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## Synthesis, characterization and properties of sulfate-modified silver carbonate with enhanced visible light photocatalytic performance†

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Sulfate-modified  $\text{Ag}_2\text{CO}_3$  was successfully synthesized *via* a simple precipitation method. Its visible light photocatalytic performance against the removal of Orange G was found to be significantly enhanced in comparison with the one of pure  $\text{Ag}_2\text{CO}_3$ . While  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$  ensured a removal efficiency of 100% of OG within 30 min, the unmodified  $\text{Ag}_2\text{CO}_3$  exhibited a degradation threshold at hardly 60%. Likewise, the degradation rate constant in the presence of  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$  photocatalyst was assessed to be twice that determined upon the involvement of pristine  $\text{Ag}_2\text{CO}_3$ . Furthermore, Total Organic Carbon (TOC) measurements evidenced the occurrence of a quasi-total mineralization of the dye pollutant upon the use of  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$  photocatalyst. Scavenger experiments highlighted the dominant role of photo-induced  $\text{h}^+$  along with  $\text{O}_3^-$  ozonide radicals in the OG photocatalytic oxidation mechanism. Reuse cycles revealed that the modification by  $\text{SO}_4^{2-}$  is a promising route to improve the stability of silver carbonate against photocorrosion. All these improvements could be ascribed to electronic transfer from the upper  $\text{SO}_4^{2-}$  HOMO to the lower  $\text{Ag}_2\text{CO}_3$  conduction band.

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## 1 Introduction

Great attention was recently paid to silver based photocatalysts such as  $\text{Ag}_2\text{O}$ ,<sup>1</sup>  $\text{AgX}$  ( $\text{X} = \text{Cl}$ ,  $\text{I}$  and  $\text{Br}$ ),<sup>2</sup>  $\text{Ag}_3\text{PO}_4$  (ref. 3) and  $\text{Ag}_2\text{CO}_3$ .<sup>4</sup> This is due to their high visible light absorption that yields an effective photocatalytic degradation of organic pollutants from aqueous media.<sup>5,6</sup> Nevertheless, their photoactivity efficiency depends on the anion nature since for instance, Ag-oxosalt photocatalytic performances increased in the order  $\text{Ag}_3\text{AsO}_4 > \text{Ag}_3\text{PO}_4 > \text{Ag}_2\text{CO}_3 > \text{Ag}_2\text{SeO}_4 > \text{Ag}_2\text{SO}_4$ .<sup>7</sup> However, this order seemed to be controversial in that a recent study reported that  $\text{Ag}_2\text{CO}_3$  appeared more photoactive and photostable than  $\text{Ag}_3\text{PO}_4$ .<sup>8</sup> Likewise, this order depended on the nature of the pollutant.<sup>8</sup> Despite this,  $\text{Ag}_3\text{PO}_4$ , has been the most studied in photocatalysis with about 900 research papers dedicated to this compound compared to about 150 for  $\text{Ag}_2\text{CO}_3$  in the same period.<sup>9</sup> This highest interest for  $\text{Ag}_3\text{PO}_4$  was likely due to its better thermal stability and higher photoactivity, which could be further enhanced by doping.

In this context, several studies reported  $\text{Ag}_3\text{PO}_4$  doping with  $\text{Ni}^{2+}$  (ref. 10) or  $\text{Cu}^{2+}$  (ref. 11) cations, and  $\text{SO}_4^{2-}$  (ref. 12) or  $\text{CO}_3^{2-}$  anions.<sup>13</sup> Considering anion doping, it is difficult to

claim the achievement of the doping of an Ag-oxosalt by a polyatomic anion since the authors do not clearly explain how 5 ions ( $\text{S}^{6+}$  and  $\text{O}^{2-}$ ) issued for instance from  $\text{SO}_4^{2-}$  group were distributed in the crystalline matrix. A more generic term than doping could be activation or treatment of the photocatalyst. For example, a so-called doping by  $\text{SO}_4^{2-}$  could be similar to a doping by sulfur. Anyway, in the particular case of  $\text{Ag}_3\text{PO}_4$  doping by  $\text{SO}_4^{2-}$ , it was suggested that an electronic transfer occurred between  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , more precisely from atomic orbitals  $\text{S } 3s^2 3p^4$  to  $\text{P } 3s^2 3p^3$ .<sup>12</sup> The photocatalyst  $\text{Ag}_2\text{CO}_3$  crystallizes in a monoclinic structure significantly different than the cubic structure of  $\text{Ag}_3\text{PO}_4$ . In addition, it presents an optical band gap ( $\approx 2.4$  eV) in the same order of magnitude as the silver phosphate and thus is photoactive under visible light irradiation.<sup>4</sup> Nonetheless, in comparison with  $\text{Ag}_3\text{PO}_4$ , it was less studied as photocatalyst, probably due to the fact that, as other silver oxosalts, it exhibited drawbacks related for instance to a lower transfer rate of charge carriers<sup>14</sup> and a higher sensitivity to photocorrosion.<sup>15</sup> By contrast with  $\text{Ag}_3\text{PO}_4$ , fewer strategies have been explored to improve the performance of  $\text{Ag}_2\text{CO}_3$ .

To overcome these issues, several routes have been proposed such as heterojunctions between  $\text{Ag}_2\text{CO}_3$  and another semiconductor, which can promote high separation of the photo-generated electrons-holes pairs. This approach has been extended to nanocomposites with metal nanoparticles as Ag to produce Schottky junctions. For this purpose, beneficial heterojunctions were reported for  $\text{TiO}_2/\text{Ag}_2\text{CO}_3$ ,<sup>16</sup>  $\text{ZnO}/\text{Ag}_2\text{CO}_3$ ,<sup>17</sup> Ag/ $\text{Ag}_2\text{CO}_3$ ,<sup>18</sup>  $\text{Ag}_2\text{O}/\text{Ag}_2\text{CO}_3$ ,<sup>19</sup>  $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$  (ref. 20) and  $\text{AgX}$  ( $\text{X} = \text{Cl}$ ,  $\text{I}$  and  $\text{Br}$ )/ $\text{Ag}_2\text{CO}_3$ .<sup>21</sup> Another way<sup>22</sup> reported the effect of

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varying types and ratios of solvents upon the synthesis in tuning the size and morphology of  $\text{Ag}_2\text{CO}_3$  and consequently improving its photocatalytic activity and photostability. In another route, it was reported that the immobilization of  $\text{Ag}_2\text{CO}_3$  particles on supports with a large specific surface area such as graphene oxide,<sup>23</sup>  $\text{C}_3\text{N}_4$  (ref. 24–26) and some clay minerals like palygorskite<sup>27</sup> was also a promising way. Surprisingly, in contrast to  $\text{Ag}_3\text{PO}_4$ , anionic modification of  $\text{Ag}_2\text{CO}_3$  was not investigated. In particular, the route of modification by  $\text{SO}_4^{2-}$  was not yet reported for improving photocatalytic properties of  $\text{Ag}_2\text{CO}_3$ .

Since both Ag-oxosalts differ in their crystallographic structure and anion nature (size, charge, composition), the response of these photocatalysts to a strategy will not necessarily be the same from one to another. The fact that  $\text{SO}_4^{2-}$  presents an ionic radius of the same order of magnitude than  $\text{CO}_3^{2-}$  (ref. 2–28) should facilitate bulk modification of  $\text{Ag}_2\text{CO}_3$ . However, the differences both in crystallographic structure between  $\text{Ag}_2\text{CO}_3$  and  $\text{Ag}_3\text{PO}_4$ , and in charge transfer expected between the modifying anion ( $\text{SO}_4^{2-}$ ) and crystal lattice anion ( $\text{CO}_3^{2-}$ ), does not allow to think that the effects of the modification by  $\text{SO}_4^{2-}$  should be similar for  $\text{Ag}_2\text{CO}_3$  and  $\text{Ag}_3\text{PO}_4$ .<sup>12</sup> These differences increase the interest of exploring  $\text{Ag}_2\text{CO}_3$  modification with  $\text{SO}_4^{2-}$  as a route to enhance photocatalytic properties and paving a new way to improve the stability against photo-corrosion for practical applications.

