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C-N-S tridoping into TiO_2 matrix for photocatalytic applications: Observations, speculations and contradictions in the codoping process†

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SUPPLEMENTARY MATERIALS

Table S1 Comparison of Phase Transformation Pathways between TiO_2 and C-N-S-TiO_2 with different dopant precursors.

Preparation Methods	TiO_2	C-N-S-TiO_2	Dopant Precursor	Ref.
Fluoride-induced self-transformation	A	A	Cysteine	[18]
Hydrothermal	A-R	A	Cysteine	[24]
Sol-gel	A	A	Cysteine	[31]
Sol-gel & ball-milling	A-R	A	Thiourea	[16]
Hydrothermal	A	A	Thiourea	[17]
Modified Sol-gel	A	A	Thiourea	[19]
Sol-gel	A-R	A	Thiourea	[20]
Sol-gel	A-R	A	Thiourea	[22]
Surfactant assisted Sol-gel	A	A-R	Thiourea	[25]
Sol-gel	A-B	A-B with no change in phase content	Thiourea	[26]
Sol-gel	A-B-R	A-B-R with increased A content	Thiourea	[27]
Sol-gel	A	A	Thiourea	[29]
Simple Hydrolysis	A	A	Thiourea	[30]
Sol-gel	A-R	A	Thiourea	[32]
Hydrothermal	A	A	Thiourea	[34]
Hydrothermal	A-R	A-R with slight increase in R content	Cystine	[21]
Hydrothermal	A-R	A-R with slight increase in R content	Cystine	[23]
Hydrothermal	A	A	Cystine	[28]
Sol-gel	A-B-R	A	Cystine	[33]
Sol-gel	A-R	A	Cystine	[35]

Note: A-Anatase; B-Brookite; R-Rutile

Table S2 Doping modes of Carbon, Nitrogen and Sulfur occupying cationic and anionic sites in titania.

Ti^{4+} lattice sites	O^{2-} lattice sites	Ref.
	C, N, S	[18, 29]
C, S	N	[17]
C, S	$N_i + N_s$	[16, 20, 23, 28]
C, S	N_i	[27, 34]
C	N, S	[19]
S	N	[26, 30]
S	C	[32]
S	$N_i + N_s$	[21, 33, 35]
S	N_i	[22]
	N, S	[24]
	S	[25, 31]

Note: N_i- Interstitial nitrogen doping; N_s-Substitutional nitrogen doping. The surface segregation of dopant species (without doping) is not considered.

Table S3

Various surface states originated from carbon doping with different precursors

Thiourea	Cysteine	Cystine
Ti-C	Ti-C	
Ti-O-C		Ti-O-C
C-O	C-O	C-O
C=O	C=O	C=O
C-OH	C-OH	
		C-C
		O-C=O

Various surface states arised from nitrogen doping with different precursors

Thiourea	Cysteine	Cystine
O-Ti-N	O-Ti-N	O-Ti-N
Ti-O-N	Ti-O-N	Ti-O-N
Ti-N-O	Ti-N-O	
Ti-N	Ti-N	
NH_3	NH_3	
NH_4^+	NH_4^+	
O-N-Ti		
N-Ti-N		
C-N		
N-H		
N-N		
N-O	N-O	
	NO_2	

Various surface states arised from nitrogen doping with different precursors

Thiourea	Cysteine	Cystine
Ti-S	Ti-S	
Ti-O-S (VI)		Ti-O-S
SO_4^{2-}	SO_4^{2-}	
Ti-O-S (IV)		

Note: Surface states coordinated with titanium indicates the doping modes, while rest corresponds to the surface species.