The role of strontium on the enhancement of photocatalytic response of TiO2 nanotubes – application in methylene blue and formic acid photodegradation under visible light and UV-A

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ABSTRACT
The influence of ferroelectric strontium nanoparticles on the photocatalytic performance of 1D TiO2 nanotubes (NT) was herein highlighted. The effect of adding various amounts of Sr nanoparticles onto NTs was therefore deeply characterized by means of Raman, UV-vis diffuse reflectance, photoluminescence (PL) and X-ray photoelectron spectroscopies, X-ray diffraction, N2 adsorption-desorption measurements and scanning electron microscopy coupled with energy-dispersive X-ray analysis as well as determining dielectric properties. The different xwt%Sr-NTs with x=(0.2, 0.4, 0.6, 0.8 and 1 wt%) were investigated for the photodegradation of Methylene Blue (MB) under visible light and formic acid under UV-A. Results emphasize that the kinetic study fits well with Langmuir-Hinshelwood (LH) model; for the same surface coverage (θ=0.99), the rate constant kLH increases versus Sr loading with an optimum at 0.8 wt% Sr. Under UV-A light, photodegradation increases versus Sr loading. As evidenced by PL, impedance and XPS measurements, the presence of ferroelectric strontium generates structural defects (Ti3+ and Ov) with strong opportunity to monitor the separation the photogenerated (electron- hole) pairs regardless of the synthesis limitations. Herein, the molar ratio O2-/Ti4+ increases vs strontium loading. Hence, Sr-NTs opens new route for "assisted" photocatalysts.

1. Introduction
Several dyes are employed in different industries such as textiles, food, printing, medicine, plastic, and mainly the paper industry for numerous purposes (Alencar et al., 2020). Nevertheless, these activities generate large amounts of wastewater containing toxic dyes, inadequate for human and plants consumption (Pandey et al., 2020). Among them, the textile manufactory remains the most methylene blue (MB) consuming industry (Derakhshan et al., 2013). The textile wastewater treatment was the topic of numerous literature reports (Bilinska & Gmurek, 2021; Wang et al., 2020). When low biodegradability is concerned, advanced Oxidation Processes (AOPs) have been used as an alternative method for MB degradation, among them, heterogeneous photocatalysis, in which radiation (UV and/or visible) is used by a semiconductor (photocatalyst) to create free hydroxyl radicals, known to be responsible of the degradation of large spectrum of organic compounds until complete mineralization into CO2 and H2O (Ahmad et al., 2015). Many innovative catalysts have been successfully employed to achieve maximum degradation efficiency. Typically, semiconductors and semiconductor heterojunctions like ZnS (Rao et al., 2016), TiO2 (Zhu, Hong & Ho, 2015), ZnO (Barnes, Molina, Xu, Dobson, & Thompson, 2013), carbon-based catalysts such as graphene, graphene oxide, and carbon nitrides (Lu et al., 2017; Sarfraz et al., 2021), plasmonic metals (such as gold, silver, platinum) (Sarfraz et al., 2021; Zhang et al., 2018). These systems have demonstrated high efficacy in oxidizing MB through redox reactions. Nevertheless, strong differences in absolute rate constant values were observed due to: different reactor profiles, different lamps used with different emission spectra (Alkaykh, Mbarek, & Ali-Shattle, 2020). There is no standard condition to perform the photodegradation test. Moreover, the rate of the reaction can vary with:
(i) MB concentration (Salama, Mohamed, Aboamera, Osman, & Khattab, 2018), (ii) the pH (Alkaim et al., 2014) and (iii) the surface charge of the catalyst (Singh et al., 2020). In fact, MB is a cationic dye, mainly adsorbs onto highly negatively charged photocatalyst (Azeez et al., 2018). Hence, the pH zero
charge is unfortunately an important key parameter, H⁺ ions competes with cationic MB dye at the surface of the photocatalyst at pH lower than pH of zero charge (pHzc). Therefore, the test must be performed at pH slightly higher than pHzc. On the other hand, preparing an efficient, wide bandgap photocatalyst is still challenging. Therefore, an efficient strategy to decrease the rate of recombination of photogenerated electron-hole of the applied photocatalyst is of high interest. Different approaches have been investigated to boost the TiO₂ response to photoexcitation: like photosensitization of TiO₂ by dye (Li, Liang, Zhou, & Pan, 2020), metal ion doping (Liu, Jiang, Song, Duan, & Zhu, 2020), or creating heterojunction with metal oxides (Mohammed Redha, Abdulla Yusuf, Amin, & Bououdina, 2020). Another approach, by doping with metal oxides like transition and noble metals which showed a great influence on the photocatalyst efficiency and yields to the creation of electronic trap-centres (like oxygen vacancies) which quell the electron-hole recombination (Chakhtouna, Benzeid, Zari, & Bouhfid, 2021). However, all these synthesis methods led to limited success in photocatalytic activity enhancement. One way to improve the efficiency of photocatalytic materials is to develop “assisted” photocatalysis processes. In this respect, charge separation can be compelled by induced electric field coming from the energy discontinuity at the semiconductor/electrolyte interface. Tuning the electronic band structure in the interfacial region therefore appears as a very effective approach to enhance charge separation efficiency. In this respect, ferroelectric polarization is a promising strategy to modify band structures and charge transport performance in heterojunction-based semiconductors. The built-in electric polarization can lead to tremendous redistribution of charges in adjacent semiconductors. Generating locally such spontaneous polarization by addition of a ferroelectric material to the photocatalyst would provide a strong opportunity (to the best of our knowledge, not used up to now) to monitor the charge separation regardless of the synthesis limitations.

