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**Interfacial coupling effects on adsorptive and photocatalytic performances  
for photoresponsive graphene wrapped- SrTiO<sub>3</sub>@Ag under UV-visible  
light: experimental and DFT approach**

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**Abstract**

Understanding the graphene/semiconductor/metal interactions is crucial to design innovative photocatalytic materials with efficient photocatalytic activity for environmental cleanup applications. SrTiO<sub>3</sub> on reduced graphene oxide (rGO) with various graphene contents was successfully synthesized in this study utilizing a simple hydrothermal method, followed by decorating the surface with Ag particles by using the photodeposition process. Under UV-visible light irradiation, the resulting composites were tested for their improved photocatalytic

activity to decompose methylene blue (MB). The prepared photocatalysts were characterized by XRD, SEM, EDX, DLS, FT-IR, Raman spectroscopy, and DRS. First-principles density functional theory calculations (DFT) were also carried out by using the generalized gradient approximation (GGA) and PBE functional with the addition of on-site Coulomb correction (GGA + U). The obtained SrTiO<sub>3</sub>/rGO@Ag composites showed great improvement in the photocatalytic performances over pristine SrTiO<sub>3</sub>. For the degradation reaction of MB, SrTiO<sub>3</sub>/rGO<sub>20%</sub>@Ag<sub>4%</sub> composites yielded the best photocatalytic activity with efficacy reach 94 %, which was also shown that it could be recycled up to four times with nearly unchanged photocatalytic activity.

**Keywords:** SrTiO<sub>3</sub>, photoresponsive graphene, Ag nanoparticles, Adsorption, Photocatalysis, DFT, Pollutants elimination.

## 1. Introduction

Research in photocatalysis has much increased in the last years due to its potential use in environmental applications such as hydrogen generation, organic synthesis and water treatment technologies (Fadlalla et al. 2019; Phoon et al. 2019a). Due to its environmental friendliness and energy sustainability, semiconductor photocatalysis has gained a lot of attention as one of the most important solar energy technologies (Wang et al. 2014). The charge carriers on the semiconductor surface can be generated under light radiation and then accelerate the thermodynamic reaction upward to breakdown organic contaminants or produce chemical fuels with high energy density. They are principally caused by the generation of reactive oxygen-containing radicals with a short-lived (e.g.,  $\text{OH}^\bullet$ ,  $\text{HOO}^\bullet$ , and  $\text{O}_2^{\bullet-}$ ) (Natarajan et al. 2018). Because the photocatalyst is such an important component of semiconductor photocatalysis, synthesizing nanomaterials with a unique hierarchical structure and excellent photocatalytic activity has become a hot topic. The research work in the area of photocatalytic water splitting into hydrogen and oxygen has led to the development of many photocatalytic systems (Zuo et al. 2016; Li et al. 2019; Jebaranjitham and Kumar 2020). Heterogeneously dispersed photocatalysts, such as  $\text{TiO}_2$ ,  $\text{SrTiO}_3$ ,  $\text{ZnO}$ ,  $\text{CdS}$  and  $\text{Fe}_2\text{O}_3$  have been extensively studied (Qi et al. 2017; Inamuddin et al. 2019; Ali et al. 2019; Xie et al. 2020). Perovskite materials are a diverse group of promising semiconductor photocatalysts that have been extensively investigated for use in Photocatalysis due to their structural, cost-effectiveness, tenability, excellent stability, and photocatalytic efficiency (Kanhere and Chen 2014; Hu et al. 2020; Bhattacharjee et al.). The strontium titanate ( $\text{SrTiO}_3$ ) is a cubic ternary perovskite-type oxide with a significant nonlinear optical coefficient; it is considered one of the best n-type semiconductor photocatalysts known due to durable photostability, corrosion resistance and low cost, which exhibits great potential in splitting water into hydrogen and oxygen, as well as degrading organic compounds (Huang et al. 2014; Kayaalp

2019). SrTiO<sub>3</sub> has a comparable electronic structure with TiO<sub>2</sub> but with a more negative conduction band edge, making it more suitable for photocatalytic reduction. Furthermore, in regard of crystallographic texture, SrTiO<sub>3</sub>'s cubic perovskite structure is more stable than TiO<sub>2</sub>. (A. Abdel-Latif 2019). It has been reported that pure SrTiO<sub>3</sub> (Huang et al. 2014; Xie et al. 2018; Gao et al. 2018) or ions doped SrTiO<sub>3</sub> (Konta et al. 2004; Wu and He 2018a; Li et al. 2020) can show effective photocatalysis of organic pollutants under UV or Visible light irradiation.

The high performance of SrTiO<sub>3</sub> in reaction to heterogeneous photocatalysis requires an effective architecture that maximizes the absorption of photons and reduces electron losses during excitation state (Coletto et al. 2019; Ferreira et al. 2020). Major efforts are required to further develop heterogeneous photocatalysis of SrTiO<sub>3</sub> under Ultraviolet, visible and solar illumination, in order to further improve the transfer of charge carriers during excitation state. Actually, interesting and unique features of the binary photocatalyst mechanism have drawn more attention from researchers and have become a favorite subject of research among different groups of scientists across the globe (Ahlem et al. 2018; Boulkroune et al. 2019; Du et al. 2021c, b). It was reported that the properties of the photocatalyst system depend primarily on the nature of the surface properties, the surface morphologies and the role of the optimum amount of doping incorporated in the SrTiO<sub>3</sub> (Hu et al. 2020).

Graphene, with its exceptional properties have established itself as a promising supporting material for the manufacture of such hybrid material (Zhu et al. 2010a). The conduction band contacts with the valence band at two points in the Brillouin zone makes graphene having high carrier mobility. In the visible light spectrum, graphene shows excellent optical transparency (97%) and refractive index (2.6-3.0). Its high extinction coefficient in the near IR range also provides graphene with a high photothermal conversion ability (Yu et al. 2021), graphene also have an excellent specific surface area (2630 m<sup>2</sup>.g<sup>-1</sup>) and unique structural

features(Zhu et al. 2010b; Li et al. 2018a).These unique properties allow the use of graphene to produce hybrid materials with superior photo-responsive properties.These properties could be used to enhance the performance of conventional organic and inorganic polymers for enhanced optical performance (Zhang et al. 2011a). A major problem is the solubility and the processability of graphene-based materials, but it can be reduced by using GO (Graphene Oxide) (Jiang et al. 2013). Further chemical modification is also possible for GO as it has hydrophilic functional groups such as epoxide, carboxyl and hydroxyl groups on both edge and surface.

