢) 50 wt %, and (⬟) 90 wt %. The isotherms are vertically offset by arbitrary number for clarity

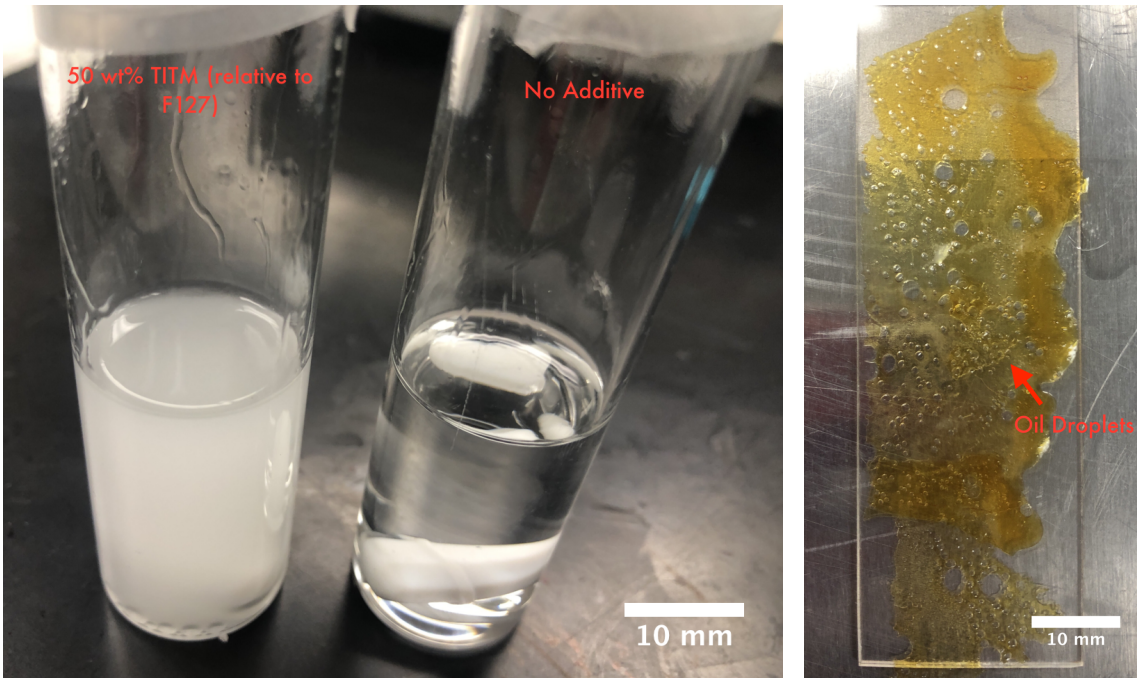

Figure S4. (A) Image of precursor solution showing cloudy appearance of solution for 50 wt% TITM (left vial) and the clear solution when there was no added swelling agent (right vial). The solutions with other swelling agents appear similar to that without any swelling agent (right vial) . (B) Oil drops can be observed on the surface of the crosslinked resol-silica-Pluronic F127 film that was fabricated with 50 wt% TITM. The TITM that phase separated from the film does not evaporate through the thermopolymerization of the resol at 100 °C. This film was cast on quartz slide to improve the visualization of the drops, but these drops are also observed for the films cast on PET.

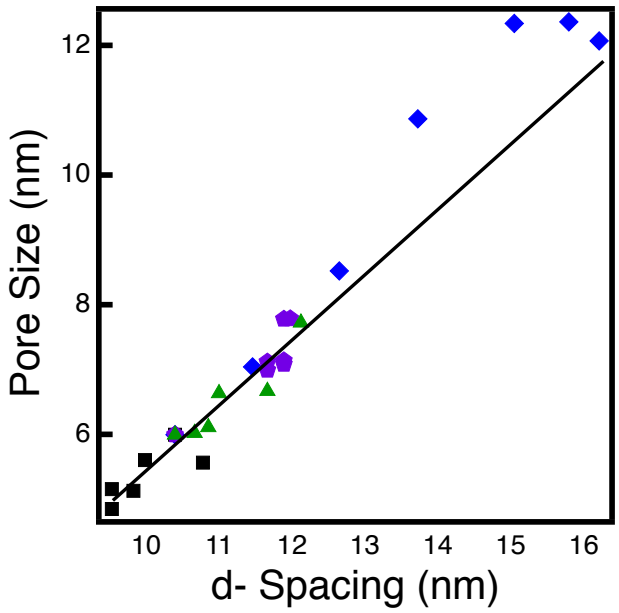

Figure S5. Relationship between pore size from N_2 adsorption isotherms and d-spacing from SAXS for the mesoporous carbon silica fabricated using (◆) DOP, (▲) TMB, (■) GTA and (⬟) TITM.