In this paper, the photocatalytic performances were assessed (i) by measuring the degradation rate of a model pollutant under visible light irradiation (kinetic data), (ii) by analyzing the extent of mineralization (TOC analysis), (iii) by determining the nature of photogenerated oxidizing species responsible of the dye photocatalytic degradation through scavenger experiments (resulting in hypothesis on the reaction mechanism) and (iv) by studying the photo-stability in reuse experiments.

## 2 Experimental

### 2.1 Synthesis of the photocatalysts

All reagents were of analytical grade and used without further purification. Pure  $\text{Ag}_2\text{CO}_3$  was synthesized according to a method previously published.<sup>4,27</sup> For  $\text{Ag}_2\text{CO}_3$  treatment with  $\text{SO}_4^{2-}$ , the method was adapted from that already reported for sulfate-doped  $\text{Ag}_3\text{PO}_4$ .<sup>12</sup> In a typical procedure, 20 mL of a translucent mixture of  $\text{AgNO}_3$  (0.272 M) and  $\text{Na}_2\text{SO}_4$  (0.0125 M) was prepared at room temperature in distilled water and stirred during 10 min for homogenization. Then 40 mL of  $\text{Na}_2\text{CO}_3$  (0.068 M) was added dropwise under continuous stirring. The formed precipitate (*i.e.*  $\text{SO}_4^{2-}$ -modified  $\text{Ag}_2\text{CO}_3$ ) was collected by centrifugation, washed with distilled water and ethanol three times to remove reaction byproducts mainly  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$  and traces of remaining reactants. The samples were dried at 60 °C overnight, then stored in the dark at room temperature before being used. With these synthesis conditions, the theoretical  $\text{SO}_4^{2-}$  content of the photocatalyst cannot exceed 9 at% since this was the value of the  $\text{SO}_4^{2-}/\text{CO}_3^{2-}$  anion ratio used.

### 2.2 Characterization techniques

The phase identification was carried out by X-ray diffraction (D8 Advance Diffractometer Bruker) with  $\text{Cu K}\alpha$  radiation source. The scanning was performed at room temperature in the  $2\theta$  range from 5° to 70° with a step size of 0.05° for 1 s. Infrared spectroscopy analysis was performed on a pellet of KBr-photocatalyst mixture ( $\approx 1$  wt%) using a PerkinElmer FTIR in the range 400–4000  $\text{cm}^{-1}$ . The SEM microscopy observations were performed using a scanning electron microscope VEGATE-SCAN3 coupled with an EDAX analyzer for elemental analysis. UV-vis Diffuse Reflectance Spectra (DRS) were recorded with respect to PTFE as standard using a Cary 5000 UV-vis-NIR spectrophotometer for wavelengths ranging from 200 to 800 nm. The zeta potential of the synthesized Ag-oxosalt powders was measured at room temperature in an aqueous suspension using a Zetasizer apparatus from Nano ZS, Malvern instruments.

### 2.3 Photocatalytic tests under visible light

The photocatalytic activity was evaluated by recording the temporal variation of Orange G (OG) concentration during its degradation under visible light irradiation in presence of the photocatalyst. OG is an anionic azo dye with the formula  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{Na}_2\text{O}_7\text{S}_2$ . It was selected as model pollutant because it is frequently used as dye in textile industry, and it does not undergo photolysis under the conditions of this test. The visible light irradiation was provided by 4 light color/840 lamps (13 W each) coupled with a UV cut-off filter ( $\lambda < 400$  nm). Practically, 25 mg of the photocatalyst was dispersed into a quartz photo-reactor containing 25 mL of OG ( $10^{-5}$  M) aqueous solution. It should be noted that such conditions were the same as the ones already established by Lakbita *et al.*<sup>27</sup> to be optimal for the study of photocatalytic performances under visible light of  $\text{Ag}_2\text{CO}_3$  supported palygorskite clay mineral in a similar slurry reactor. Afterwards, the suspension was stirred in the dark for 30 min to achieve adsorption–desorption equilibrium before to start the photocatalytic test by switching on the lamps. At regular time intervals, aliquots were picked up, centrifuged and OG concentration in supernatant was determined using UV-vis spectrophotometer from the intensity of the OG absorption band in the range 470–500 nm. It should be noted that a calibration curve in the Beer–Lambert linearity domain was checked beforehand in the low concentration range ( $10^{-7}$ – $10^{-4}$  M) that includes the test value ( $10^{-5}$  M). The experimental data reported here were the average of 3 photocatalytic tests and an error bar represented the dispersion of data.

To check if the photocatalytic degradation of OG organic dye pollutant led to its partial or total mineralization, the Total Organic Carbon (TOC) corresponding to remaining organic dye plus possibly organic byproducts was determined after the test using a TOC analyzer (TOC-L CPH/CPN, Shimadzu). For this purpose, after the test, photocatalyst dispersion was centrifuged at 12 000 rpm during 5 min and the resulting supernatant was analyzed.

To further investigate the photocatalytic mechanism that would ensure the OG photocatalytic degradation, isopropanol



(IPA) was utilized to quench hydroxyl radicals ( $\cdot\text{OH}$ ),<sup>12</sup> trichloromethane (TCM) served as scavenger of superoxide radical anions ( $\cdot\text{O}_2^-$ ),<sup>29</sup> indigo carmine (IC) used to trap the ozonide radicals ( $\cdot\text{O}_3^-$ )<sup>8</sup> and ethylenediamine tetra-acetic acid disodium (EDTA) was used as a hole ( $\text{h}^+$ ) scavenger.<sup>30</sup> Before adding  $\text{Ag}_2\text{CO}_3$  or  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  powders and running photocatalysis experiment, 1 mM of each scavenger was added to the OG dye solution.<sup>31</sup>

### 3 Results and discussion

#### 3.1 Bulk modification of $\text{Ag}_2\text{CO}_3$ by $\text{SO}_4^{2-}$

As shown in Fig. 1, XRD patterns recorded on unmodified and  $\text{SO}_4^{2-}$  modified  $\text{Ag}_2\text{CO}_3$  appeared quite similar with several diffraction peaks amongst which the ones at  $2\theta$  around  $18.32^\circ$  ( $d_{100} = 4.85 \text{ \AA}$ ),  $18.54^\circ$  ( $d_{020} = 4.78 \text{ \AA}$ ),  $20.5^\circ$  ( $d_{110} = 4.32 \text{ \AA}$ ),  $32.74^\circ$  ( $d_{\bar{1}01} = 2.73 \text{ \AA}$ ),  $33.81^\circ$  ( $d_{130} = 2.65 \text{ \AA}$ ),  $37.07^\circ$  ( $d_{200} = 2.42 \text{ \AA}$ ) and  $39.60^\circ$  ( $d_{031} = 2.27 \text{ \AA}$ ). These peaks were indexed on the basis of the stable monoclinic  $\text{Ag}_2\text{CO}_3$  phase (ICDD file no. 01-070-2184). This result confirmed that the  $\text{Ag}_2\text{CO}_3$  treatment by  $\text{SO}_4^{2-}$  had no effect on the crystallographic structure of the silver carbonate that remained monoclinic while several polytypes exist.<sup>27</sup> Furthermore, the non-appearance of additional peaks in the  $\text{SO}_4^{2-}$  modified  $\text{Ag}_2\text{CO}_3$  pattern denoted the absence of any crystallized secondary phases as byproducts from the base reactions (*e.g.*  $\text{Ag}_2\text{SO}_4$ ) or from side decomposition reactions (*e.g.*  $\text{Ag}_2\text{O}$ ,  $\text{Ag}$ ). Regarding  $\text{Ag}_2\text{SO}_4$ , the corresponding main XRD peaks, expected at  $31.13^\circ$  (311) and  $28.08^\circ$  (040), were not present (Fig. 1). This is consistent with the fact that it is water-soluble and was therefore washed away from the final photocatalyst powder (see Section 2.1).