A semiconductor irradiated with photons containing energy equal to band gap energy contributes to the creation of electron hole ( $e^-$ ,  $h^+$ ) pairs during photocatalysis. The quick recombination of photogenerated electron-hole pairs limits the applicability of photocatalysis technologies in the industry, the substantial amount of scientific research is to extend life time (Zhang et al. 2012). The electron-hole recombination can be suppressed using a variety of strategies, this entails lowering the diffusion length by shrinking the size and creating various nanostructures interaction with other semiconductor materials that have a band location, which is appropriate for a smooth charge transfer, and connection with a conductor such as graphene(Zhang et al. 2011b; Li et al. 2018a; Du et al. 2021a).Conducting materials such as graphene furnished support for catalytic particles and operate as an acceptor of electrons provided the photocatalyst conduction band must be more negative than the graphene band(Atout et al. 2017). Graphene's new role as a photosensitizer macromolecular has been investigated where graphene interacts as an organic dye-like photosensitizer for wide band gap semiconductors(Chi et al. 2019). The semiconductor cannot form an electron and a hole in this mechanism, but it is theoretically possible to photoexcite graphene under visible light. To put it another way, graphene becomes a semiconductor. The photoexcited electrons are moved from the CB of Graphene to the CB of the semiconductor, resulting in the separation

of electrons and holes and resulting in visible-light photo-responsive (Bajorowicz et al. 2015). A good photosensitizer might exhibit high optical absorption at a large range of wavelengths, especially in the visible region, and a sufficiently long life of the excited state to react with the semiconductors. In addition, the construction of metal semiconductor composites by the introduction of noble metal nanoparticles is also a promising method (Konta et al. 2004; Li et al. 2020). For instance, Attout and colleagues created a bimetallic complex Au-Ag, which they grafted on the surface of P25-TiO<sub>2</sub> NPs and then incorporated into rGO sheets, resulting in an increase in visible light absorption and a reduction in the bandgap, which improved charge carrier separation and thus improved photocatalytic activity. The primary function of noble metal is illustrated as follows: used as electrons sink to facilitate the transfer of the interfacial electron to the composites; and the Surface Plasmon Resonance (SPR) of the noble metal enhances the light absorbance of the composite (Zada et al. 2019).

Herein, SrTiO<sub>3</sub> on reduced graphene oxide (rGO) with various graphene contents was successfully synthesized in this study utilizing a simple hydrothermal method. Then, the surface coated with Ag particles by using the photodeposition process; the synthesized sample's photocatalytic properties were examined in the degradation of methylene blue (MB) as a typical organic contaminant. As far as we know, the majority of the literature only focusses on charge migration in the system graphene/semiconductor and/or metal/semiconductor nanocomposite. Hence, certain parts of reaction mechanisms are still unknown. Therefore, the goal of this study was to look into the involvement of rGO and Ag metal in the UV-visible light photocatalytic activity of SrTiO<sub>3</sub>/rGO@Ag nanocomposite. Moreover, the composite structure, morphological, electronic, and absorption properties were examined in detail and correlated to photocatalytic experiments. For this, several experimental characterizations and theoretical computational based on density functional

theory (DFT) were employed by using the generalized gradient approximation (GGA) and PBE functional with the addition of on-site coulomb correction (GGA + U).

## 2. Materials and methods

### 2.1 Materials

The precursors for the preparation of graphene oxide: natural flake graphite (carbon content: 99.8% -325 mesh) was purchased from Alfa Aesar, potassium permanganate  $\text{KMnO}_4$  (Panreac). Hydrogen peroxide  $\text{H}_2\text{O}_2$  (30%), sulfuric acid  $\text{H}_2\text{SO}_4$  (97%) and hydrochloric acid  $\text{HCl}$  37% were purchased from Scharlau, potassium nitrate  $\text{KNO}_3$  (analytical grade) and, barium chloride  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (Biochem).

Titanium (IV) isopropoxide (97%, Aldrich), strontium nitrate  $\text{Sr}(\text{NO}_3)_2$  (>99,0%, Fluka Analytical), poly ethylene glycol (PEG), acetone and ethanol were used as precursors for the preparation of  $\text{SrTiO}_3$ . Methylene blue was purchased from Sigma Aldrich; all of the compounds were analytical reagents, and they were employed without further purification or treatment. All reactions and treatment experiments were carried out with deionized water. For the photocatalytic tests, the concentrations of the samples were measured before and after adsorption using a UV-visible spectrophotometer (Shimadzu Spectrophotometer UV-vis 1700) at  $\lambda_{\text{max}} = 664$  nm of MB. The Infrared spectra were carried out on an Agilent Technologies Fourier Transform Spectrophotometer (FTIR) driven by a microcomputer and the infrared spectra are performed in the spectral domain between 4500 and 400  $\text{cm}^{-1}$ . The morphology of semiconductor compounds was investigated with FEI QUANTA 250 FEG scanning electron microscopy (SEM; FEI, Hillsboro, OR, USA) working in high vacuum. The diffuse reflectance spectroscopy (DRS) is a tool suitable for quantifying the optical properties of powders; the optical transmission and absorption were measured using a UV-Vis spectrometer. X-ray diffraction was used to identify the crystallographic phases with a



Siemens D5000 diffractometer, a Bragg-Brentano-geometry and vertical 2-theta goniometer and operated at 45 kV using Cu K $\alpha$ 1 radiation. Diffractograms were carried out in a 2-theta range from 4 ° to 85 ° with an angular step of 0.0167° and an accumulation time of 6.985 s per step. The formation of graphene sheets were studied by Raman spectroscopy (LabRAM HR Evolution - HORIBA Jobin Yvon, OLYMPUS BX41) supplied by a laser source operating at 473 nm wavelength at room temperature.