Few attempts have been done in the literature to build devices combining ferroelectrics and semiconductor materials by growing the strontium titanate (SrTiO₃) phase onto TiO₂ systems. Different methodologies were envisaged like TiO₂ anodization (Janczarek & Kowalska, 2021) or rutile TiO₂ nanowires obtained by controlled alkaline hydrothermal treatment (Zhang, Jing, Tan, Yu, & Ma, 2018) followed in all cases by in situ substitution by Sr or Ba under hydrothermal conditions. However, these methods suffer from a low scale production of anodized TiO₂ materials or use of inappropriate low active rutile phase. TiO₂ microspheres were also used but their very large size limits the proportion of TiO₂ semiconductor phase influenced by ferroelectric domains (Hamisu, Gaya, & Gaya, 2020). Generally, improved photocatalytic performances were observed but without distinguishing the p-n heterojunction effects or induced ferroelectric polarization effects (if even considered). For example, the conduction band (CB) of SrTiO₃ is lower than TiO₂ (CB) which limits to some extend the recombination rate; but the role played by ferroelectricity was rarely considered in this case because SrTiO₃ is generally considered paraelectric. This simplistic statement was however recently denied since under optical excitation, SrTiO₃ was found to become ferroelectric (Liu, Lv, Fan, Xing, & Jia, 2019).

The objective here is to demonstrate the interest of assisted photocatalysis process. The photocatalytic activity will be enhanced by an adequate combination of ferroelectric strontium with TiO₂ semiconductor of optimized 1D morphology. To the best of our knowledge, Sr-doped TiO₂ nanotubes for “assisted” photocatalysis has not yet been investigated. In this respect, charge separation can be boosted by the electric field created by strontium. In the first part, different wt% of strontium loadings were doped onto 1D TiO₂ nanotubes. The second part is devoted to characterization of Sr-NTs nanomaterials. Finally, kinetics models were applied for the photodegradation of model molecules (MB and Formic acid (FA)) and correlated to the structural, textural, morphological and electrical properties of Sr-NTs nanomaterials.

2. Experimental
2.1. Elaboration of Sr-doped TiO₂ nanotubes

Firstly, 1D TiO₂ nanotubes material (NT) is obtained using a hydrothermal procedure as described in (Meksi et al., 2016). Secondly, NT was subsequently doped with different amounts of Strontium (0.2, 0.4, 0.6, 0.8 and 1.0 wt %) using dry impregnation method. The desired amount of strontium precursor, Sr(NO₃)₂ was first suspended in a volume of water corresponding to twice the porous volume (Vp) of the TiO₂ nanotubes before being contacted with an adequate quantity of NT. The obtained paste was then dried in vacuum-oven at 40°C for 24h. The resulting nanomaterials are named x Sr-NT (with x the weight loading of strontium). Further post-thermal treatment was then conducted for the Sr-NT samples once again at 400°C under air using a heating ramp of 2°C/min. Samples were then named as x wt%Sr-NT.
2.2. Materials characterization

2.2.1. Catalyst characterization

XRD data were collected on an automatic diffractometer (XRD-7000, Shimadzu, Japan) using a Ni-filtered Cu Kα radiation source (λ = 1.54184 Å). The samples were measured at 2 theta range between 10 and 80° using a scan speed of 1°/min. x wt%Sr-NT nanomaterials structural environment was studied using Raman spectroscopy at excitation wavelength of 632 nm (iHR320, HORIBA, Japan). The textural properties of x wt%Sr-NT nanomaterials and their Sr free counterpart were measured using QUANT ACHROME Nova 1200e, USA. Prior to analysis, the samples were outgassed at 200°C for 2 h. The UV–Vis DRS measurements were recorded on UVD-3200, Labomed Inc, USA. Bandgap energy values were evaluated using the Kubelka–Munk method. F(R)hv1/2 versus hv plots were built with F(R) = (1 – R)/2R, assuming an indirect bandgap transition. Transmission Electron Microscopy (TEM) was performed on a JEOL 2010 (200 kV) microscope to reveal the morphology of the different samples. The TEM analysis specimens were first dispersed in ethanol before dropwise addition and drying onto a holey carbon film supported on a Cu grid (300 mesh). The SEM images and SEM mapping of 0.2 wt% and 0.8 wt% Sr loaded TiO2 were studied using Scanning electron microscope at 20 kV (FEI, Inspect S50, USA). Photoluminescence (PL) of Sr-NTs are measured directly from the intensity and spectrum content of the photoluminescence (Shimadzu spectrofluorometer, RF5301 PC) with excitation wavelength of 290 nm. X-ray photoelectron spectroscopy (XPS) studies were carried out using a Thermo Scientific ESCALAB 250Xi equipped with a dual Al/Mg anode and a hemi-spherical analyzer operating at fixed pass energy of 50 eV. A 150 W monochromatic source (Al Ka = 1486.6 eV) was used to excite the samples. Impedance measurements were performed using PalmSens4 instrument. Samples (0.2 wt%Sr-NT and 0.8 wt%Sr-NT powder) in the form of a 13 mm diameter and a 2 mm thickness pellet were used. The material is placed between two glass coated with a conductive FTO electrodes. The complex impedance measurements were carried out at room temperature by scanning a frequency range from 0.1 Hz to 1 MHz with a voltage of 0.5 V.