Further detailed analysis of the diffractograms interestingly revealed a slight shift of the peaks towards smaller  $2\theta$  angles. Indeed, in the  $2\theta$  region between  $32.0^\circ$  and  $34.5^\circ$ , ( $\bar{1}01$ ) and (130) peaks were observed respectively at  $32.74^\circ$  and  $33.81^\circ$  for pure  $\text{Ag}_2\text{CO}_3$  while they appeared at  $32.64^\circ$  and  $33.69^\circ$  for  $\text{SO}_4^{2-}$  modified  $\text{Ag}_2\text{CO}_3$  (Fig. 1b). The values of  $a$ ,  $b$ , and  $c$  lattice

parameters and  $\beta$  angle of unmodified- and  $\text{SO}_4^{2-}$  modified  $\text{Ag}_2\text{CO}_3$  samples, were calculated from all the XRD peaks, using the Unit Cell software.<sup>32</sup> They were reported in Table S1 (ESI).† They revealed an increase of the lattice parameters for  $\text{SO}_4^{2-}$ -modified  $\text{Ag}_2\text{CO}_3$  with respect to unmodified  $\text{Ag}_2\text{CO}_3$  corresponding to a volume expansion of the unit cell of *ca.* 1.0%, which was certainly due to the higher ionic radius of  $\text{SO}_4^{2-}$  (0.218 nm) compared to the one of  $\text{CO}_3^{2-}$  (0.189 nm).<sup>28</sup> This finding ascertained that  $\text{CO}_3^{2-}$  anions in the crystal lattice were substituted by modifying  $\text{SO}_4^{2-}$  anions larger by 15% and hence confirmed the achievement of a bulk modification of  $\text{Ag}_2\text{CO}_3$  by sulfate anions. This ruled out a simple surface functionalization by  $\text{SO}_4^{2-}$  anions grafted on  $\text{Ag}_2\text{CO}_3$  particles, which should not induce an expansion of the crystal lattice.

To complete the crystallographic analysis, the two photocatalysts were characterized by FTIR spectroscopy. In addition to the presence of  $\text{H}_2\text{O}$  molecules that was revealed by absorption bands around  $3200$  and  $1650 \text{ cm}^{-1}$ , both FTIR spectra exhibited characteristic absorption bands of  $\text{Ag}_2\text{CO}_3$  (Fig. 2). The two intense bands at  $1442$  and  $1377 \text{ cm}^{-1}$ , as well as those at  $879$  and  $697 \text{ cm}^{-1}$  may be assigned to the distinctive vibrations of the planar  $\text{CO}_3^{2-}$  groups, *i.e.* deformation and stretching, respectively.<sup>33</sup> Additional bands were exclusively detected in  $\text{SO}_4^{2-}$ -modified  $\text{Ag}_2\text{CO}_3$  sample with bands at  $1113$ ,  $1056$ , and  $606 \text{ cm}^{-1}$  attributed to the stretching mode of S-O and O-S-O bonds in  $\text{SO}_4^{2-}$  tetrahedra, as reported for  $\text{Ag}_2\text{SO}_4$  elsewhere.<sup>34</sup> Except the bands of  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  anions (and  $\text{H}_2\text{O}$  traces), no other absorption band was observed in the sulfate modified  $\text{Ag}_2\text{CO}_3$  photocatalyst. This result further supported the beforehand mentioned statement issued from XRD analysis according to which on one hand a bulk modification of  $\text{Ag}_2\text{CO}_3$  with  $\text{SO}_4^{2-}$  anions was successfully achieved rather than a sulfate anion grafting on the surface of  $\text{Ag}_2\text{CO}_3$  particles and on the other hand the absence of secondary phases formation.

SEM analyses showed that pure  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  samples exhibited the same microstructure with micron-size

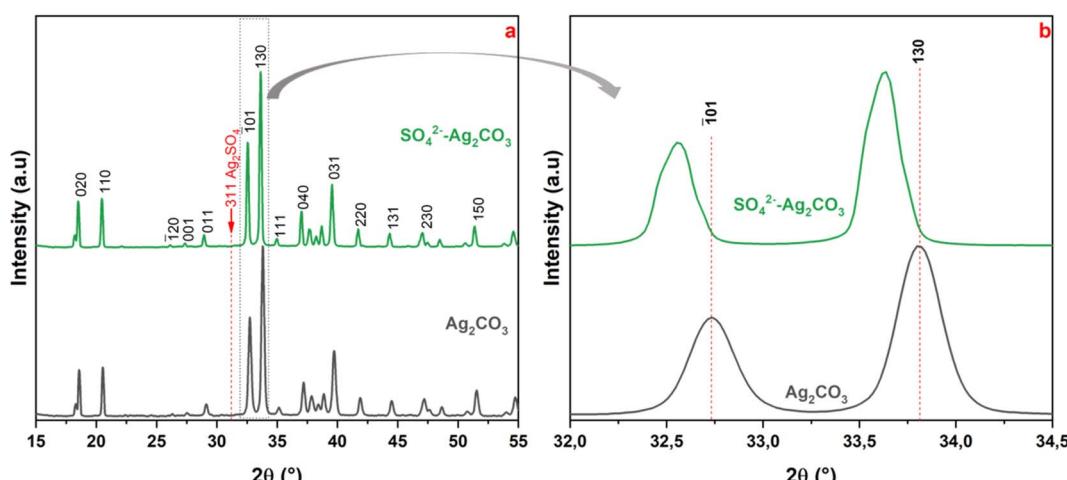


Fig. 1 X-ray diffraction patterns of pure  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}$  modified  $\text{Ag}_2\text{CO}_3$  (left) and zoom in the  $32.0^\circ$ – $34.5^\circ$  angular region corresponding to ( $\bar{1}01$ ) and (130) reflection planes of both  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  (right).



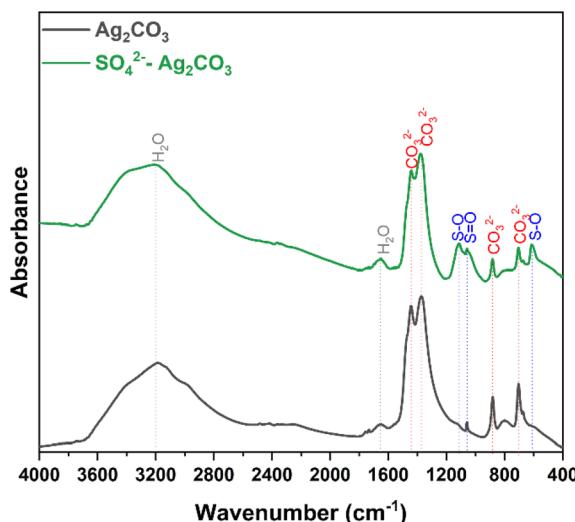


Fig. 2 FTIR spectra of pure  $\text{Ag}_2\text{CO}_3$  (bottom) and  $\text{SO}_4^{2-}$  modified  $\text{Ag}_2\text{CO}_3$  (top). The absorption bands were assigned according to literature data of carbonates and sulfates including  $\text{Ag}_2\text{CO}_3$ <sup>33</sup> and  $\text{Ag}_2\text{SO}_4$ .<sup>34</sup>

and monodisperse particles with pretty similar polyhedral shapes (Fig. 3). They appeared well crystallized, in the form of faceted rhombohedra with an average size of  $0.3\text{ }\mu\text{m}$  according to the Dynamic Light Scattering (DLS) particle size distribution analysis (Fig. S1†). This microstructure was similar to that previously reported for silver carbonate synthesized by the same method.<sup>27</sup> Therefore,  $\text{SO}_4^{2-}$ -modification did not change the

microstructure of  $\text{Ag}_2\text{CO}_3$  particles (Fig. 2). This should be consistent with the incorporation into the  $\text{Ag}_2\text{CO}_3$  crystal lattice of only a very small amount of  $\text{SO}_4^{2-}$  anions. This assumption was further supported by EDS analysis showing the  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$  sample was mainly composed of Ag, C, O. Very small peak, corresponding to sulfur, was detected in the energy range (Fig. 3d). Moreover, the SEM-EDS elemental mapping of the  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$  powder spread on the sample holder did not reveal any evidence for S-rich regions, which additionally confirmed the absence of secondary phase such as  $\text{Ag}_2\text{SO}_4$  (Fig. 3). Thus, the S amount in  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$  sample was estimated to be around 1.8 atomic% fraction, which is way lower than the 9% allowed by the initial proportion of reagents and confirms the  $\text{Ag}_2\text{CO}_3$  modification with  $\text{SO}_4^{2-}$ .