## **2.2 Synthesis of graphene oxide (GO) and cubic SrTiO<sub>3</sub>**

The modified Hummers method was used to prepare graphene oxide (GO), which is discussed in detail in the paper (Guediri et al. 2020b). Strontium titanate SrTiO<sub>3</sub> was synthesized adopting the hydrothermal method (Xie et al. 2018; Zhou et al. 2020). An amount of titanium (IV) isopropoxide was mixed with a stoichiometric amount of Sr(NO<sub>3</sub>)<sub>2</sub> powders to obtain mixed phases, a solution of acetic acid as a lubricant were separately dissolved in minimum volume of distilled water; to obtain a homogeneous metal ion distribution, stoichiometric proportions of the required metal and acetic acid were utilized. Following total dissolution, acetic acid solution was poured onto the metal precursors followed by Polyethylene Glycol (PEG, 2 g/90 mL) addition. The addition of PEG controls the nanoparticle's growth, leads to the prevention of agglomeration and the production of nanoparticles of uniform size. After one hour stirring, and under continuous stirring, the NaOH aqueous solution was added drop by drop until the pH value reached 13. Indeed, the suspension was transferred to Teflon sealed autoclave and maintained at 180°C for 24 hours. Finally, it was washed in ethanol and distilled water multiple times before being dried in a 60°C oven for 24 hours.

## **2.3 Preparation of SrTiO<sub>3</sub>/rGO<sub>20</sub>@Ag photocatalysts**

The Preparation of SrTiO<sub>3</sub>/rGO photocatalysts with different weight ratios of rGO were obtained via the hydrothermal method, Figure 1 (Bajorowicz et al. 2015). Firstly, 200 mg of

SrTiO<sub>3</sub> powder and appropriate weight ratios of GO to SrTiO<sub>3</sub> (x = 0, 5, 10, 15 and 20 wt.%) was dispersed in a mixing solution of ethanol and water (2:1) by ultrasonic treatment for 1 hour. Then, the mixing solution was agitated for additional 30 minutes to get homogenous suspension. The suspension was placed in Teflon-sealed autoclave at 120°C for 12 hours. The obtained photocatalyst was centrifuged three times with distilled water before being dried in a 60°C oven for 24 hours. A simple photo-deposition method was used to prepare the SrTiO<sub>3</sub>/rGO<sub>20</sub>@Ag<sub>x</sub> photocatalyst with 1, 2, 3 and 4 wt.% of metallic Ag (Tang et al. 2019). For this purpose, an amount of synthesized SrTiO<sub>3</sub>/rGO<sub>20</sub> nanocomposite powder was dispersed into 100 mL of deionized water, then 9.27 x10<sup>-5</sup> M of AgNO<sub>3</sub> solution was suspended in the mixture solution and diluted to 0.5 L with distilled water accompanied by 30 minutes of ultrasound treatment and 2 hours magnetic stirring under 300 W Xenon lamp for the photoreduction of Ag<sup>+</sup> to Ag<sup>0</sup>. The powder was then collected and dried under vacuum.

#### **2.4 Kinetics of adsorption and equilibrium modeling**

The adsorption dynamics study identifies the rate of solute adsorption (Guediri et al. 2020a). This rate controlled the residence time of adsorption at the solid-solution interface. Several kinetic models such as pseudo-first-order, pseudo-second order and pseudo n<sup>th</sup> order models were applied to fit experimental data Table 1. The correlation coefficients were used to assess how well the experimental results matched those predicted by the models. In the dark, the procedure was carried out as follows: 100 mg of SrTiO<sub>3</sub> and SrTiO<sub>3</sub>/rGO<sub>x</sub> (x = 5, 10, 15 and 20 %) in a 200 mL solution of methylene blue (MB) at a concentration of 10 mg/L was stirred at room temperature for 180 minutes. Samples were taken at 10-minute intervals until equilibrium was reached to track the change of the adsorbed quantity (Q<sub>ads</sub>). The yield was calculated using the following formula:

$$R(\%) = \frac{(c_0 - c_e)}{c_0} \times 100 \quad (1)$$

R represents the percentage of MB fixed on the adsorbent,  $C_0$  is the MB solution's initial concentration (mg/L) and  $C_e$  is the MB solution's at-equilibrium residual concentration (mg/L).

## 2.5 Photocatalytic tests

Photocatalytic tests were performed at room temperature using a batch photo-reactor, an open-air double-walled beaker of 200 mL with a cooling water jacket, which keeps the temperature at  $(25 \pm 2)$  °C equipped with a Xenon lamp (150W), positioned above 30 mm of light-exposed surface  $32.17 \text{ cm}^2$ . The operating parameters used were the same as in the adsorption kinetic. To establish the adsorption desorption balance, the solution was agitated in the dark for 40 minutes before the Xenon lamp was turned on; each 20 minutes, 1 mL of the suspension was removed, diluted five times, and immediately centrifuged to separate the catalyst from the solution, the solution was then analysed using UV-Vis spectroscopy. To assure photocatalyst photostability, all photocatalytic experiments were duplicated.

## 2.6 Computational Details

The electronic and structural properties of  $\text{SrTiO}_3$  bulk, density functional theory (DFT) computations was used to examine pristine  $\text{SrTiO}_3$ , graphene and hybrid  $\text{SrTiO}_3/\text{rGO}/\text{Ag}$  composite to comprehend the mechanisms of its enhanced photocatalytic activity under visible light irradiation. The use of DFT calculations to decipher the nature of electronic interactions at composite interfaces is pretty helpful. (Diao et al. 2019). Exchange and correction energies were described by using the Generalized Gradient Approximation (GGA) and PBE functional with the addition of on-site coulomb correction (GGA + U), by employing the Cambridge Serial Total Energy Package (CASTEP), which is based on plane-wave pseudopotential DFT methods[39][40]. It has been reported that GGA methods provide a better prediction of lattice constants and electron structure than LDA, especially for surface layers (Chen et al. 2020). However, (GGA+U) has been known generally to prevent the

unwanted delocalization of the *d* or *f* electrons and to underestimate the energy gap of semiconductor (Hu and Metiu 2011), resulting into an overestimate for photoinduced electrons transfer in photocatalytic processes. The required Hubbard U values for Ti 3*d*, Sr 4*d*, and O 2*p* were 5.0, 5.0, and 5.0 eV (Yang et al. 2015), respectively, to correct the SrTiO<sub>3</sub> band gap problem.