2.2.2. Photocatalytic experiments

The photocatalytic activity of Sr doped TiO2 nanomaterials were applied in the photodegradation of methylene blue (MB) under visible light and formic acid (FA) under UV-A. The photodegradation of MB was performed using visible lamp (HQI-E 400 W/n) having a maximum emission at 520 nm and coated with UV filter. Typically, 30 mg of xwt% Sr-NT catalyst was added to 30 mL of 20 ppm aqueous solution of MB. The solution was stirred under dark for an hour to reach adsorption equilibrium and then the lamp was turned on. The methylene blue samples were withdrawn at different time intervals (t) and analyzed by UV-visible spectrophotometer. In order to elucidate the photodegradation kinetic model, the concentrations of MB were varied between 5 and 50 mg.L⁻¹ (0.014 to 0.14 mmol.L⁻¹). The photodegradation of FA was performed in a photoreactor (pyrex, 100 ml) with 12.5 cm² of optical window area. Sr-NTs concentration was maintained at 1.0 g.L⁻¹. The solution pH was in the range of 3.0 ± 0.2. A PL-L (18 W) lamp with emission at 365 nm was used for UV irradiation. An optical Corning filter 0.52 was employed to cut-off wavelength below 340 nm. A radiant flux of 5 mW.min⁻¹ was fixed for all experiments. Before the study, the suspensions were facilitated to reach equilibrium condition by stirring well in darkness for 30 min. The formic acid concentration of the solution after equilibration was then measured and used as the initial concentration (C₀). Formic acid samples were taken for analysis at different intervals (t) from the photoreactor while the photocatalyst was separated from the liquid phase by filtration. Withdrawn samples were then analyzed with a HPLC Shimadzu Nexera i-series equipped with Hypersil Gold column (5 mm, 150 × 4.6 mm); using acetonitrile/water (30/70 v/v) as mobile phase and UV-visible detector (λ = 210 nm) at a flow rate of 0.8 mL.min⁻¹.

Figure 1. XRD patterns of: (A) x wt% Sr-NT, x = {0, 0.2, 0.4, 0.6, 0.8 and 1.0} and (B) zoom of (101) peak.
Table 1. Textural and structural properties of x wt% Sr-NT catalysts, x = {0, 0.2, 0.4, 0.6, 0.8 and 1}.

| Catalysts   | S BET (m^2 g^-1) | Pore diameter (nm) | E g (eV) | Crystallite sizes (nm) | EDAX Sr/Ti atomic ratio |
|-------------|------------------|--------------------|----------|------------------------|-------------------------|
| NT          | 128              | 22.2               | 3.20     | 12.0                   | –                       |
| 0.2 wt% Sr-NT | 107              | 22.8               | 3.42     | 11.0                   | 0.0067                  |
| 0.4 wt% Sr-NT | 95               | 22.1               | 3.71     | 11.2                   | –                       |
| 0.6 wt% Sr-NT | 117              | 21.8               | 3.46     | 11.2                   | –                       |
| 0.8 wt% Sr-NT | 106              | 21.7               | 3.41     | 11.1                   | 0.020                   |
| 1 wt% Sr-NT  | 108              | 21.5               | 3.41     | 11.1                   | –                       |

3. Results and discussion

3.1 X-Ray diffraction (XRD)

Figure 1A illustrates the X-ray diffraction patterns of xwt% Sr-NT; x = (0.2%, 0.4%, 0.6%, 0.8%, 1.0%) and their free strontium material TiO2 (NT) taken as reference. The NT displayed the presence of crystalline TiO2 nanostructure typical to that of anatase phase and agrees with JCPDS No. 21-1272. Moreover, the addition of strontium does not lead to the appearance of new peaks corresponding to SrO (32.85°, 38.74°, 46.95° and 58.40°). Nevertheless, Sr doping induced slight shift in (101) plane of anatase phase (Figure 1B), which indicates distortion in lattice of TiO2 (Keerthana et al., 2022) by creation of defects (Ti3+) and/or oxygen vacancies. Hence, PL and XPS measurements were used in the later section to highlight this hypothesis. In our case, the presence of strontium oxide or strontium titanates (SrTiO3) is highly probable even if we do not detect their corresponding rays in the XRD patterns of doped samples. This could be explained by (i) the low content of strontium which is lower than XRD sensitivity or (ii) Sr could be explained by (i) the low content of strontium in the XRD patterns of doped samples. This probable even if we do not detect their corresponding rays in the XRD patterns of doped samples. This could be explained by (i) the low content of strontium which is lower than XRD sensitivity or (ii) Sr might be highly dispersed onto TiO2. Similarly, doping TiO2 with large ionic radius like rare elements lanthanides (e.g. La, Ce) anatase crystallite size and generates surface defects like oxygen vacancies (Xue et al., 2011). Following this finding, calculations were established, in the case of our materials, and determined from the broadening of (101) plane of anatase phase by using Scherrer formula (Secundino-Sánchez et al., 2022):

\[ L = \frac{K \lambda}{\beta_i \cos(\theta/2)} \]  

(1)

Where L is the crystallite size; K is taken 1; \( \lambda \) is the wavelength of the X-Ray radiation (CuK\( \alpha_1 = 0.15406 \text{nm} \)) and \( \beta_i \) is the line width at half-maximum height considering the correction \( \beta_i = ((\beta_{\text{measured}})^2 - (\beta_{\text{instrumental}})^2)^{0.5} \). After taking into account all parameters, crystallites size results of samples are summarized in Table 1.