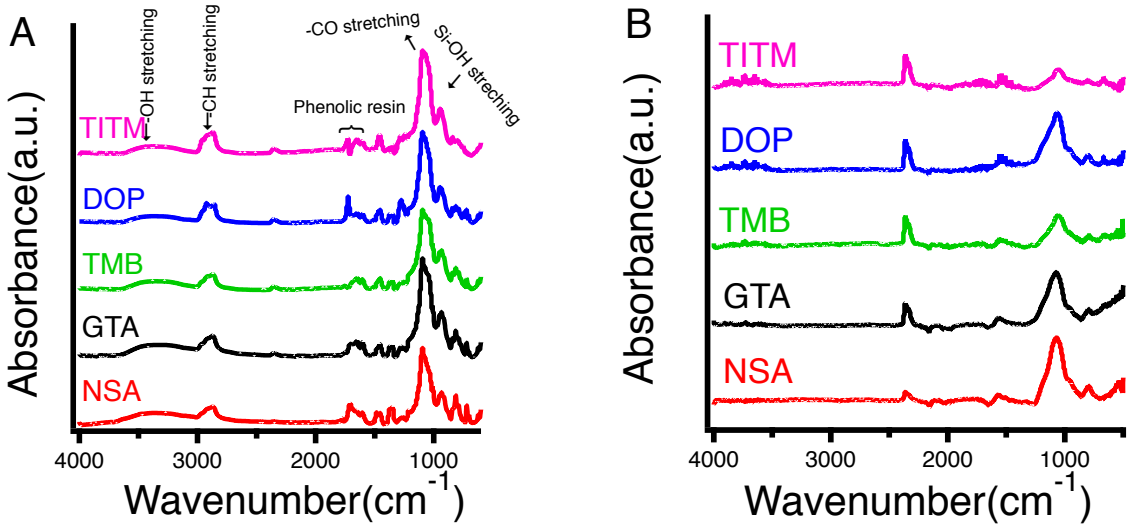

Figure S6. Comparison of FTIR spectra of the films fabricated using 50 wt% (relative to F127) GTA, TMB, DOP and TITM for (A) as made samples (crosslinked) and B) carbonized samples (800°C). A reference sample without swelling agent (NSA) was also examined for comparison. There are limited difference in the spectra as expected.

Table S2. Elemental composition of the S-doped mesoporous carbon silica prepared without swelling agent (NSA) and with 50 wt% swelling agents as determined from XPS survey data.

Swelling agent	S (at%)	Si (at%)	O (at%)	C (at%)
NSA	2.5	10.1	21.6	65.7
GTA	2.2	10.9	23.6	63.3
TMB	2.3	10.7	22.5	64.5
DOP	2.1	11.0	23.9	63.1
TITM	2.3	10.6	23.1	64.0