The SrTiO<sub>3</sub> bulk, pristine rGO, and SrTiO<sub>3</sub>/rGO@Ag composite structures were constructed using Material Studio software, by choosing a cubic SrTiO<sub>3</sub> (100) surface: in a supercell (8.16 × 7.59 × 25 Å<sup>3</sup>), a 5 × 3 single layer of rGO containing 60 carbon atoms sits on a 3 × 2 five atomic layer STO (100) and 5 × 5 top layer Ag metal (200) surface slab. A Monkhorst-Pack mesh of k points, 4×4×1, 8×8×1 and 2×2×1 point, was used to sample the two-dimensional Brillouin zone for geometry optimization and for calculating the density of states of SrTiO<sub>3</sub>, rGO and SrTiO<sub>3</sub>/rGO@Ag composite, respectively. The plane wave cutoff energy was set at 571 eV. All geometrical structures were totally relaxed until the convergence criteria of force and energy were less than 0.03 eV/Å and 10<sup>-6</sup> eV/atom, respectively. Total energy tolerance at 105 eV/atom for convergence parameters, maximum force tolerance was chosen at 0.03 eV/nm, and maximum stress component at 0.05 GPa.

### **3. Results and discussion**

#### **3.1 Structural analysis**

The XRD pattern of SrTiO<sub>3</sub>/rGO<sub>x</sub> (*x* = 0, 5, 10, 15 and 20 %) composites are shown in the Figure 2(a). The composites presented almost the same profiles and the peaks were localized at the angular positions: 2θ = 22.74, 32.38, 39.95, 46.47, 52.36, 57.79, 67.83, 77.21, 81.76 and 86.22 °; these peaks were identified according to (JCPDS card No. 35-0734) as respectively (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), (3 1 0), (3 1 1) and (2 2 2) Bragg's planes of the cubic perovskite SrTiO<sub>3</sub> structure (Huang et al. 2014). The Figure 2(a)

also shows the XRD patterns of SrTiO<sub>3</sub>/rGO<sub>20</sub>@Ag<sub>x</sub> composites for 2 and 4 % weight ratio of Ag; the most significant peaks appeared at the angular positions  $2\theta = 38.12^\circ$  and  $44.28^\circ$ , which corresponded to the (111) and (200) Bragg's planes of cubic Ag phase (JCPDs No. 04-0783) (Wu and He 2018a). The development of metallic Ag<sup>0</sup> particles adhered to the surface of the composites was evidenced by the extra diffraction peaks detected in Ag deposited samples. Furthermore, metallic Ag had an atomic radius of  $1.44\text{\AA}$ , which was significantly more than the ionic radius of Ti<sup>4+</sup> ( $0.68\text{\AA}$ ) (Nithya and Devi 2019a). Consequently, without causing crystal structural distortion, Ag cannot easily diffuse into the SrTiO<sub>3</sub> lattice. No diffraction peaks related to other impurities were detected on the XRD patterns, suggesting a high purity of the crystalline phases. Moreover, the characteristic crystalline parameter (a), the average grain sizes (D), microconstraint ( $\xi\%$ ) and dislocation density ( $\delta$ ) were calculated according to the relations (i), (ii), (iii) and (iv) (Abdel-Latif et al. 2017; Yousaf et al. 2019; Huang et al. 2019) and the corresponding results are illustrated in Table 2.

$$(i) \quad 2d_{hkl} \sin\theta = n\lambda \quad \text{and} \quad d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

$$(ii) \quad D = \frac{K\lambda}{\beta \cos\theta}$$

$$(iii) \quad \xi\% = \frac{\beta}{4 \tan\theta}$$

$$(iv) \quad \delta = \frac{1}{D^2}$$

The largest lattice parameter was estimated for pristine SrTiO<sub>3</sub>. Subsequently, the deposit of rGO on SrTiO<sub>3</sub> caused a shrinkage of the unit cell; small but noticeable, a decrease in the lattice parameter (a) was observed with increasing the rGO weight ratio. It is seen from both the Figure 2(b) and the Table 2 that the fixation of rGO sheets on SrTiO<sub>3</sub> decreased the average grain size (D), obviously accompanied by a rise in microconstraints ( $\xi\%$ ) and caused

significant structural defects as measured by an increase in dislocation density ( $\delta$ ); this indicates that the rGO induced stress in the SrTiO<sub>3</sub> crystal structure. On another hand, the lattice strain values and the grain size were affected by the Ag decoration.

### **3.2 Scanning Electron Microscopy (SEM)**

The shape of SrTiO<sub>3</sub> and the formation of the junction between SrTiO<sub>3</sub> and rGO were studied by SEM analysis. As shown in the Figure 3 (a and b), the SrTiO<sub>3</sub> had a cubic form and the sizes distribution was fitted with Gaussian function which is shown in the Figure 3(x); this latter proved that the average size of SrTiO<sub>3</sub> nanocubes was about 51 nm, with a width at half height of about 12 nm, this value was compatible with the result found by XRD analysis (Gao et al. 2018; Phoon et al. 2019b). In addition, a perfect cubic particle can only be formed with six equivalent {100} facets of a crystal with a cubic structure (Grimbergen et al. 1998; Zhou and Greer 2016). The Figure 3 (c–h) shows SEM images of SrTiO<sub>3</sub>/rGO<sub>x</sub>; it can be seen that the cubic structure of SrTiO<sub>3</sub> was retained and the SrTiO<sub>3</sub> particles were well dispersed on the overall surface of the graphene sheets. These results revealed that SrTiO<sub>3</sub>/rGO<sub>x</sub> heterojunction was successfully prepared.