From Table 1, Anatase crystallite sizes are similar for all the xwt% Sr-NT nanomaterials with values around 11.12 ± 0.06 nm showing the absence of crystallite size variation compared to the Sr-free 0NT reference (12 nm). This result might be explained by better stabilizing of the structural properties in presence of Strontium.

3.2. Raman spectroscopy

Raman spectra of pure NT nanotubes and x wt%-Sr-NT nanomaterials are shown in Figure 2. The appearance of peaks at 143, 394, 514 and 638 cm\(^{-1}\) are assigned to active modes E1g, B1g, A1g and E\(_g\) of anatase phase. The Raman signature clearly shows the presence of anatase phase, in good agreement with XRD results. However, a red shift was observed corresponding to the E1g mode of the anatase phase. NT has a mode of vibration at 149 cm\(^{-1}\) against 152 cm\(^{-1}\) for 0.6 wt% Sr-NT and 153 cm\(^{-1}\) for 0.8 wt% Sr-NT (Figure S1 supplementary information). Such shift was ascribed to the creation of surface defects like oxygen vacancies (Scepanovic, Grujic-Brojcin, Dohcevic-Mitrovic, & Popovic, 2007). Moreover, spectra of low doped materials (0.2 and 0.4 wt%Sr) show a small blue shift and extending of the principal peak (144 cm\(^{-1}\)). This effect was explained in literature by the distortion of anatase crystalline lattice or also the non-uniform distribution of the particle size and to the co-existence of several phases (Zhang, Bang, Tang, & Kamat, 2010). However, according to XRD patterns, distortion of the anatase crystalline lattice is eliminated but possibility of co-existence of other phases like SrTiO3 or SrO are not excluded.

3.3. UV-vis diffuse reflection

UV-vis DRS spectra were also acquired for NT and different wt% Sr doped NT catalysts (Figure 3). The spectra showed a strong absorption band at about 360 nm corresponding to TiO2. Sr-doped TiO2 showed a wavelength shift to lower values (340 nm for 0.2 wt% Sr-NT against 240 nm for 1 wt% Sr-NT) (Figure 3). Furthermore, the band gap energies were determined for doped and undoped strontium samples (Table 1) using Kubelka-Munk method (Machado & da Hora Machado, 2020) by plotting F(R) x h\(\nu\)^{1/2} against Energy (E) (Figure S2 supplementary information).

From Table 1, the undoped TiO2 NT material shows a band gap energy about 3.20 eV, value near to anatase one E\(_g\) (~3.17 eV) which agrees with XRD and Raman spectroscopies results. For doped samples, E\(_g\) increases slightly to reach 3.43 ± 0.02 eV. It should be noted that this absence of Eg shift can be expected if SrTiO3 is formed at the surface of TiO2.
3.4. Textural properties

The textural changes of NT with different wt% Sr loadings (0.2–1.0) was analyzed using N₂ adsorption-desorption measurement. The results are summarized in Table 1 and Figure S3 in supplementary information. NT shows a type IV isotherm pattern with H₃ hysteresis loop at p/p₀ range of 0.45, while with different wt% loading, the hysteresis loop tends to extend at higher p/p₀/C². Such isotherm with narrow and broad hysteresis indicates presence of micropore and mesopores and are characteristic of intergranular porosity resulting from particles aggregation to form slot like pores (Lei et al., 2001). The textural properties of NT and xwt% Sr-NT materials (Table 1) show a slight decrease of the surface area from 128 m² g⁻¹ NT to 95 m² g⁻¹ after doping with 0.4 wt% Sr. Compared to NT, the surface area varies in the range of 8.5%–17% for respectively 0.6 wt% Sr and 0.8 wt% Sr-NT materials. This suggests that some porosity vanished probably by partial blockage in the presence of strontium oxide species. The pore diameter obtained from BJH method varies slightly (22 ± 0.65 nm). Based on previous X-ray results the particle size (or coherent domain) is constant ~11 nm. Therefore, this homogeneous pore diameter distribution is most probably related to intergranular porosity resulting from physical agglomeration of xwt% Sr-NT materials by Van der Waals interaction.

3.5. Morphological properties

The morphological properties of representative nanomaterials NT and 0.8 wt% Sr-NT was examined with TEM and HRTEM (Figure 4).

From Figure 4, NT possess a tubular morphology with an outer diameter of ca. 15 nm (Figure 4a). HR-TEM image of NT shows an interlayer space of 0.34 nm corresponding to the (101) plane of the anatase phase (Figure 4b), being in good agreement with X-ray diffraction and Raman observations. By contrast, doping NT with Sr ions followed by post-thermal treatment (calcination at 400 °C) yields to mixture of nanotubes and nanorods (Figure 4c).

The FE-SEM-EDS mapping of 0.8 wt%Sr-NT (Figure 5a) and Ti, Sr and O elements are presented in Figure 5(b–d). The mapping shows the presence of Sr coexisting with NT nanoparticles. The presence of elements Sr, O and Ti are homogeneously distributed.

From EDAX results, the atomic molar ratio Sr/Ti are 0.0067 and 0.020 for respectively 0.2 wt%Sr and 0.8 wt%Sr-NT (Figure S4, Supplementary information). This result clearly indicates that dry impregnation method yields to excellent Sr ions distribution onto the surface of NT material.

3.6. Photoluminescence (PL) emission spectroscopy measurements

Photoluminescence (PL) spectra were also acquired for the same series of xSr-NT samples with x = 0, 0.2 and 0.8 (Figure 6). Results were recorded using an excitation source centred at 330 nm while spectra are herein presented in the 330–700 nm wavelength range.