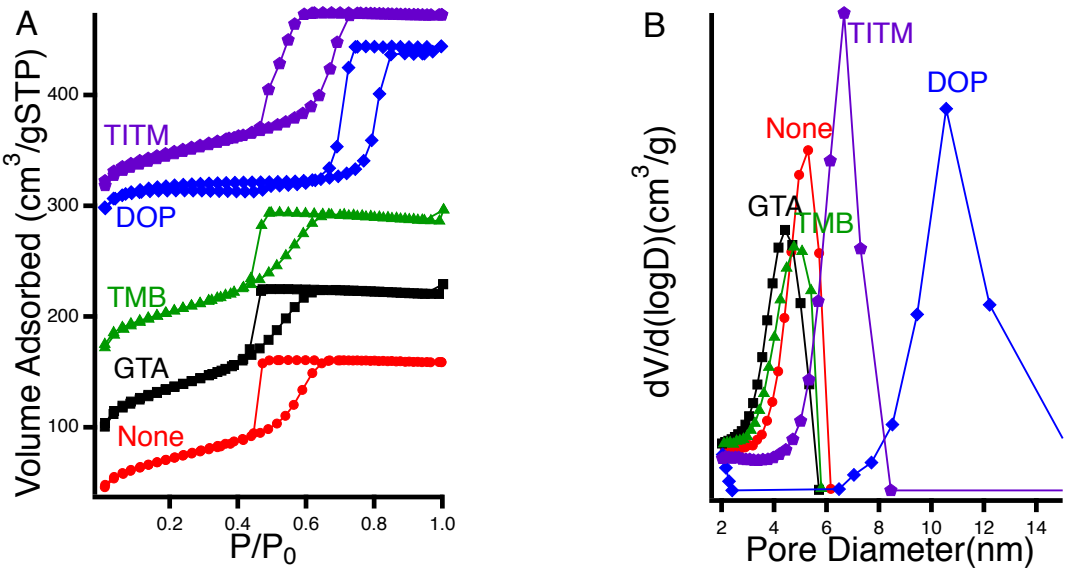

Figure S7. (a) N_2 adsorption-desorption isotherm for sulfur-doped mesoporous carbon silica fabricated without swelling agent (NSA)(●) and using 50 wt% (relative to F127) GTA(■), TMB(▲), DOP(◆), and TITM(⬟). (b) The adsorption isotherms were used to calculate the pore size distributions.

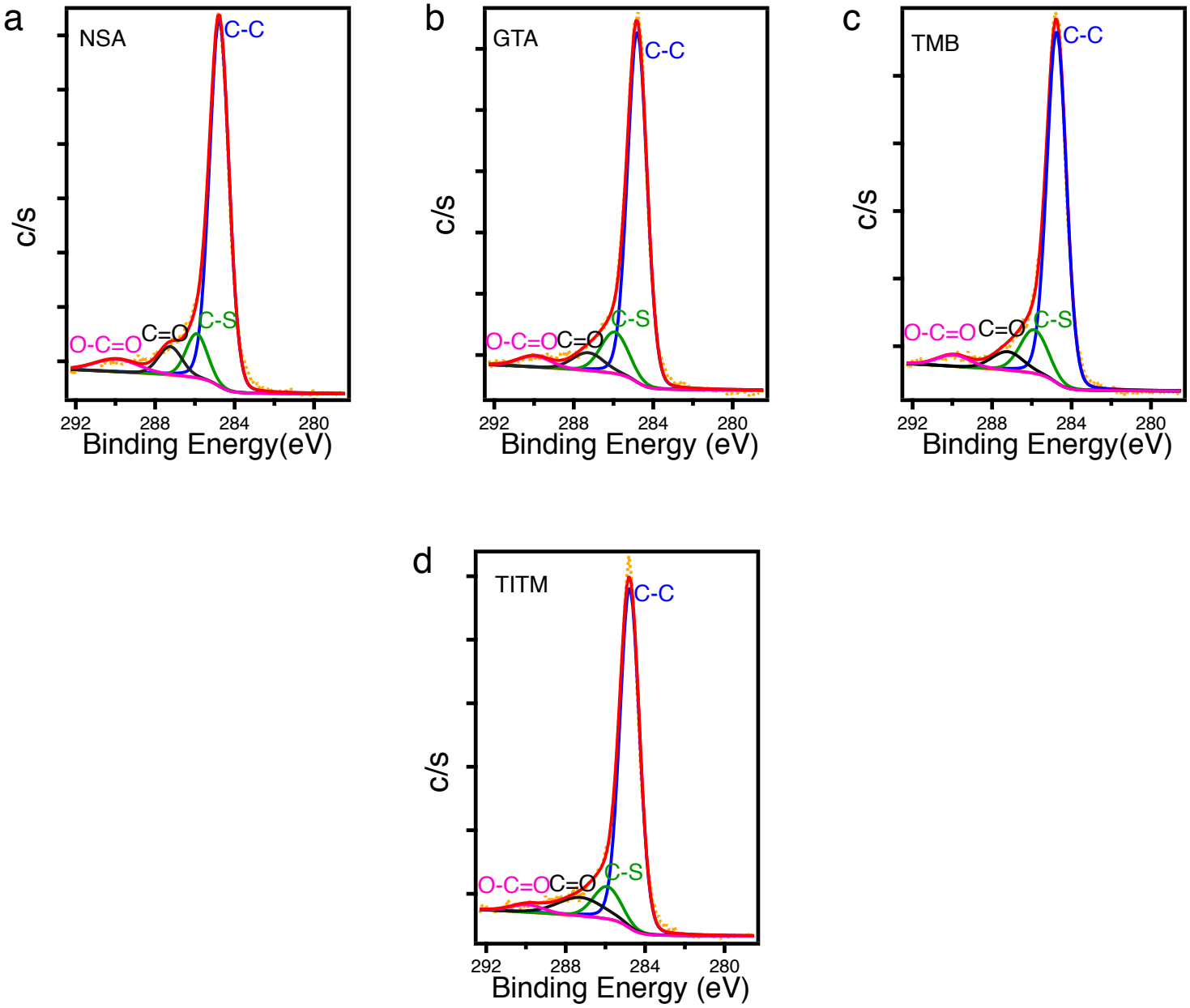

Figure S8. High resolution XPS spectra associated with C1s for mesoporous S-doped carbon silica fabricated (a) without any solvent additive, with 50 wt% (b) GTA, (c) TMB, and (d) TITM. The raw data is shown by orange dashed line and the red curve corresponds to the best fit.