UV-vis diffuse reflectance spectra recorded on pure  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}$  modified  $\text{Ag}_2\text{CO}_3$  samples did not reveal significative differences. For both the samples, they displayed a high and sharp absorption below 500 nm, in the visible light range, denoting as expected their wide band gap semiconductor characters (Fig. 4a). In both the cases, there was no evidence of absorption band above 500 nm that could be due to plasmonic effect induced by Ag nanoparticles as reported elsewhere.<sup>35</sup> The recorded UV-vis spectra herein were in good agreement with those previously reported for monoclinic  $\text{Ag}_2\text{CO}_3$ .<sup>4,8,15</sup> The absorption edges, corresponding to the intersection of the extrapolation of the linear part of the absorption curve with the wavelength axis, were determined to be around 509 nm (2.44 eV) and 533 nm (2.33 eV) for pure  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}$ -modified  $\text{Ag}_2\text{CO}_3$  samples, respectively (Fig. 4a).

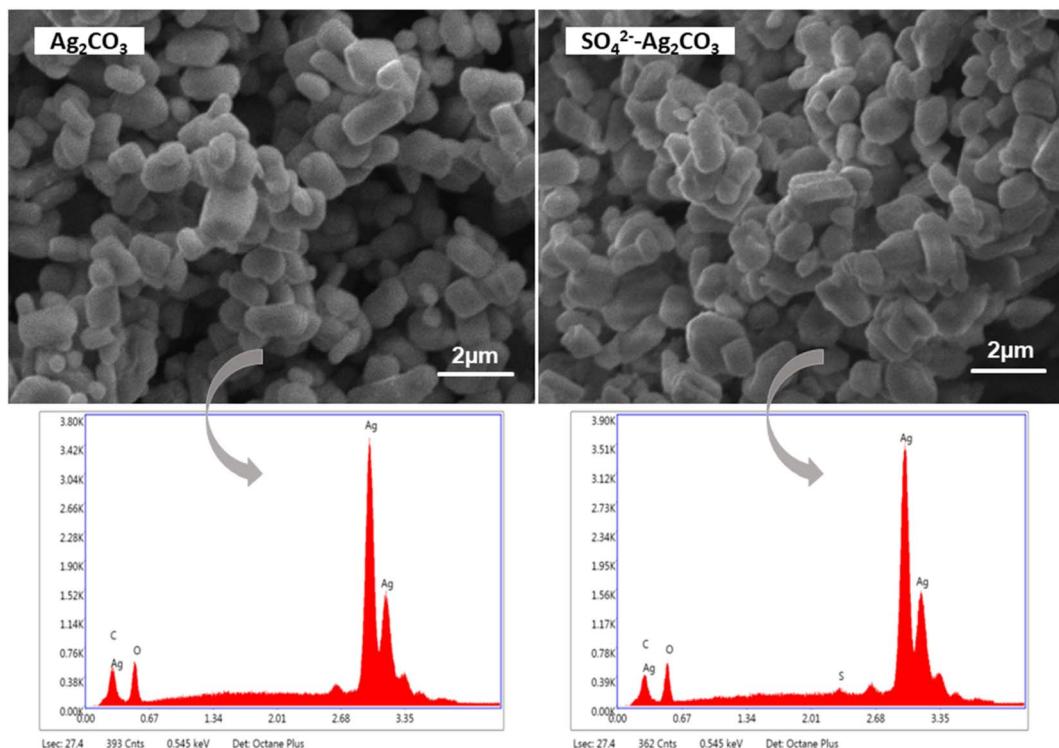


Fig. 3 SEM micrographs of pure  $\text{Ag}_2\text{CO}_3$  (left) and  $\text{SO}_4^{2-}$  modified  $\text{Ag}_2\text{CO}_3$  (right), and the EDS spectra corresponding to each image.



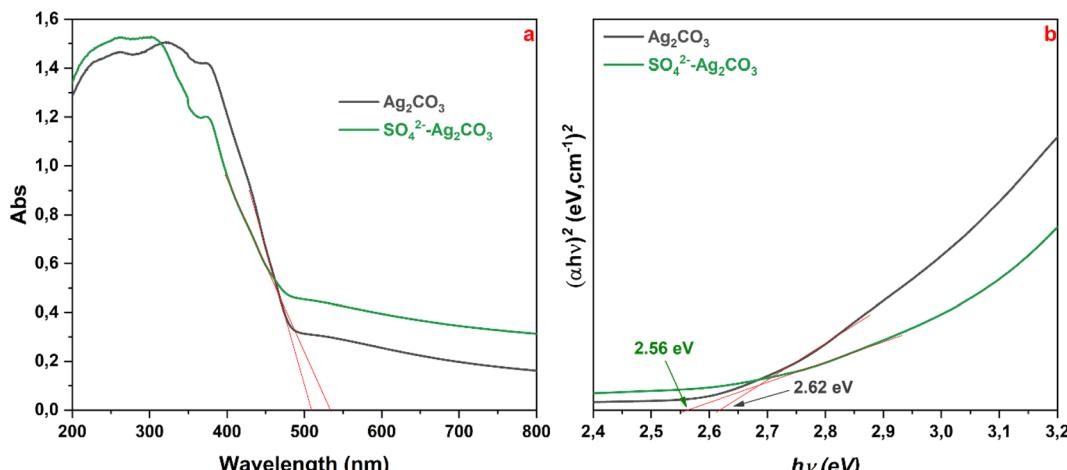


Fig. 4 UV-vis DRS spectra of  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$  samples (a), and corresponding plot  $(\alpha h\nu)^2$  vs. energy  $h\nu$  (b). Red straight lines are extrapolations to determine optical gap (absorption edge) from (a) and the Tauc band gap energy from (b).

As both the  $\text{Ag}_2\text{CO}_3$ -based compounds are indirect semiconductors according to previously reported studies,<sup>4,7,8</sup> the corresponding band gap energies ( $E_g$ ) determined by the Tauc method<sup>4</sup> were found to be about 2.62 and 2.56 eV, for unmodified and  $\text{SO}_4^{2-}$  modified  $\text{Ag}_2\text{CO}_3$  respectively (Fig. 4b). These  $E_g$  values were consistent with those of  $\text{Ag}_2\text{CO}_3$  which were reported over a fairly wide range from 2.30 eV<sup>15</sup> to 2.62 eV<sup>20</sup> depending on the synthesis method, the crystallographic structure, the microstructure and purity (Table S2 in ESI†). In this respect, as beforehand evidenced that the treatment by  $\text{SO}_4^{2-}$  did change neither the structure (Fig. 1) nor the microstructure of  $\text{Ag}_2\text{CO}_3$ , the slight decrease of  $E_g$  ( $\approx 2.3\%$ ) between both the band gap energies may result from the anionic modification effect. This  $\text{SO}_4^{2-}$  effect contrasted with that exerted by  $\text{Ag}_3\text{PO}_4$  doping by  $\text{SO}_4^{2-}$  yielding rather to a slight increase of  $E_g$  as reported elsewhere.<sup>12</sup> Therefore,  $\text{SO}_4^{2-}$ -modified  $\text{Ag}_2\text{CO}_3$  photocatalyst exhibited a slightly better absorption of the photons in the visible range. This means that, as more discussed below, more photo-generated electrons ( $e^-$ ) were transferred from the valence band (VB) to the conduction band (CB), leaving more holes ( $h^+$ ) in the VB that will be capable of oxidizing more organic species in primary reactions.