Otherwise, the composition of SrTiO<sub>3</sub> obtained by EDX analysis, the Figure 3(y) illustrates the presence of the Ti, Sr and O elements, which confirmed the product's purity. The chemical formula can be writing as Sr<sub>0.93</sub>Ti<sub>1.08</sub>O<sub>2.99</sub>; this formula was in good agreement with what can be expected for a perovskite structure.

### **3.3 Dynamic light scattering (DLS)**

The external surface of nanoparticles, as well as their surface state, have a significant impact on their adsorption and photocatalytic activities; the aggregated particles' surface is the effective surface exposed to the external medium. Furthermore, the aqueous solution aggregation of metal oxides is well-known and well-studied (Nam and Han 2003; Simonsen

et al. 2008). For this basis, DLS was used to characterize the SrTiO<sub>3</sub> samples, Figure 4 depicts the hydrodynamic diameter of aggregated nanoparticles suspended in distilled water and the Gaussian function was used to fit the experimental data. The fitted curve demonstrated the growth of aggregated particles of various sizes, the average hydrodynamic diameter size value was around 199 nm, with a width at half height of about 147 nm and the experimental standard deviation was about 14 nm (the measurement was performed three times), comparatively to the grain sizes estimated by XRD and SEM analysis (D = 21.4 and 51 nm respectively). The SrTiO<sub>3</sub> had a weak tendency to aggregate; this result was due to the use of PEG in the synthesis which prevent from agglomeration and leads to the production of nanoparticles of uniform shapes.

### **3.4 Fourier-Transform Infrared Spectroscopy (FT-IR)**

The FT-IR spectra obtained for GO (Graphene Oxide), SrTiO<sub>3</sub>/rGO<sub>x</sub> and SrTiO<sub>3</sub>/rGO<sub>x</sub>@Agnanocomposites are shown in the Figure 5. The spectra of GO clearly showed numerous absorption peaks that related to distinct functional groups. C–H bending vibration was attributed for the band at 934 cm<sup>-1</sup>, the peak at 1713 cm<sup>-1</sup> was assigned to C=O stretching vibration of the COOH group. The band at 1632 cm<sup>-1</sup> was due to C=C stretching vibration and the absorption peak at 1397 cm<sup>-1</sup> corresponded to C–OH bending vibration (Xian et al. 2014; Bajorowicz et al. 2015). The absorption peak at 1249 cm<sup>-1</sup> was due to C–O–C asymmetric stretching vibration, the peak at 1041 cm<sup>-1</sup> was attributed to C–O stretching vibration (Ahmadi et al. 2019). From the comparison between the spectra of the composites and the GO spectrum, the reduction of the C=O band intensity at 1713 cm<sup>-1</sup> indicated that GO was reduced to rGO after the hydrothermal treatment.

On the spectra of the SrTiO<sub>3</sub>/rGO<sub>x</sub> composites, compared to pristine SrTiO<sub>3</sub>, the Ti–O–Ti bands at 602 cm<sup>-1</sup> shifted to 545 cm<sup>-1</sup> at lower wavenumber and exhibited weaker peak

intensity; the absorption of the  $\text{TiO}_6$  group in the octahedral structure was attributed to this band. (Yang et al. 2018; Wu and He 2018b). It may be attributed to the incorporation of C atoms into the  $\text{SrTiO}_3$  and the formation of the Ti–C bond (Guo et al. 2018). In addition, a new band at  $928\text{ cm}^{-1}$  can be observed, confirming the formation of Ti–C bond; the presence of this bond indicates that during the reduction of GO, the residual carboxylic acid functional groups interact with the surface of  $\text{SrTiO}_3$  nanoparticles, and form a bonded  $\text{SrTiO}_3/\text{rGO}_x$  composite. The C=C bands at  $1632\text{ cm}^{-1}$  shifted gradually to  $1620\text{ cm}^{-1}$  with increasing ratio of rGO, indicating that the skeletal of the graphene sheets was influenced. Finally, the IR spectrum of  $\text{SrTiO}_3/\text{rGO}_x@Ag$  was comparable to that of  $\text{SrTiO}_3/\text{rGO}_x$  composites.

### 3.5 Raman spectroscopy

For the characterization of graphitic materials, Raman spectroscopy is widely employed (Bußmann et al. 2011; Karamat et al. 2016). The distinctive bands of graphene, such as D, G, and 2D, provide relevant information regarding defects,  $sp^2$  carbon atom in-plane vibrations, and stacking orders, respectively. In addition, the G band ( $1582\text{ cm}^{-1}$ ) was formed by first-order scattering of  $E_{2g}$  phonons of the  $sp^2$ -hybridized carbon atoms. While the D band ( $1350\text{ cm}^{-1}$ ) was formed by a breathing mode of  $K$ -point phonons of  $A_{1g}$  symmetry of the defects involved in  $sp^3$ -hybridized carbon bonds such as epoxide and/or hydroxyl bonds, and the graphene sheet stacking-sensitive 2D band ( $2679\text{ cm}^{-1}$ ) (Akhavan 2015). Figure 6(a) illustrate the Raman spectroscopy of  $\text{SrTiO}_3/\text{rGO}$  nanocomposites. All the composites  $\text{SrTiO}_3/\text{rGO}$  exhibits the appearance of G peak around ( $1584\text{ cm}^{-1}$ ). The D peak appear from the ratio 15% of rGO in  $\text{SrTiO}_3/\text{rGO}$  nanocomposites at ( $1352\text{ cm}^{-1}$ ), and the 2D peak is not observed so far, which might have been due to substrate screening effect and the small quantity of rGO in the composites. The repression of 2D peak is observed at ( $2697\text{ cm}^{-1}$ ) in the composite  $\text{SrTiO}_3/\text{rGO}$  (20% of rGO).



The D to G peak intensity ratio is commonly used to evaluate graphene disorder, which is an indirect indication of the material's quality (Figure 6(b)). The D/G ratio was determined to be 0.34 in this study, which is lower than the value reported in prior research (Akhavan 2015). This higher ratio can be attributable to the existence of more disordered nano-graphene. The bilayer sheets' 2D/G ratios were found to be in the range of 0.26, confirming the deposition of triple- and multi-layer (>4) graphene sheets on SrTiO<sub>3</sub> nanocubes based on the same earlier study.