In case of Sr doped NT, four emission peaks were observed in the PL spectra. At the excitation of 397 nm, the emission signalling self-electron trapping tendency by holes inside bulk titania lattice structure (Lei et al., 2001). Two emission peaks at about 457 nm and 535 nm were observed indicating a generated photoelectrons recombination with titania oxygen surface defect sites (Liu, Li, Sedhain, Lin, & Jiang, 2008). The emission peak 471 nm indicates the excited charge transfer transition from titania Ti³⁺ species to octahedral unit (TiO₆²⁻) (Li, Li, Hou, Cheah, & Choy, 2005). A much higher PL intensity is found
for Sr-NT than for NT. In addition, a high intense emission peak at about 535 nm indicates the generation of surface defects with Sr doping due to distortion of TiO$_6$ octahedra (Choudhury, Borah, & Choudhury, 2013). This phenomenon is particularly attributed to the ion size mismatch between Sr$^{2+}$ (1.18 Å) and Ti$^{4+}$ (0.68 Å) species, which eventually helps to generate oxygen vacancies and restore neutral charge. Increasing Sr loading from 0.2 to 0.8 wt% leads to the intensification of the PL intensity especially for 0.8 wt% Sr-NT with a dominant peaks at 397 nm, 471 nm and 535 nm. Such enhancement in peak intensity shows that increasing Sr loading influences the surface defect sites generation. Though an increase in surface oxygen vacancies occurs, the electrons transport from conduction to valence band (radiative recombination centres) becomes less, while act as luminescence sinkers and decreases the intensity of emission (Choudhury, Borah, & Choudhury, 2013). Overall, the PL characterization study shows that strontium doping on NT creates surface oxygen vacancies, assist trapping photogenerated electrons leaving holes for photocatalytic process. In the next section XPS analysis was used to provide more insights about the modification of surface structure in presence of strontium.
3.7. XPS measurements

XPS was employed to determine the elemental composition and surface chemical states of NT, 0.2 wt% Sr-NT and 0.8 wt% Sr-NT nanomaterials. Results are reported in Figure 7 and Table 2. As shown in Figure 7(a), Ti 2p, Sr 3d, O 1s and Ti 2s can be readily observed in the fully scanned spectra, indicating the presence of Ti, O and Sr at the surface of xwt% Sr-NT nanomaterials in good agreement with SEM mapping (Figure 5b–d). As displayed in Figure 7(b), the core O1s peak at 529.14 eV attributed to bulk oxygen (O²⁻) bound to Ti⁴⁺ is observed for all nanomaterials (Wang et al., 2021). The introduction of Sr yields to the formation of: (i) Ti-OH bonds and/or oxygenated Ti³⁺ species (530.08 eV) and (ii) oxygen vacancy (Ov) at 530.72 eV for respectively 0.2 wt%Sr-NT and 0.8 wt%Sr-NT. These results confirm PL measurements, which showed the emission peaks at 457 and 535 nm for surface oxygen defect sites. Ti₂p₃/₂ core-level spectra (Figure 7c) present a bimodal signal at 458.18 eV and 456.8 eV suggesting the presence of Ti⁴⁺ (Liu, Yang, & Wang, 2009) and Ti³⁺ species (Di Valentin, Pacchioni, & Selloni, 2009). Herein, the predominance of Ti³⁺ (defects) increases versus strontium loading in following order 10 and 14% for respectively 0.2 wt% Sr-NT and 0.8 wt% Sr-NT. From Table 2, the ratio of O²⁻/Ti⁴⁺ increases versus strontium loading and confirms the formation of surface defects (Ti³⁺); being consistent with the results of PL measurements and ascribed to lattice distortion as described by X-ray diffraction. XPS peaks of Sr 3d found at 134.2 eV in Figure 7(d) is attributed to electron binding energy of Sr 3d₅/₂, confirming the presence of Sr⁷⁺ (Wang et al., 2021) as identified by SEM mapping. Moreover, it must be pointed out that experimental ratio between the intensities of XPS peaks of Sr 3d₅/₂ for 0.8 wt% Sr and 0.2 wt% Sr (Figure 7d) is equal to 3.45, which is lower than the theoretical one of 4. This result can be explained by possible Sr ions migration inside the bulk.

3.8. Photocatalytic properties

3.8.1. MB photodegradation kinetics

The photodegradation of MB onto xwt% Sr-NT is investigated under visible light radiation. The photodegradation rate of MB can be expressed as

\[
\text{Rate} = \frac{\text{d}[\text{MB}]}{\text{dt}} = k_i \text{[MB]} \chi \quad (\text{at constant temperature}) \tag{3}
\]

In order to investigate the reaction kinetics, we apply to the experimental data to two kinetic models: (i) pseudo-first order and (ii) pseudo-second order. The results are summarized in Table 3.