Furthermore, the valence band position ( $E_{\text{VB}}$ ) and the conduction band position ( $E_{\text{CB}}$ ) of  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$  can be computed through the Mulliken electronegativity empirical equations:<sup>15</sup>

$$E_{\text{VB}} = \chi - E_0 + 0.5E_g \quad (1)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g \quad (2)$$

where  $\chi$  is the semiconductor absolute electronegativity (6.023 eV for  $\text{Ag}_2\text{CO}_3$  (ref. 8 and 15) and  $E_0$  is the free electron energy on the hydrogen scale, otherwise the Fermi level of NHE (Normal Hydrogen Electrode) with respect of the vacuum level (ca. 4.5 eV).  $E_{\text{VB}}$  and  $E_{\text{CB}}$  are the VB and CB edge potentials respectively, and  $E_g$  is the band gap of the semiconductor. The  $E_{\text{VB}}$  and  $E_{\text{CB}}$  values hence deduced for  $\text{SO}_4^{2-}$ -modified  $\text{Ag}_2\text{CO}_3$

were +2.80 and +0.24 eV, respectively. For pure  $\text{Ag}_2\text{CO}_3$  the values found were +2.83 and +0.21 eV respectively. These values were in agreement with literature data for  $\text{Ag}_2\text{CO}_3$  based compounds (Table S2†).

### 3.2 Visible-light photocatalytic properties

The variation of OG dye concentration *versus* irradiation time under visible light in presence of pure  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$  photocatalysts was reported in Fig. 5. It is worth noting that keeping beforehand in the dark during 30 min the dispersion of the two photocatalysts in OG aqueous solution did not reveal OG adsorption onto the surface of the two photocatalysts due to electrostatic repulsions between anionic OG dye molecules and negatively charged surfaces of the photocatalysts. This was confirmed by the zeta potentials measured to be  $-23$  mV for pure  $\text{Ag}_2\text{CO}_3$  and  $-27$  mV for  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$ , which was consistent with that reported elsewhere ( $-36$  mV) for the pure silver carbonate.<sup>7</sup> Furthermore, the concentration of OG solution free from photocatalyst appeared not decreasing during the whole duration of its exposure to visible light. This proved that OG dye did not undergo photolysis (Fig. 5a).

In the presence of pure  $\text{Ag}_2\text{CO}_3$ , OG concentration considerably decreased during the first 20 minutes of irradiation to reach an OG degradation plateau after a removal of *ca.* 60% (Fig. 5a) beyond which no more dye photocatalytic degradation occurred. This striking behavior could be ascribed either to (i) surface  $\text{Ag}_2\text{CO}_3$  poisoning by byproducts issued from photocatalytic reactions, or (ii) to photocorrosion of the photocatalyst induced by premature  $\text{Ag}_2\text{CO}_3$  decomposition under light irradiation. The second assumption seemed to be of minor impact since the catalyst has been found still active in reuse experiments as further discussed in the Section 3.3. The observation of photocatalytic degradation threshold has already been reported upon assays involving pure  $\text{Ag}_2\text{CO}_3$  against Methyl Orange (MO) anionic dye,<sup>7,8</sup> and Rhodamine B (RhB)<sup>7,8,18</sup> and Methylene Blue (MB)<sup>7</sup> cationic dyes despite their electrostatic attraction by negatively  $\text{Ag}_2\text{CO}_3$  surfaces. In contrast, the most



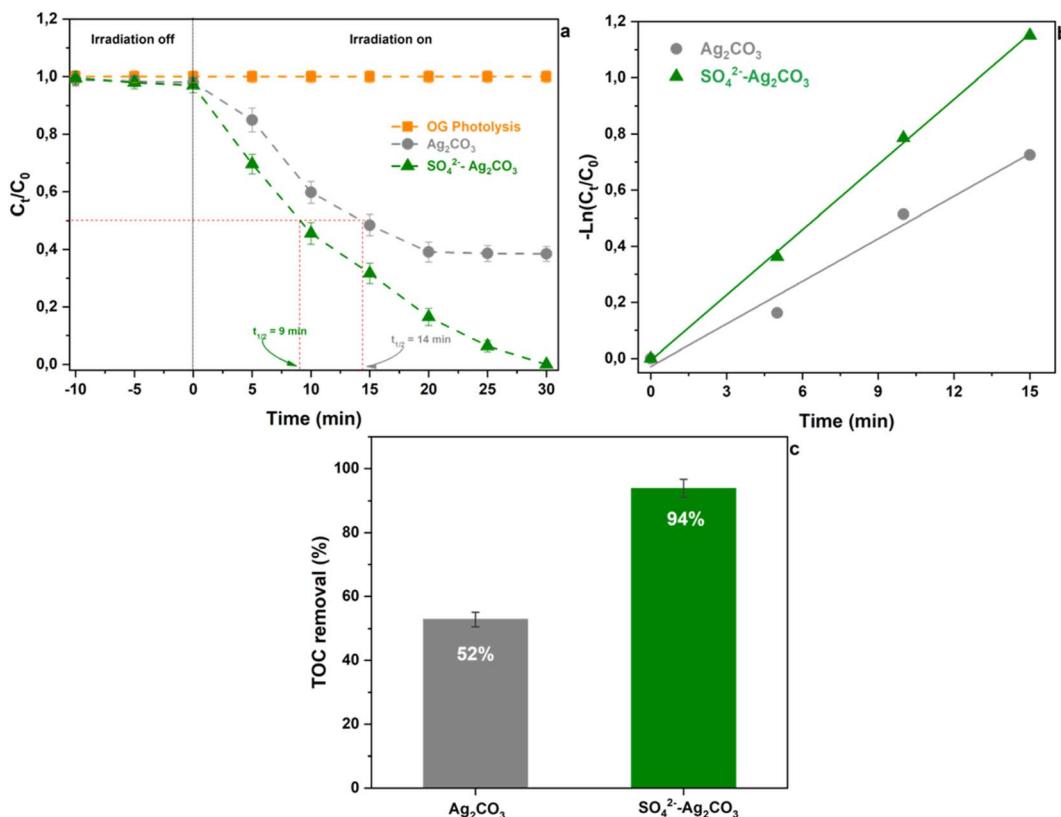


Fig. 5 Variation of the relative OG concentration vs. irradiation time over  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  (a). Plots of  $-\ln(C_t/C_0)$  vs. irradiation time for the two photocatalysts (b). Proportion of Total Organic Carbon (TOC) removal analyzed upon OG photocatalytic degradation under visible light irradiation during 30 min (c). The errors bars in (a) and (c) correspond to the data dispersion from 2 experiments.

salient result from the use of  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  photocatalyst was that the relative OG concentration continuously decreased during the photocatalytic test to reach remarkably a total removal of the dye pollutant within 30 min (Fig. 5a). This denoted its relative better photostability, *i.e.* a higher resistance to both surface poisoning and photo-corrosion issues as below evidenced in Section 3.3.

For both the pristine photocatalyst and  $\text{SO}_4^{2-}$ -modified photocatalysts, OG dye photocatalytic degradation obeyed a pseudo first-order kinetics during approximately the first 15 min of visible light illumination. The rate constant assessed in this time range was about  $5.1 \times 10^{-2} \text{ min}^{-1}$  for pure  $\text{Ag}_2\text{CO}_3$  and  $7.8 \times 10^{-2} \text{ min}^{-1}$  for  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  (Fig. 5b). This result denoted that the photocatalytic activity of the  $\text{SO}_4^{2-}$ -modified sample was *ca.* 1.5 times faster than that of pure  $\text{Ag}_2\text{CO}_3$ .