### **3.6 Electronic structure and optical properties**

#### **3.6.1 First Principle Study of the SrTiO<sub>3</sub>/rGO@Ag Heterojunction**

In order to understand the structure well, the binding and the electronic properties of SrTiO<sub>3</sub>/rGO@Ag composite were studied by DFT simulations. The optimized relaxed geometries of SrTiO<sub>3</sub>/rGO and SrTiO<sub>3</sub>/rGO@Ag are shown in the Figure 7. The electronic structure of nanocomposites is mostly defined by the components' interfacial interactions; their total (DOS) and Partial (PDOS) Density of States can evidence the variation of electronic properties of the SrTiO<sub>3</sub>/rGO@Ag composites. The band structure and PDOS plots of SrTiO<sub>3</sub> are given in the Figures 8 and S1, respectively. It can be seen that the maximum of the valence band (VBM) and the minimum of the conduction band (CBM) of SrTiO<sub>3</sub> were located at 0.00 eV and +2.98 eV respectively (Figure 8), so the band gap was about 2.98 eV. In addition, the VBM was mainly dominated by the Sr *4p* and O *2p* states; while, the main contribution in the CBM was the Ti *3d* state (Figure S1). Moreover, the band structure of rGO is shown in the Figure 8. For the rGO, its antibonding  $\pi^*$  orbitals (which makes up its conduction band) and bonding  $\pi$  orbitals (which makes up its valence band) degenerated and touch at Brillouin zone corners, making graphene a zero-band gap semi-conductor material.

When contacting the SrTiO<sub>3</sub> surface with rGO sheets, the difference in the work function of the graphene and the SrTiO<sub>3</sub> leads to electrons transfer between them to equilibrate their Fermi levels (Schusteritsch and Pickard 2014; Gogoi et al. 2015; Baran et al. 2017). Compared to the gap of pristine SrTiO<sub>3</sub>, the band gap was substantially reduced and decreased from 2.98 to 0.06 eV. The contact of SrTiO<sub>3</sub> with rGO produced some inter-levels in the band gaps of SrTiO<sub>3</sub>; these levels belonged to the C of rGO as can be seen in the Figure 8. These inter-levels (also called trap centers) can trap the electron-hole recombination which may consequently enhance the photocatalytic activity, the photogenerated electrons transfer from the VB to the CB of the SrTiO<sub>3</sub>/rGO composites become easier, which lead to red shift of the optical absorption edge. These statements can explain our experimental results.

Another important feature in the Figure S2 was the band alignment between the SrTiO<sub>3</sub> surface and rGO sheet. One can find that the main shapes of the calculated PDOS projected on the composite can be seen as a superposition of the total DOS of the SrTiO<sub>3</sub> and rGO; this can be due to the large geometrical separation space between the SrTiO<sub>3</sub> and rGO layers, the theoretical bond lengths C–O and C–Ti are about 1.42 and 2.27 Å (Wang and Zhou 2003; Lang and Smith 2014), respectively return, the separation of oxygen and titanium from carbon in the optimized structure was about 5.05 and 5.16 Å; these large values suggested a weak interaction and an absence of covalent bonding. This leads us to conclude that the van der Waals interaction is expected to be significant in these composites (Yang et al. 2015). Figure S2 displays that the VBM of the SrTiO<sub>3</sub>/rGO composite only consisted of O 2*p* states, while the CBM was formed from C 2*p* and Ti 3*d* orbitals.

The transformation of band gap upon deposit of Ag nanoparticles suggests an important fact, it enhances the photocatalytic activity under light illumination due to slow electron-hole recombination process, as compared to those of SrTiO<sub>3</sub>/rGO where the recombination happens more quickly (Humayun et al. 2020). For the sake of comparison between the

SrTiO<sub>3</sub>/rGO and decorated systems (SrTiO<sub>3</sub>/rGO@Ag), the PDOS were plotted in the Figure S3, showing significant differences in valence and conduction band states before and after deposit of Ag (the VBM and CBM of the composites SrTiO<sub>3</sub>/rGO@Ag were moved toward more positive potentials). The deposition of Ag nanoparticles on SrTiO<sub>3</sub>/rGO showed that the valence band was shifted upward and was mainly formed by Ag 5s and O 2p states, while the bottom of CB was formed from Ti 3d orbitals. Furthermore, the work function of Ag was slightly higher than that of SrTiO<sub>3</sub>/rGO composite. Therefore, in this case, the photo-generated electrons (CB) of SrTiO<sub>3</sub>/rGO are transferred to the surface of Ag nanoparticles, until the equilibrium of the Fermi level, and consequently the lifetime of photo-generated carriers increases.

### 3.6.2 Diffuse reflection spectroscopy (DRS)

UV-Vis-DRS spectroscopy is a proven tool for experimentally quantifying electronic characteristics (Nadtochenko et al. 2009). The spectra shown in the Figure 9 correspond to SrTiO<sub>3</sub>/rGO<sub>x</sub> (x = 0, 10, and 20%) and SrTiO<sub>3</sub>/rGO<sub>20</sub>@Ag<sub>x</sub> (x= 2 and 4%), the lines demonstrated that the composites had a robust and wide UV absorption band and that they are transparent in the visible range, due to the transitions from the VB to the CB. To quantify the band gap 'E<sub>g</sub>' and Urbach 'E<sub>U</sub>' energies, from the reflectance curves 'R', the absorption coefficients 'F(R)' must be derived, according to the Kubelka-Munk formula (Guediri et al. 2020b):

$$F(R) = \frac{(1-R)^2}{2R} \quad (2)$$

Figure 9 shows the variation of Urbach energy 'E<sub>U</sub>' and the band gap 'E<sub>g</sub>' according to the Kubelka-Munk method as an insert. The maximum absorbance has been used to normalize all spectra to one.