![Figure 7. XPS spectra of Sr-free and 0.2 wt% Sr and 0.8 wt% Sr-doped NT nanomaterials calcined at 400°C: (a) full scan survey of all elements and high-resolution spectra of (b) O 1s (c) Ti 2p₃/₂, (d) Sr 3d₅/₂.](image-url)
Table 3 illustrate the kinetics parameters obtained from two models. The correlation coefficient $R^2$ values of pseudo-first-order model are tad-higher with respect to those of pseudo-second order model. Hence, we can assume that the kinetic parameters of MB photodegradation over xwt%Sr-NT catalysts are best interpreted by pseudo-first order kinetic model. From Table 3, it seems that $k_1$ increases versus Sr loading. The direct photolysis of MB (2%) is quite low, the MB photodegradation increases in the following order: 0.2 wt%Sr-NT < 0.4 wt%Sr-NT < 0.6 wt%Sr-NT < 0.8 wt%Sr-NT < 1.0 wt%Sr-NT. An optimum MB degradation (56%) is observed for 0.8 wt% Sr-NT. Therefore, the photocatalytic activity is boosted mainly due to low recombination rate prompted by possible formation of heterojunction between Sr and TiO$_2$-MB. The photogenerated (electron-hole) pairs are most probably separated on the interface between ferroelectric strontium and TiO$_2$. Herein, the introduction of Sr ions induced in the creation of oxygen vacancies (O$_v$) as demonstrated earlier by PL and XPS measurements. The oxygen vacancies act as traps for photogenerated electrons which results in increase of holes lifetime. Nevertheless, we cannot discard the hypothesis that strontium might create local electric field which limits the recombination of photogenerated (e-hole) pairs and results in enhanced MB photodegradation.

### Table 2. XPS results of different xwt% Sr-NT nanomaterials: surface state, binding energy, predominance, molar ratio O$_2-/Ti^{4+}$.

| Catalysts | Elements | Surface State | Binding Energy (eV) | Predominance % | Molar ratio O$_2-/Ti^{4+}$ |
|-----------|----------|---------------|--------------------|----------------|-----------------------------|
| 0 wt% Sr-NT | O       | O$^-$         | 529.14             | 100            | 2.15                        |
| Ti        | Ti$^{4+}$ | 458.18        |                     |                |                             |
|           |          |               | 456.80             | 5              |                             |
| 0.2 wt%SrNT | O       | O$^-$         | 529.14             | 56.8           | 2.22                        |
| Ti        | Ti$^{4+}$ | 458.52        |                     |                |                             |
|           |          |               | 456.68             | 10             |                             |
| 0.8 wt%Sr-NT | O       | O$^-$         | 529.83             | 75             | 3.46                        |
| Ti        | Ti$^{4+}$ | 458.56        |                     |                |                             |
|           |          |               | 456.78             | 14             |                             |
| Sr        | Sr$^{2+}$ | 134.35        |                     |                |                             |

### Table 3. Rate constant values ($k_1$ and $k_2$) obtained using pseudo-first order and pseudo-second order models and MB photodegradation.

| Catalysts | Wt% Sr | Pseudo-first order | Pseudo-second order | MB degradation |
|-----------|--------|--------------------|---------------------|---------------|
|           |        | $k_1$ (min$^{-1}$) | $R^2$               | $k_2$ (mmol$^{-1}$ L. min$^{-1}$) | $R^2$ |$rac{C_0-C_t}{C_0}$ x 100 |
| Photolysis| 0      | 0.0002             | 0.991               | –              | –              | 2% |
| 0.2 Sr-NT | 0.2    | 0.0016             | 0.998               | 1.05 10$^{-4}$ | 0.985          | 19% |
| 0.4 Sr-NT | 0.4    | 0.0019             | 0.992               | 1.41 10$^{-4}$ | 0.984          | 24% |
| 0.6 Sr-NT | 0.6    | 0.0028             | 0.991               | 2.20 10$^{-4}$ | 0.989          | 35% |
| 0.8 Sr-NT | 0.8    | 0.0056             | 0.999               | 5.57 10$^{-4}$ | 0.988          | 56% |
| 1.0 Sr-NT | 1.0    | 0.0033             | 0.999               | 4.98 10$^{-4}$ | 0.986          | 51% |

Results are reported for xwt%Sr-NT nanocomposites with different Sr amounts. Photolysis experiment is used as reference.

#### 3.8.2. MB photodegradation isotherms-Langmuir-Hinshelwood (LH) kinetic model

The photodegradation of MB is followed at different concentrations. Herein, the initial rate ($r_0$) is plotted versus the concentration of MB at the equilibrium ($C_e$) (Figure 8).

Figure 8 reveals that the degradation rate ($r_0$) increases versus MB concentration and reaches a plateau. We can highlight mainly two domains: at low MB concentration (< 0.6 mmol.L$^{-1}$), $r_0$ increases linearly with MB concentration which fits with simplified LH model (1 $/C_0$ $k_{LH} C_e$) Eq. (2).

For high MB concentrations, ($> 1$ $/C_0$ $k_{LH} C_e$), the initial rate is zero order to MB (15) and a plateau is reached.

The linearization of Eq. (2) (Figure S5 in supplementary information) indicates that our results fit well with Langmuir-Hinshelwood model (L-H). In addition, LH model was found to be successful for the degradation of several organic compounds (Zhang, Yang, Xie, Zhang, & Li, 2009).

$$r_0 = \frac{k_{LH} C_e}{1 + k_{LH} C_e} = k\theta$$  \hspace{1cm} (2)

$$r_0 = kK_{LH} C_e$$ since ($1 \gg k$ K$_{LH}$ C$_e$)  \hspace{1cm} (3)

$$r_0 = \frac{kK_{LH} C_e}{1 + K_{LH} C_e} = k$$ since ($1 \ll k$ K$_{LH}$ C$_e$)  \hspace{1cm} (4)

$$\theta = \frac{K_{LH} C_e}{1 + K_{LH} C_e}$$  \hspace{1cm} (5)
The photocatalytic activity of Bi$_2$MoO$_6$/TiO$_2$ was investigated onto NT material. The photocatalytic activities vary in the order: NT < 0.2 wt% Sr-NT < 0.4 wt% Sr-NT < 0.6 wt% Sr-NT < 0.8 wt% Sr-NT < 1.0 wt% Sr-NT. Above 0.8 wt% Sr, the activity slightly decreases by possible charges accumulation.