The mineralization of OG, *i.e.* its ability to be converted into  $\text{H}_2\text{O}$  and  $\text{CO}_2$  upon photocatalytic degradation, was also investigated. Fig. 5c depicted the total organic carbon (TOC) removal analyzed in the supernatant aqueous solution after a 30 min photocatalytic test using each photocatalyst. In presence of  $\text{Ag}_2\text{CO}_3$ , only around 52% of the TOC was removed, otherwise the proportion of OG and eventually its organic byproducts originated from photocatalytic reactions which was able to be mineralized. It should be noted that this OG amount was of the same magnitude order than that ( $\approx 60\%$ ) previously assessed by

*in situ* UV-VIS spectrophotometry during the photocatalyst test. Nevertheless, it is worth noting that upon the use of  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$ , almost 94% of the TOC was removed, indicating a relatively huge mineralization of OG dye. Interestingly, it should be noted that this amount was fairly close to the 100% of OG photo-catalytically degraded assessed above by UV-VIS spectrophotometry.

### 3.3 Effect of $\text{SO}_4^{2-}$ modification on $\text{Ag}_2\text{CO}_3$ stability

The above presented results highlighted that modification of  $\text{Ag}_2\text{CO}_3$  by  $\text{SO}_4^{2-}$  could be an efficient route to enhance the photocatalytic activity under visible light with (i) a higher degradation rate, (ii) an almost complete decomposition of the organic pollutant and (iii) a high efficiency of mineralization of the OG dye. However, the effect of  $\text{SO}_4^{2-}$  anions on both the stability of the photocatalyst and the photocatalytic oxidation mechanism needed to be investigated for further improvement and practical applications.

To investigate the behavior of pure and sulfate-modified  $\text{Ag}_2\text{CO}_3$  photocatalysts towards photo-corrosion issue, cycling experiments were performed. Fig. 6a reported the relative variation of OG concentration *versus* irradiation time under visible light recorded in presence of both the photocatalysts during three successive runs of 30 min each one. As previously mentioned, when using pure  $\text{Ag}_2\text{CO}_3$ , the dye photocatalytic

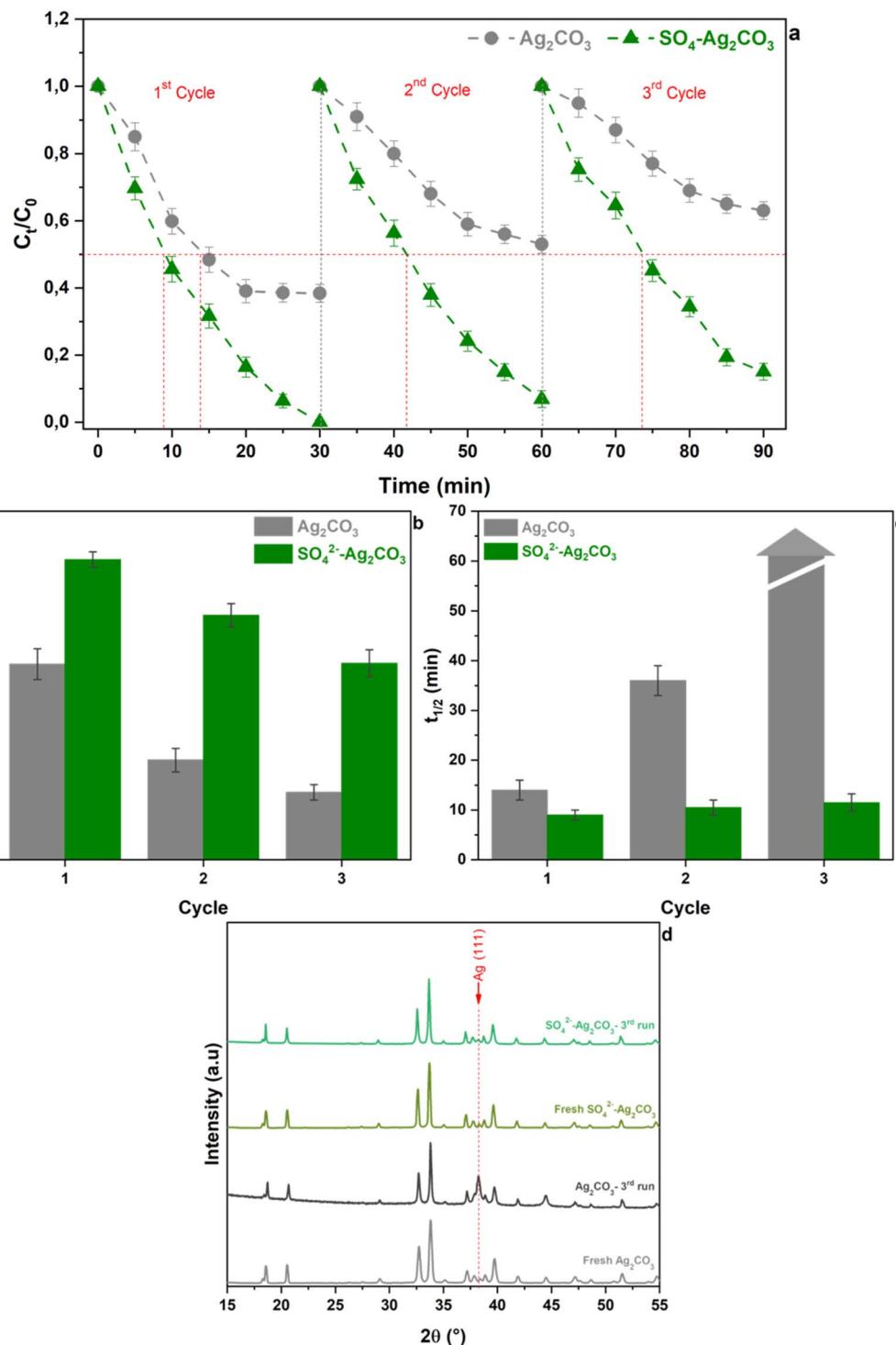


Fig. 6 Cycling runs for OG photodegradation under visible light irradiation over pure  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$  (a). Rate constant (b) and half-photodegradation time of OG ( $t_{1/2}$ ) versus cycling of pure  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}$ - $\text{Ag}_2\text{CO}_3$  photocatalysts (c). X-ray diffraction patterns of unmodified  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}$  modified  $\text{Ag}_2\text{CO}_3$  after the 3rd cycle (d). The errors bars in (a)–(c) correspond to the data dispersion from 2 experiments.

degradation curve reached a plateau after 20 min of irradiation in the 1st cycle and the same behavior tended to be exhibited during the 2nd and 3rd cycles. It should be noted that as the cycles number increased, the maximal amount of OG removed decreased from approximately 60% at the end of the 1st cycle, to

45 and 35% after the 2nd and 3rd ones respectively. Accordingly, the corresponding rate constants deduced over the first 15 minutes, labelled  $R_{15}$ , also rapidly decreased from  $5.1 \times 10^{-2} \text{ min}^{-1}$  for the 1st cycle to  $2.6 \times 10^{-2}$  and  $1.7 \times 10^{-2} \text{ min}^{-1}$  for the 2nd and 3rd ones, respectively (Fig. 6b). This steady



decline of rate constants corresponded to an efficiency loss with respect to the 1st cycle of 50 and 65% for the 2nd and 3rd ones respectively. These results ascertained the poor stability of pure  $\text{Ag}_2\text{CO}_3$  in agreement with elsewhere reported studies.<sup>8,15</sup> The variation of the OG half-degradation time ( $t_{1/2}$ ) *versus* cycling recorded upon the use of  $\text{Ag}_2\text{CO}_3$  (Fig. 6) showed that  $t_{1/2}$  of about 14 min for the 1st cycle strongly increased to 35 min for the 2nd one while it cannot be determined after 3 cycles since the total amount of OG removed did not exceed 35% (Fig. 6c). These results further supported previous deductions (Section 3.2) regarding the low stability and/or deactivation, by being sensitive to photo-corrosion and/or poisoning issues respectively, of the unmodified  $\text{Ag}_2\text{CO}_3$ .