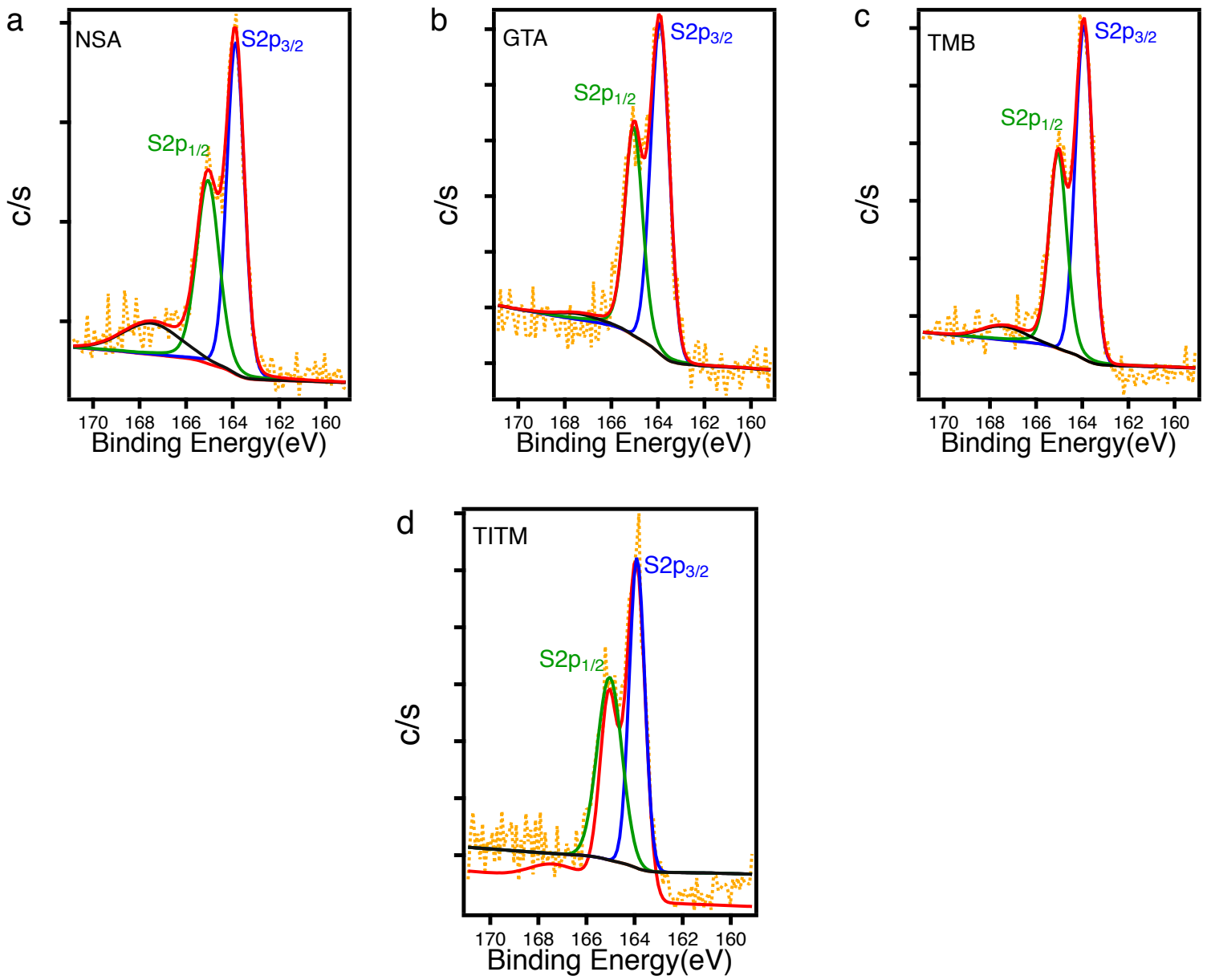

Figure S9. High resolution XPS spectra associated with S2p for mesoporous S-doped carbon silica fabricated (a) without any solvent additive, with 50 wt% (b) GTA, (c) TMB, and (d) TITM. The raw data is shown by orange dashed line and the red curve corresponds to the best fit.