Our results indicate the beneficial effect of Strontium doped TiO$_2$ NTs. In fact, at the same surface coverage ($\theta = 0.999$), the rate of MB degradation is reflected by enhancement of $k_{\text{LH}}$ values vs strontium loading (Figure S6 in supplementary information).

The degradation kinetics of MB under visible light can be described by the apparent first-order kinetics model. Wu et al. 2017 has demonstrated that pseudo-first order of MB photodegradation onto g-C$_3$N$_4$ –RGO-TiO$_2$ is about 4.7 and 3.2 times higher than those of the pure g-C$_3$N$_4$ (0.0029 min$^{-1}$) and direct Z-scheme g-C$_3$N$_4$-TiO$_2$ (0.0043 min$^{-1}$), respectively. The photocatalytic activity of Bi$_2$MoO$_6$/TiO$_2$ nanofiber heterojunction film is enhanced by increasing Bi$_2$MoO$_6$ loading (Li et al., 2017). Hence, 0.08Bi$_2$MoO$_6$/TiO$_2$ nanofiber (0.035 min$^{-1}$) is about 25 and 2.8 times more active than pure TiO$_2$ nanofiber (0.0043 min$^{-1}$) and 0.02 Bi$_2$MoO$_6$/TiO$_2$ (0.0123 min$^{-1}$) respectively. Recently, Waimbo et al. 2020 has demonstrated that the photodegradation of MB onto CuWO$_4$ nanoparticles under visible light shows a pseudo-rate constant of 0.00235 min$^{-1}$ using H$_2$O$_2$ as oxidant. In this study, the generated OH radicals act as the dominant reactive oxygen species (ROS) and is responsible for the degradation of MB until complete mineralization into carbon dioxide (CO$_2$) and water (Zong et al. 2021, Okla et al. 2022). 0.8 wt%-NT catalyst shows good activity in absence of hydrogen peroxide, thus Sr-NT materials will be promising candidate for water treatment in the industrial effluents at low cost.

Furthermore, to avoid any competitive adsorption between MB molecule and its by-products onto the surface of xwt%Sr-TiNT materials; the formic acid (HCOOH) was selected as target pollutant. Because of its simple chemical formula (C$_1$), the degradation leads to the formation of carbon dioxide (CO$_2$) and water. In addition to that, Formic Acid is one of the final intermediate products of most of the organic pollutant degraded, so it could be interesting to learn about the kinetic photodegradation of this by-product. The properties of Sr-NT nanomaterials under UV-A light, subsequently, formic acid photodegradation was investigated onto NT, 0.2 wt%Sr-NT and 0.8 wt%Sr-NT materials (Figure 9). The predominance of Ti species (Ti$^{4+}$, Ti$^{3+}$) and oxygen vacancies obtained from XPS are summarized in Figure 9b.

From Figure 9a, the initial photodegradation rate is obviously enhanced in presence of Sr. In fact, the initial rate increases in the following order: NT < 0.2 wt%Sr-NT < 0.8 wt%Sr-NT; here NT material is taken as reference catalyst. The catalyst 0.8 wt%Sr-NT shows a degradation rate of 98 mmol.L$^{-1}$.min$^{-1}$ against 51 mmol.L$^{-1}$.min$^{-1}$ for 0.2 wt%Sr-NT. Therefore, the photocatalytic activity was enhanced mainly by factor of two due to the high efficiency of charge separation induced by the synergistic effect between Sr and TiO$_2$. Figure 9b, shows that the percentages of defects (Ti$^{3+}$) and oxygen vacancies (from XPS) increase vs strontium loading. The highest amount of oxygen vacancies is obtained for 0.8 wt% Sr-NT catalyst. Therefore, the photocatalytic

![Figure 8. Kinetic study of MB photodegradation: rate vs equilibrium concentration for a. 0 wt% Sr, b.0.2 wt% Sr, c. 0.4 wt% Sr, d. 0.6 wt% Sr, e. 0.8 wt% Sr and f. 1.0 wt% Sr.](image)

\[ \frac{1}{r_0} = \left( \frac{1}{k} \times \frac{1}{K_{\text{LH}}} \right) \times \frac{1}{C_e} + \frac{1}{k} \]  

(6)
properties are indirectly affected by strontium ions. Hence, the rate of recombination of photogenerated electron-hole decreases due to the creation of oxygen vacancies onto Sr-NT nanomaterials and results in electron trapping. Most notably, the holes are used to produce hydroxyl radicals (OH•/C14•) which are highly reactive electrophilic oxidants. So, they decompose directly formic acid to CO₂ and H₂O.

For better understanding, the electrical properties of Sr-NT materials was thoroughly discussed in the next paragraph.

### 3.9. Electrical properties

To attempt to explain of the changes in catalytic properties between 0.2 wt%-Sr NT and 0.8 wt%Sr-NT catalysts, additional impedance measurements were performed. The complex impedance measurements were performed at room temperature by scanning from low to high frequencies (from 0.1 Hz to 1 MHz) using a voltage of 0.5 V. The experimental and theoretical curves were summarized in Figure 10.