By contrast, the OG concentration variation curves *versus* cycling, recorded in presence of  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  photocatalyst, showed a continuous and very noticeable OG photocatalytic degradation *versus* irradiation time under visible light regardless the cycling run number (Fig. 6a). In fact, while OG dye was completely removed after 30 min during the 1st cycle, denoting 100% of removal efficiency, the efficiency remained greater than 90% and 80% over the same period upon the 2nd and the 3rd cycles, respectively. Likewise, the corresponding  $R_{15}$  rate constants slightly decreased from  $7.8 \times 10^{-2} \text{ min}^{-1}$  after the 1st

cycle to  $6.3 \times 10^{-2} \text{ min}^{-1}$  after the 2nd and to  $5.1 \times 10^{-2} \text{ min}^{-1}$  after the 3rd cycle, which corresponded to a thorough efficiency loss of about 35% being slighter than that (65%) previously computed for pure  $\text{Ag}_2\text{CO}_3$  (Fig. 6b). The better stability of  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  photocatalyst was also illustrated throughout the assessment of  $t_{1/2}$  values *versus* cycling. Fig. 6c revealed that  $t_{1/2}$  remained quite of the same magnitude order around 10 min regardless the cycle run number. Furthermore, powder XRD carried out on unmodified  $\text{Ag}_2\text{CO}_3$  sample, recovered after the 3rd cycle, revealed the appearance of a very intense peak ascribed to (111) metallic silver (Ag) (Fig. 6d). This observation denoted that bare  $\text{Ag}_2\text{CO}_3$  underwent photo-corrosion issue. Nevertheless, it is worth noting that such Ag peak was very hardly observed in  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  after the same run of photocatalysis test. The whole of these results concorded for proving that  $\text{Ag}_2\text{CO}_3$  modification by  $\text{SO}_4^{2-}$  likely appeared to be an effective and efficient way to improve the resistance of  $\text{Ag}_2\text{CO}_3$  against photo-corrosion as well as poisoning issues, and thus to enhance photocatalytic activity.

### 3.4 Photocatalytic mechanism

In order to explore the photocatalytic mechanism of both  $\text{Ag}_2\text{CO}_3$  and  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  photocatalysts, reactive species

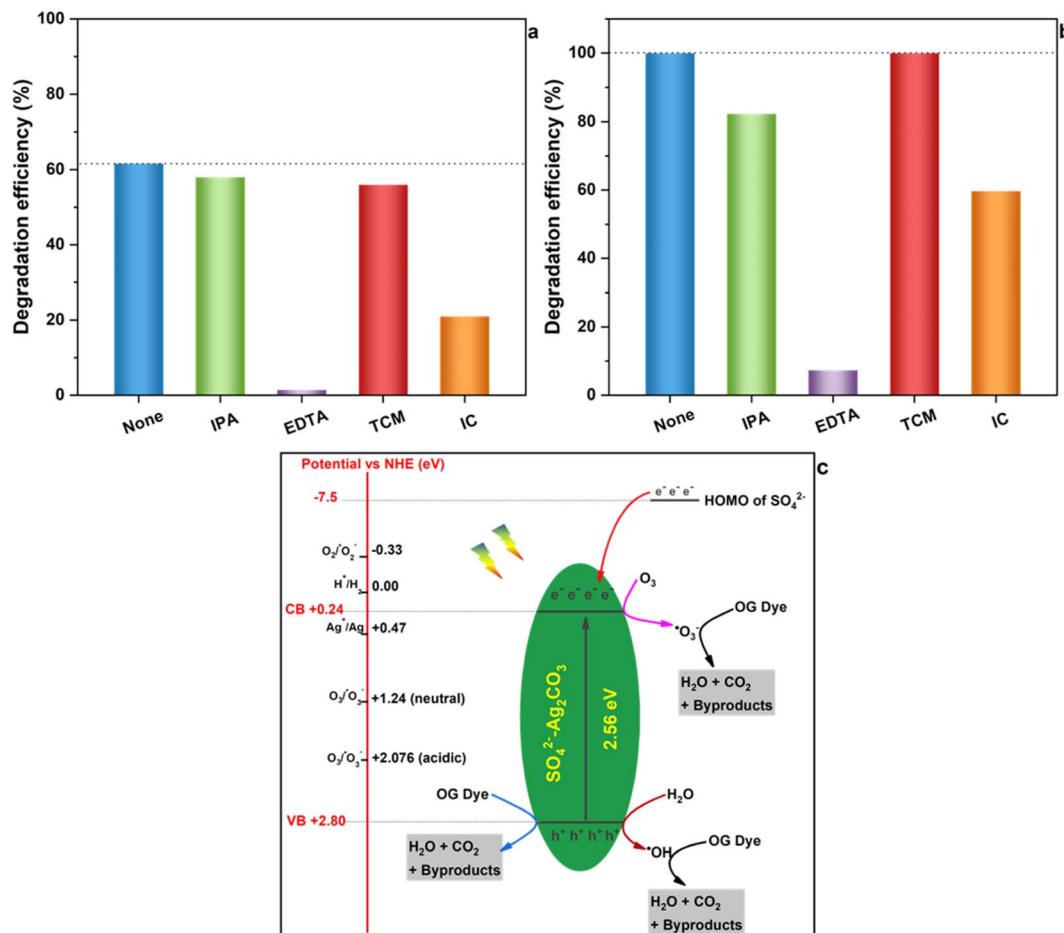


Fig. 7 Photocatalytic degradation of OG by  $\text{Ag}_2\text{CO}_3$  (a) and  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  (b) under visible light irradiation in the presence of scavengers: IPA, EDTA, TCM and IC. Schematic illustration of the plausible mechanism of OG degradation in presence of  $\text{SO}_4^{2-}\text{-Ag}_2\text{CO}_3$  photocatalyst (c).

trapping experiments were performed to elucidate the main oxidants responsible of OG degradation under visible light irradiation, including hydroxyl radical ( $\cdot\text{OH}$ ), superoxide radicals ( $\cdot\text{O}_2^-$ ), ozonide radicals ( $\cdot\text{O}_3^-$ ) and photoinduced holes ( $\text{h}^+$ ). The obtained results, gathered in Fig. 7(a) and (b), did not reveal significant differences in the behavior of both the investigated  $\text{Ag}_2\text{CO}_3$  based photocatalysts towards the radicals trapping agents above-mentioned. Indeed, the addition of TCM, as  $\cdot\text{O}_2^-$  scavenger, had no noticeable effect on OG photocatalytic degradation since the efficiency almost remained constant in both the cases like before using the trapper. This likely stood for the noninvolvement of  $\cdot\text{O}_2^-$  in OG degradation. The use of IPA, as hydroxyl radical trapper, yielded a small decrease in the photocatalytic degradation efficiency of OG within 30 min from initially almost 62% and 100% to around 58% and 82% over unmodified and modified  $\text{Ag}_2\text{CO}_3$  respectively. Hence,  $\cdot\text{OH}$  radicals seemed to play a minor role in OG photocatalytic degradation. Nevertheless, it is noteworthy that using IC quencher of  $\cdot\text{O}_3^-$  provoked a relatively huge decrease of the OG degradation efficiency estimated at almost 40% in both the cases. This denoted that the contribution of  $\cdot\text{O}_3^-$  radicals in OG photocatalytic degradation may be substantial. The most salient effect was that of the addition of EDTA as  $\text{h}^+$  trapper which thoroughly made both the  $\text{Ag}_2\text{CO}_3$  based photocatalysts unactive towards the OG removal. This likely ascertained that photoinduced holes ( $\text{h}^+$ ) was the major reactive species responsible of OG photocatalytic oxidation over both the investigated photocatalysts.

