Supplementary Information

Synthesis, Characterizations and Properties of Sulfate-doped Silver Carbonate SO_4^{2-}-Ag_2CO_3 with Enhanced Visible Light Photocatalytic Performances

Sara Ghazi[a,b], Benaissa Rhouta[a*], Claire Tendero[b], Francis Maury[b]

a) *IMED-Lab, Sciences and Technologies Faculty, Cadi Ayyad University, Avenue Abdelkrim Khattabi, Box 549, Marrakech, Maroc.*

b) *CIRIMAT, Université de Toulouse, CNRS-UPS-INP, ENSIACET, 4 allée Emile Monso, BP 44362, 31030 Toulouse, cedex 4, France.*

Corresponding author e-mail address: b.rhouta@uca.ma

CONTENT

1- XRD data of photocatalysts

Table S1: Lattice parameters of the monoclinic cell of pure Ag_2CO_3 and SO_4^{2-} modified Ag_2CO_3 photocatalysts assessed from all the peaks of XRD patterns of Fig. 1 using the Unit Cell software [1].

Lattice constants	Pure Ag_2CO_3	SO_4^{2-}-Ag_2CO_3	Relative difference
***a* (Å)**	4.7822	4.8098	+0.6%
***b* (Å)**	9.6118	9.6395	+0.3%
***c* (Å)**	3.2128	3.2178	+0.2%
***β* (°)**	93.22	93.28	+0.1%
***Unit cell Volume* (Å^3)**	147.45	148.95	+1.0%

2- Grain size distribution

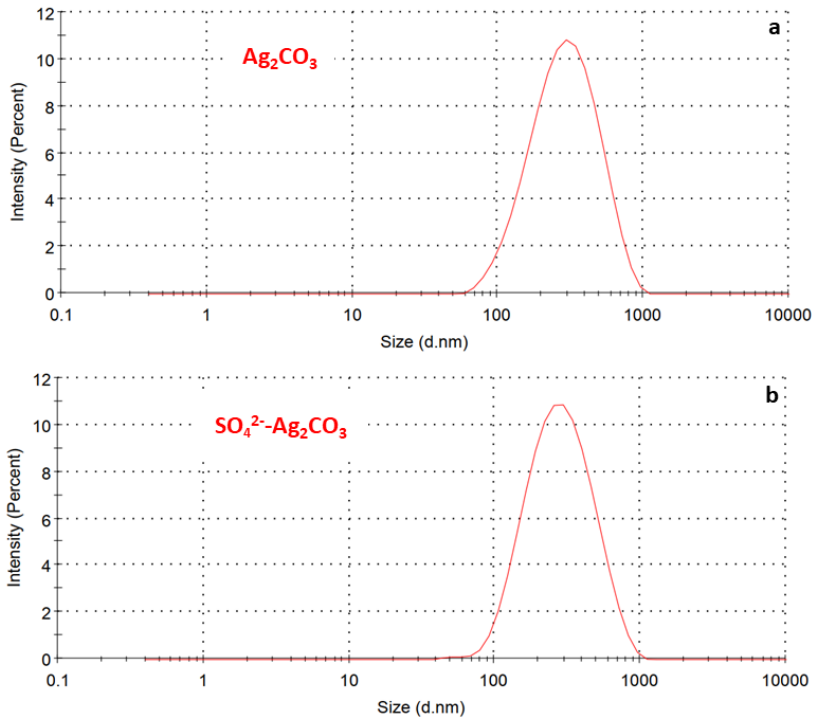

Fig. S1: DLS grain size distribution of (a) pure Ag_2CO_3 and (b) SO_4^{2-}-Ag_2CO_3.

3- Optical properties of photocatalysts

Table S2: Literature data giving representative values of experimental band gap energy (E_g) of Ag_2CO_3, as well as energy of the top of valence band (E_{VB}) and that of the bottom of the conduction band (E_{CB}). When they were not available in the cited references, E_{VB} and E_{CB} were calculated with the equations given in the sub-section 3.1 of the paper using values of E_g and the absolute electronegativity.

Semiconductor compounds	E_g (eV)	E_{VB} (eV)	E_{CB} (eV)	Ref.
Ag_2CO_3	2.30	2.67	0.37	[2]
	2.31	2.69	0.37	[3]
	2.37	2.70	0.30	[4]
	2.46	2.75	0.29	[5]
	2.50	2.77	0.27	[6]
	2.62	2.83	0.21	[7]
	2.62	2.83	0.21	*This work*
SO_4^{2-}-Ag_2CO_3	2.56	2.80	0.24	*This work*

4- Calculation of Ag^+-anion interaction (Pearson model)

According to R.G. Pearson [8], in a system comprising 2 entities, the difference in electronegativity (χ) drives the electron transfer. Therefore, considering a cation Ag^+ and an anion (CO_3^{2-} or SO_4^{2-}) that are brought together, electrons will flow from that of lower electronegativity to that of higher χ until the chemical potentials are equal. The absolute electronegativity and the absolute hardness (η) regarding the entities forming sulfate-doped Ag_2CO_3 are reported in Table S3.