Figure 10 shows the electrical response of Sr-NT materials by the Nyquist diagram, the points representative of the complex impedance Z are arranged in an approximately circular arc. The equivalent electrical circuit of the Sr-NT catalysts (shown in the inset of Figure 10). The impedance model cannot be often represented by combining resistance (R) and capacitance (C) circuit. However, Constant Phase Element CPE are usually regarded as circuit-fitting parameters (Liu, 1985). The application of R-CPE circuit (instead of R-C circuit) allowed researchers to overcome the distortion of the impedance semicircles due to the inhomogeneities of defects distribution and to grain boundaries (Komornicki, Radecka, & Rekas, 2001).

The total impedance of the circuit is given by Eq. (7)

\[ Z' = ReZ' + ImZ' = Z' + jZ'' = \left( \frac{1}{R} \right) + \left( \frac{1}{Z_{CPE}} \right) \]

(7)

where the impedance of the CPE is defined via Eq. (8) (Jorcin, Orazem, Pébère, & Tribollet, 2006):

\[ Z_{CPE} = \frac{1}{A_0(j\omega)^n} \]

(8)

where \((j^2 = -1)\) and \(\omega\) is the angular frequency \((\omega = 2\pi f)\), \(A_0\) is a constant independent of frequency, and \(0 < n < 1\) is a dimensionless parameter determining the degree of deviation from an exact semicircle (Sdiri, Elhouichet, Azeza, & Mokhtar, 2013). When \(n = 1\), Eq. (7) yields the impedance of a capacitor, where \(A_0 = C\). The resistance \(R\) is the intercept of the impedance curve with \(Z'\) axis. The experimental semicircles have been fitted by the ORIGINLAB software based on the following relationships.

\[ Z' = \frac{R(1 + RA_0\omega^n\cos(\frac{\pi n}{2}))}{1 + 2RA_0\omega^n\cos(\frac{\pi n}{2}) + (RA_0\omega^n)^2} \]

(9)

\[ Z'' = \frac{R^2A_0\omega^n\sin(\frac{\pi n}{2})}{1 + 2RA_0\omega^n\cos(\frac{\pi n}{2}) + (RA_0\omega^n)^2} \]

(10)

From Figure 10, the maximum Imaginary impedance spectra \(Z''\) slightly shifted to high frequency by increasing the percentage of Sr. The modeling of the...
impedance results gives us the parameters of the equivalent circuit (Table 5).

From Table 5, a slight decrease in resistance (8%) with simultaneously marked increase in capacitor are observed when going from 0.2 wt% Sr-NT to 0.8 wt% Sr-NT. While the electron lifetime \( \tau \) increases from 269 \( \mu \)s to 5450 \( \mu \)s. Herein, \( \tau \) parameter could be considered as the time required to discharge the capacitor. This means that the \( \tau \) parameter also reflects the time that photogenerated charges remain available at the semiconductor interface for generating reactive oxygen species (ROS) able to degrade organic pollutants such as: formic acid and MB. This observation helps us to understand the enhancement of photocatalytic activity as observed in the photodegradation of MB under visible light and FA under UV-A light. For MB photodegradation, \( k_{\text{MB}}=0.0054 \text{mmol.L}^{-1}.\text{min}^{-1} \) is obtained for 0.8 wt% Sr-NT against 0.0013 mmol.L\(^{-1}.\text{min}^{-1} \) for 0.2 wt% Sr-NT. A high charges accumulation is obtained with 0.8 wt%Sr-NT (high capacitor) due to highest number of oxygen vacancies (identified by PL and XPS). In addition, the conductivity increases slightly from 0.2 Sr to 0.8 Sr (the reverse of resistance value).

4. Conclusion

In the present study, the addition of low amounts of strontium to TiO\(_2\) nanotubes was herein studied in order to determine its potential role in enhancing the photooxidation ability of 1D titanium oxide semiconductor. Attention was therefore paid here to the influence of strontium on the structural, textural, optical, morphological and electrical properties of the resulting materials named as xSr-NT, with x between 0.2 and 1.0 wt% Sr. Results emphasize interesting textural and structural properties of xSr-NT nanomaterials. X-ray diffraction patterns shows that Sr doping induces slight shift of the main (101) diffraction peak of the anatase phase, indicating a possible distortion in the TiO\(_2\) lattice in good agreement with Raman results. UV-visible DRS highlights the absence of any Eg shift (3.43 ± 0.02 eV) as expected if SrTiO\(_3\) is formed at the surface of TiO\(_2\). While the photoluminescence and XPS analysis show that the role of strontium is mainly to generate surface oxygen vacancies able to trap photogenerated electrons and leaving photogenerated holes available for oxidation reactions. Finally, photodegradation of MB yields to mineralization and the electric properties of xSr-NT clearly show that photogenerated charges remain available for longer time at the semiconductor interface for generating reactive oxygen species.

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Credit authorship contribution statement

Dr. Nuhad Alomair contributed in conceptualization, methodology, investigation and writing original draft and approving final version.

Disclosure statement

No potential conflict of interest was reported by the authors.

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| Catalysts | R (k\(\Omega\)) | \(A_0\) \(10^{-10} \text{ F cm}^2 \text{s}^{-1}\) | n | \(\tau\) (\(\mu\)s) |
|-----------|---------------|---------------------------------|---|-----------|
| 0.2 wt%Sr-NT | 1213          | 2.22                            | 0.750 | 269       |
| 0.8 wt%Sr-NT | 1117          | 48.80                           | 0.870 | 5450      |
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