These results were further supported by the values of redox potentials of the top of valence band (VB) and the bottom of conduction band (CB) beforehand computed for both the  $\text{Ag}_2\text{CO}_3$  based photocatalysts studied herein (Section 3.1) that were reported in Fig. 7c on which were also placed potentials of different reactive species in photocatalysis. In fact, the potential of photoelectrons on CB is too positive (0.24 eV) to be able to permit the reduction of dissolved  $\text{O}_2$  in aqueous medium into  $\cdot\text{O}_2^-$  species whose potential is  $-0.33$  eV. Therefore,  $\cdot\text{O}_2^-$  entities cannot come into play in the OG photocatalytic degradation over  $\text{Ag}_2\text{CO}_3$  based photocatalysts, and must be excluded as also emphasized by W. Jiang *et al.*<sup>8</sup> This deduction was in contrast to results reported by several authors<sup>4,34</sup> proposing the involvement of  $\cdot\text{O}_2^-$  in the photodegradation of rhodamine B and/or Methylene Orange and/or Methylene Blue over silver carbonate although the potential of photoelectrons they estimated was 0.29 eV and 0.37 eV respectively, *i.e.* too positive with respect to the negative one characterizing  $\text{O}_2/\cdot\text{O}_2^-$  couple. Nevertheless, the ozone, able to be provided from dissolved oxygen upon solution illumination,<sup>8</sup> present an electrode potential in neutral and acidic medium of 1.24 eV and 2.076 eV respectively so that it can be reduced by photoelectrons generated herein (0.24 eV) to yield the formation of oxidative  $\cdot\text{O}_3^-$  radicals which assured OG photocatalytic degradation onto both the investigated photocatalysts. Furthermore, taking into account the strongly oxidative electrode potential of photoholes ( $\text{h}^+$ ) herein estimated of about 2.80 eV, these photoinduced entities assured direct OG degradation. Likewise,  $\text{h}^+$  species could also hardly oxidize  $\text{H}_2\text{O}$  to provide  $\cdot\text{OH}$  radical

whose the potential is close to its own (2.8 eV). This denoted that a part of  $\text{h}^+$  may indirectly participate through a minor amount of  $\cdot\text{OH}$  radical in the OG photodegradation onto both the studied photocatalysts. In light of all these results, the OG photocatalytic degradation under visible light seemed to be achieved according to on the whole a similar mechanism illustrated in Fig. 7c onto unmodified and sulfate modified  $\text{Ag}_2\text{CO}_3$ . The plausible mechanism likely mainly implied photoholes acting as latent oxidative entities along with to a relatively lesser extent  $\cdot\text{O}_3^-$  reactive radicals and finally a minor participation of  $\cdot\text{OH}$  hydroxyl radicals. Nonetheless, in view of the so proposed mechanism, one can ask how  $\text{Ag}_2\text{CO}_3$  modification by  $\text{SO}_4^{2-}$  improved photostability as well as photocatalytic efficiency beforehand evidenced (Section 3.2 and 3.3)?

One beneficial key role of  $\text{SO}_4^{2-}$  anions would be their ability to contribute with 32 valence electrons to the lattice of the sulfate-modified  $\text{Ag}_2\text{CO}_3$  photocatalyst, instead of 24 electrons for  $\text{CO}_3^{2-}$  anions, providing therefore a surplus of 8 valence electrons. As reported by Bishop *et al.*,<sup>36</sup> the Highest Occupied Molecular Orbital (HOMO) of  $\text{SO}_4^{2-}$  is located at around  $-7.5$  eV, so that sulfate electrons can be transferred to lower  $\text{AgCO}_3$  conduction band. Thus, these excess electrons provided by  $\text{SO}_4^{2-}$  together with those photogenerated in  $\text{AgCO}_3$  upon illumination can reduce more ozone to produce more  $\cdot\text{O}_3^-$  reactive entities which can act as additional reactive species as evidenced above by IC trapping experiments. Consequently, the OG photocatalytic degradation could speed up as proved by corresponding higher rate constant with respect to that of the pristine  $\text{Ag}_2\text{CO}_3$  above-computed in Section 3.2.

Another possible key effect of  $\text{SO}_4^{2-}$  on the improvement of  $\text{Ag}_2\text{CO}_3$  photostability, beforehand evidenced upon photocatalytic tests (Section 3.2) and cycling experiments (Section 3.3), may be its capacity of electrons transfer to  $\text{Ag}^+$  higher than that permitted by  $\text{CO}_3^{2-}$ . In fact, as widely reported, primary mechanism of photocorrosion of pure  $\text{Ag}_2\text{CO}_3$  could be attributed to the reduction of  $\text{Ag}^+$  cations, issued from  $\text{Ag}_2\text{CO}_3$  solubilizing, by photoinduced  $\text{e}^-$ , which produced metallic Ag and, over time, a progressive  $\text{Ag}_2\text{CO}_3$  depletion into Ag cations resulting at the end in the photocatalyst degradation.<sup>2,4,15</sup> Considering an isolated  $\text{Ag}^+$ –anion interaction, the fractional number of electrons transferred from the anion to  $\text{Ag}^+$  cation can be estimated, according to the Pearson model<sup>37</sup> (details reported in the ESI†), to be about 0.29 and 0.21 for  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  respectively. This indicated that an interaction of  $\text{SO}_4^{2-}$  with  $\text{Ag}^+$  cation was 38% greater than that of  $\text{CO}_3^{2-}$ . Such an effect can contribute to improve the stability of the photocatalyst because  $\text{Ag}^+$  would be less reactive towards photoelectrons to form metal Ag, hence yielding photocorrosion issue to get mitigated.

## 4 Conclusion

$\text{Ag}_2\text{CO}_3$  modification with sulfate was achieved according to a simple precipitation method. This was confirmed by XRD that revealed a volume expansion of the monoclinic  $\text{Ag}_2\text{CO}_3$  unit cell due to the substitution of  $\text{CO}_3^{2-}$  groups by the larger  $\text{SO}_4^{2-}$  anions. This was hence consistent with a bulk modification

rather than a simple surface grafting of  $\text{SO}_4^{2-}$  ions on  $\text{Ag}_2\text{CO}_3$  particles. However,  $\text{Ag}_2\text{CO}_3$  modification with  $\text{SO}_4^{2-}$  did not significantly affect the  $\text{Ag}_2\text{CO}_3$  band gap. The evaluation of the photocatalytic degradation of OG dye under visible light revealed that the sulfate modified  $\text{Ag}_2\text{CO}_3$  was more active than bare  $\text{Ag}_2\text{CO}_3$  leading to the achievement of a quasi-total mineralization within 30 min of irradiation. In addition, evidence for poisoning and/or photocorrosion issues observed for pure  $\text{Ag}_2\text{CO}_3$  did not occur for the modified photocatalyst. The active species trapping experiments revealed that the OG photocatalytic degradation seemed to be assured over both the photocatalysts by photoinduced holes ( $\text{h}^+$ ) along with  $\text{O}_3^-$  radicals, while  $\text{OH}$  radicals would play a minor role. Improvements allowed by  $\text{Ag}_2\text{CO}_3$  modification by  $\text{SO}_4^{2-}$ , in terms of increase of photocatalytic rate and enhancement of  $\text{Ag}_2\text{CO}_3$  stability, could be due to valence electrons added to photoinduced electrons, as a result of their transfer from  $\text{SO}_4^{2-}$  HOMO to  $\text{Ag}_2\text{CO}_3$  conduction band, which may together assure the formation of much active  $\text{O}_3^-$  radicals entities. This proposed mechanism ought to be further validated by using more sophisticated characterization technique such as ESR and PL analyses and DFT calculations. On the whole, in view of the simple synthesis route of  $\text{SO}_4^{2-}$  modified  $\text{Ag}_2\text{CO}_3$  photocatalyst and its promising performances, in term of enhancement of photoactivity and photostability under visible light at laboratory scale, this study should be carried on by evaluating its photocatalytic properties in an outdoor solar pilot. This will increase its prospect of application in the field of tertiary treatment of wastewater.

## Conflicts of interest

There are no conflicts of interest to declare.

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