The band gap ‘E<sub>g</sub>’ was estimated using a Tauc plot on linear part of  $(\alpha \cdot hv)^n \propto (hv - E_g)$ , where  $n = 1/2$  for indirect band gap, and  $n = 2$  for direct gap (insert of Figure 9); Table 3 represents the calculated band gap energies.

The Urbach energy ‘E<sub>U</sub>’ was calculated by the Eq.3 (Entradas et al. 2014), where  $\alpha_0$  and  $E_0$  are constants in relation to the substance being studied:

$$F(R) = \alpha_0 \exp\left(\frac{hv - E_0}{E_U}\right) \quad (3)$$

The value of ‘E<sub>U</sub>’ is calculated from the slope of the linear part  $[\ln(F(R)) \propto (hv - E_0)]$  of the plot  $[\ln(F(R)) \text{ vs } hv]$  (insert of Figure 9); Table 3 summarizes the results.

‘E<sub>U</sub>’ characterizes the shift in the electronic band structure generated by several sources. (dislocation, lattice strain, vacant or interstitial sites...). These sources produce extra states in the band gap near HOMO and LUMO levels, which can be seen as CB and VB tails; ‘E<sub>U</sub>’ is approximately equivalent to the average tail width (Guediri et al. 2020b). Table 3 shows that depositing rGO sheets and Ag particles over SrTiO<sub>3</sub> increased the Urbach energy, in good agreement with theoretical calculation, which were observed inter-levels. In the band gap caused by the deposit of rGO and metallic Ag, UV-Vis-DRS and XRD analyses confirmed that the deposit of rGO sheets and Ag particles induces stress and defects within SrTiO<sub>3</sub> nanocrystals. Furthermore, decreasing ‘E<sub>g</sub>’ by adding rGO sheets changed the Fermi level, which boosts photogenerated electron migration while suppressing the recombination electron hole, implying an improvement in photocatalytic activity.

### **3.7 Adsorption kinetic and modeling**

According to the adsorption curves shown in the Figure 10, the equilibrium time for the five samples was about 40 minutes. The adsorbed quantities (Q<sub>ads</sub>) increased for increasing rGO content in the composites SrTiO<sub>3</sub>/rGO<sub>x</sub> and varied from Q<sub>ads</sub> = 5.15 mg/g to Q<sub>ads</sub> = 12.57 mg/g

for  $x = 0$  to  $x = 20\%$  respectively, which means that the rGO was responsible for MB adsorption due to its high specific surface area.

The modeling results are shown in the Figure 10. The constants obtained from the adsorption models, namely the rate constants  $K$ , Table 4 lists the  $R^2$  correlation coefficients and the maximum theoretical amount adsorbed  $Q_{ads}$ . The best-established model for the kinetic study was chosen according to the highest correlation factor  $R^2$ .

The adsorbed quantities  $Q_{ads}$  derived by the pseudo-first-order model were not comparable to those obtained experimentally, and the correlation coefficients  $R^2$  for all composites were between 0.949 and 0.984, according to the values quoted in Table 4.. On another hand, the adsorbed quantities calculated  $Q_{ads}$  by the pseudo-second-order model were close to the experimental results with correlation coefficients  $R^2$  between 0.979 and 0.995. For the pseudo- $n^{th}$  order model, the correlation coefficients  $R^2$  were between 0.986 to 0.996 with adsorbed quantities  $Q_{ads}$  determined experimentally close to those calculated. In conclusion, and according to the fits carried out, the pseudo  $n^{th}$  order model was the most suitable for describing the adsorption kinetics of MB on SrTiO<sub>3</sub>/rGO.

### **3.8 Photocatalytic activity under UV-visible light illumination**

The overall elimination curves of MB by adsorption and photocatalysis are shown in the Figure 11. For SrTiO<sub>3</sub>/rGO<sub>x</sub> composites, it was found that the elimination of MB increased as the rGO content rose; the obtained yields were  $R = 6, 31, 53, 63$  and  $67\%$  for  $x = 0, 5, 10, 15$  and  $20\%$  respectively. This was owing to rGO's large specific surface area, which enhanced the interface (solid solution) and thus improved photocatalytic activity. In other words, Graphene used kinetically to enhance the efficiency of photocatalysis owing to the high adsorption capacity of organic/inorganic contaminants by facilitating the access to the active sites (Guediri et al. 2020b). This occurred in two stages: (i) in the dark, mostly by MB

adsorption on rGO sheets due to its high specific surface, and (ii) Electron-hole pairs produced within SrTiO<sub>3</sub>/rGO<sub>x</sub> can oxidize MB via photocatalysis after adsorption saturation and under UV-visible light. An exponential function was used to fit the rate constants of the photocatalytic kinetic curves. (Insert of Figure 11 (a)), and were  $K \cdot 10^{-4} = 2.81, 15.8, 24.7, 32.3$  and  $38.4 \text{ min}^{-1}$  for the composites SrTiO<sub>3</sub>/rGO<sub>x</sub> (with  $x = 0, 5, 10, 15$  and  $20\%$ ) respectively. It is worth mentioning that in the absence of the photocatalyst (SrTiO<sub>3</sub>/rGO<sub>x</sub>); the concentration of MB did not change significantly, demonstrating that MB cannot be decomposed by photolysis.

The removal yields for the composites SrTiO<sub>3</sub>/rGO<sub>20</sub>@Ag<sub>x%</sub> increased with increasing Ag weight ratio and were about  $R = 67, 75, 83, 88$  and  $94 \%$  for  $x = 0, 1, 2, 3$  and  $4 \%$ , respectively.