For the complex anions, the values were calculated according to the Pearson equations:

$$\chi = q/R \quad (1)$$

$$\eta = 1/2R \quad (2)$$

where q = the charge of the ion and R is the polyatomic radius [9,10].

The χ□values show that when Ag^+ and an anion are brought, electrons will flow from the complex anion to Ag^+ (the anions SO_4^{2-} and CO_3^{2-} are donor D). Assuming only isolated systems, the fractional number of e^- transferred in these initial Ag^+-D interactions ($\Delta N_{Ag\text{-}D}$) can be approximated by [8]:

$$\Delta N_{Ag\text{-}D} = (\chi_{\square\square+} - \chi_{\square}) / [2(\eta_{Ag+} + \eta_{\square})] \qquad (3)$$

The values reported in Table S3 indicate that $\Delta N_{Ag\text{-}D}$ is 38% bigger with SO_4^{2-} compared to CO_3^{2-}, which reveals a stronger interaction of the sulfate with the Ag_2CO_3 crystal lattice.

Table S3: Key data of cation (Ag^+) and anions pertinent for the SO_4^{2-} doped Ag_2CO_3 photocatalyst. The anions PO_4^{3-} is given for comparison. Data were determined from the Pearson approximation [8] using equations reported above and ionic radius□that □□□□□□□□□s□□□□□ [9,10].

Ion	Ionic radius R (nm)	Absolute electronegativity χ (eV)	Absolute hardness η (eV)	□□□□□□□□□□□□□□□□□□□□□□□□□□ □□□□□□□□r□□□□($\Delta N_{Ag\text{-}D}$)	Ref.
Ag^+	0.126	14.53	6.96	N/A	[8]
CO_3^{2-}	0.189	10.58	2.65	0.21	[9,10]
SO_4^{2-}	0.218	9.17	2.29	0.29	[9,10]
PO_4^{3-}	0.230	13.04	2.17	0.08	[9,10]

5- References

[1] T. J. B. Holland, S. A. T. Redfern, Unit cell refinement from powder diffraction data: the use of regression diagnostics, Mineralogical Magazine. 61 (1997) 65–77. https://doi.org/10.1180/minmag.1997.061.404.07.

[2] G. Dai, J. Yu, G. Liu, A New Approach for Photocorrosion Inhibition of Ag_2CO_3 Photocatalyst with Highly Visible-Light-Responsive Reactivity, J. Phys. Chem. C. 116 (2012) 15519–15524. https://doi.org/10.1021/jp305669f.

[3] W. Jiang, Y. Zeng, X. Wang, X. Yue, S. Yuan, H. Lu, B. Liang, Preparation of Silver Carbonate and its Application as Visible Light-driven Photocatalyst Without Sacrificial Reagent, Photochemistry and Photobiology. 91 (2015) 1315–1323. https://doi.org/10.1111/php.12495

[4] Y. Li, L. Fang, R. Jin, Y. Yang, X. Fang, Y. Xing, S. Song, Preparation and enhanced visible light photocatalytic activity of novel g-C_3N_4 nanosheets loaded with Ag_2CO_3 nanoparticles, Nanoscale, 7 (2015) 758-764. https://doi.org/10.1039/C4NR06565D

[5] H. Dong, G. Chen, J. Sun, C. Li, Y. Yu, D. Chen, A novel high-efficiency visible-light sensitive Ag_2CO_3 photocatalyst with universal photodegradation performances: Simple synthesis, reaction mechanism and first-principles study, Applied Catalysis B: Environmental. 134–135 (2013) 46–54. https://doi.org/10.1016/j.apcatb.2012.12.041.

[6] E. Nyankson, B. Agyei-Tuffour, E. Annan, A. Yaya, B. Mensah, B. Onwona-Agyeman, R. Amedalor, B. Kwaku-Frimpong, J.K. Efavi, Ag_2CO_3-halloysite nanotubes composite with enhanced removal efficiency for water soluble dyes, Heliyon. 5 (2019) e01969. https://doi.org/10.1016/j.heliyon.2019.e01969.

[7] W. Fa, P. Wang, B. Yue, F. Yang, D. Li, Z. Zheng, Ag_3PO_4/Ag_2CO_3 p–n heterojunction composites with enhanced photocatalytic activity under visible light, Chinese Journal of Catalysis. 36 (2015) 2186–2193. https://doi.org/10.1016/S1872-2067(15)61004-X

[8] R.G. Pearson, Absolute electronegativity and hardness: application to inorganic chemistry, Inorg. Chem. 27 (1988) 734–740. https://doi.org/10.1021/ic00277a030

[9] H.K. Roobottom, H.D.B. Jenkins, J. Passmore, L. Glasser, Thermochemical Radii of Complex Ions, J. Chem. Educ. 76 (1999) 1570. https://doi.org/10.1021/ed076p1570

[10] M.C. Simoes, K.J. Hughes, D.B. Ingham, L. Ma, M. Pourkashanian, Estimation of the Thermochemical Radii and Ionic Volumes of Complex Ions, Inorg. Chem. 56 (2017) 7566–7573. https://doi.org/10.1021/acs.inorgchem.7b01205.