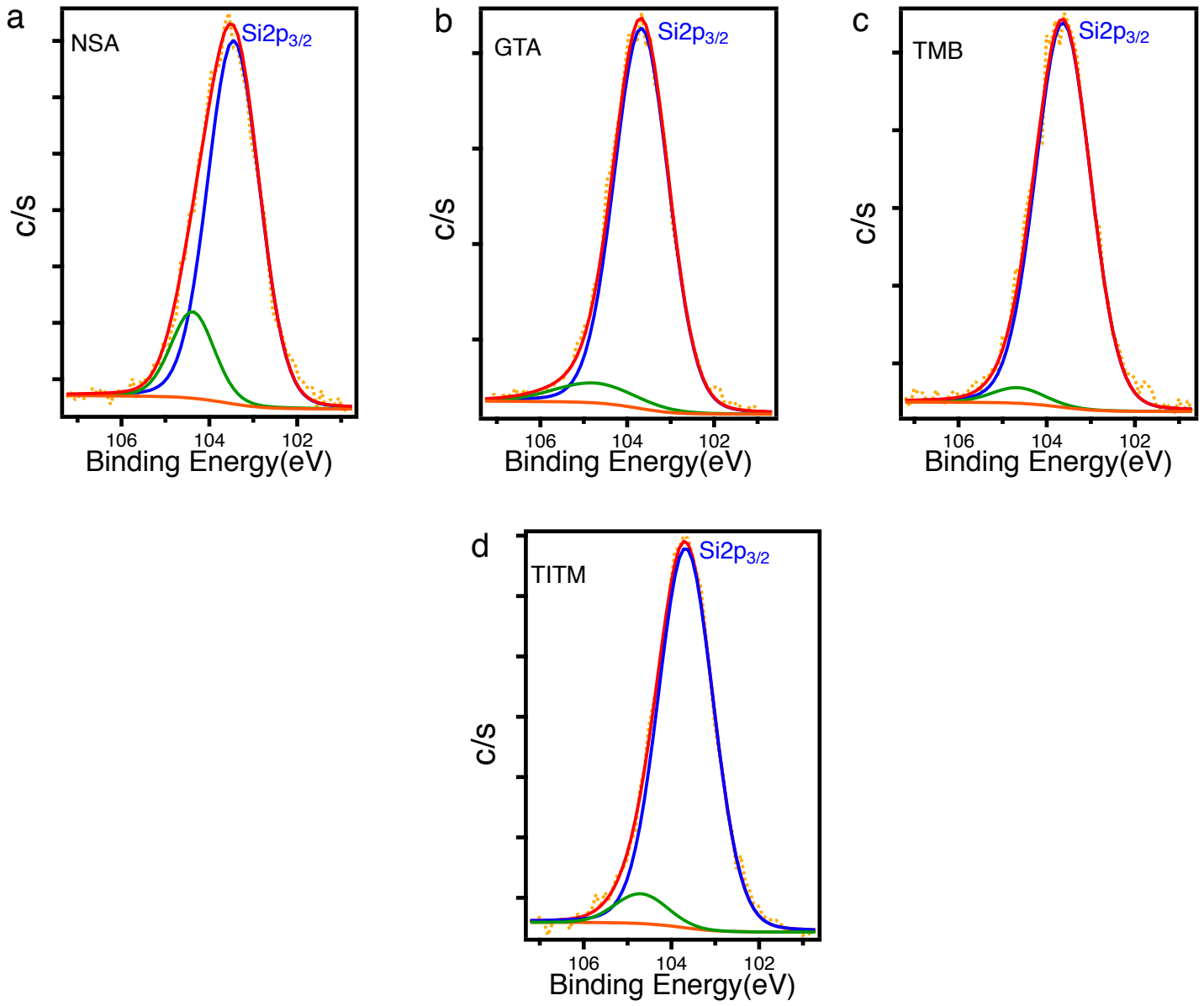

Figure S10. High resolution XPS spectra associated with Si2p for mesoporous S-doped carbon silica fabricated (a) without any solvent additive, with 50 wt% (b) GTA, (c) TMB, and (d) TITM. The raw data is shown by orange dashed line and the red curve corresponds to the best fit.