Moreover, the rate constants of the kinetics (insert of Figure 11 (b)) were  $K \cdot 10^{-4} = 38.4, 54.6, 80.0, 108.3$  and  $145.7 \text{ min}^{-1}$  for  $x = 0, 1, 2, 3$  and  $4 \%$  respectively. The obtained SrTiO<sub>3</sub>/rGO@Ag composites showed high improvement in the photocatalytic performance over pristine SrTiO<sub>3</sub> and SrTiO<sub>3</sub>/rGO, which could be linked to graphene's function as a photosensitizer in p-n heterojunctions SrTiO<sub>3</sub>/rGO composites, as well as the benefit from the localized surface plasmon resonance caused by Ag nanoparticles in SrTiO<sub>3</sub>/rGO@Ag composites. For the commercial application of the photocatalyst, it is necessary to test the photocatalyst across numerous cycles. Figure 12 illustrates the recycled SrTiO<sub>3</sub>/rGO<sub>20</sub>@Ag<sub>2</sub> photocatalyst four times, for each cycle three hours ( $4 \cdot 3 \text{ h} = 12 \text{ h}$ ) of irradiation, which photocatalytic activity remained almost unaltered.

### **3.9 Proposed mechanism**

A putative mechanism for the photocatalytic process is given based on the previous findings and depicted by a scheme in Figure 13. In the SrTiO<sub>3</sub>/rGO@Ag system, the wide bandgap of

SrTiO<sub>3</sub> prevents it from being photoexcited by visible light (3.19 eV §3.5.2). However, in the pristine graphene, its antibonding  $\pi^*$  orbitals and bonding  $\pi$  orbitals degenerated and reaching Brillouin zone corners (Li et al. 2018b), rendering graphene a zero band gap semi-metallic material and hence it can behave as a photosensitizing compound under visible light irradiation. In addition, the junction with SrTiO<sub>3</sub> broke the lattice symmetry and open the band gap, thus converting semi-metallic character of graphene into a pure semiconductor character due to the formation of gap between  $\pi$  and  $\pi^*$  bands; it has been demonstrated previously theoretically and experimentally that rGO semiconductor can directly act as photocatalysts for water splitting (Jiang et al. 2013; Bantawal et al. 2019; Ahmadi et al. 2019; Chi et al. 2019; Chang and Hu 2020; Bajorowicz et al.). Therefore, when exposed to UV-visible light, rGO in SrTiO<sub>3</sub>/rGO<sub>x</sub> composites is photoexcited from the ground state (rGO) to the excited state (rGO\*), during which electrons are photogenerated. The excited state of rGO\* injects electrons into SrTiO<sub>3</sub>'s conduction band (CB); the photoexcited electrons react with dissolved oxygen and water molecules to produce oxidative species such as hydroxyl radicals (OH<sup>•</sup>) and peroxide radical anions (O<sup>2•-</sup>); the Reactive Oxygen Species (ROS) can drive mineralization and oxidize totally MB into CO<sub>2</sub> and H<sub>2</sub>O. Otherwise, SrTiO<sub>3</sub>/rGO<sub>x</sub> composites are also expected to be efficient photocatalysts excited by UV light irradiation, with rGO acting as an electron acceptor rather than a photosensitizer.

When an Ag metal is coated on a semiconductor (SrTiO<sub>3</sub>/rGO@Ag), the semiconductor electrons' work function must match that of the metal electrons at the interface, as well as the Fermi levels for the two materials (Nithya and Devi 2019b). In this case, there is a state in the energy gap that penetrates deeper into the semiconductor; it is actually the metal's band states that are deeply buried into the semiconductor's states (Wan et al. 2019).

In the present case, the work function of the Ag metal was near to the CB and acted as an electron acceptor from the SrTiO<sub>3</sub>/rGO. The semiconductor's work function can be divided

into two parts(Nithya and Devi 2019a; Li et al. 2020): first, the internal work function ( $W_I$ ) is defined as the energy difference between Fermi energy and the CB's bottom; and second, external work function ( $W_E$ ) refers to the amount of work required to extract a free electron from SrTiO<sub>3</sub>/rGO. As a result, the total work function of the SrTiO<sub>3</sub>/rGO ( $W_S$ ) can be written as  $(W_S) = (W_I) + (W_E)$ . Let ( $W_M$ ) be the deposited Ag's work function, the donor levels in the SrTiO<sub>3</sub>/rGO are totally ionized when the SrTiO<sub>3</sub>/rGO and the Ag metal come into contact, the electrons in these states ( $W_M > W_S$ ) should flow into the Ag metal in the CB of SrTiO<sub>3</sub>/rGO until the Fermi energies of the metal and the semiconductor approach equilibrium. At equilibrium, the energy levels of the SrTiO<sub>3</sub>/rGO are dropped by the amount ( $W_M - W_S$ ) since the Fermi energies are at the same level, and Schottky barrier ( $W_{SK}$ ) formed at the SrTiO<sub>3</sub>/rGO@Ag interface.



#### 4. Conclusions

In conclusion, by using a simple hydrothermal technique, a series of SrTiO<sub>3</sub>/rGO nanocomposites with varied graphene weight ratios were successfully synthesized, followed by decorating the surface with Ag nanoparticles by using the photodeposition process, and tested for the photocatalytic degradation and adsorption of MB dye under irradiation of UV-visible light. The XRD analysis proved that the SrTiO<sub>3</sub> nanocrystals have a cubic crystalline structure. The rGO and the Ag<sup>0</sup> particles caused stress on the crystal structure of SrTiO<sub>3</sub> that confirmed by a notifiable decrease of the average grain sizes ( $D$ ) obviously accompanied by a rise in microconstraints ( $\xi\%$ ) and caused significant structural defects as measured by an increase in dislocation density ( $\delta$ ). Furthermore, SEM images also confirmed the establishment of the heterojunction and the superior intimate interaction between rGO sheets and SrTiO<sub>3</sub> nanocubes. The experimental gap values were about 3.21 eV and 2.82 eV for SrTiO<sub>3</sub> and SrTiO<sub>3</sub>/rGO<sub>20%</sub>@Ag<sub>4%</sub>, respectively, as determined by UV-Vis-DRS spectroscopy; whereas, the gap value of SrTiO<sub>3</sub> determined by DFT was about 2.98 eV using GGA +U computations. Due to the introduction of hybridized states, increasing the rGO and Ag metal quantities positively tuned the electronic structure with a lowered band gap, expanding the absorption to the visible region of the electromagnetic spectrum. Moreover, the adsorption kinetic curves showed that the equilibrium time was about 40 minutes and the quantity of MB adsorbed rose as the amount of rGO increased. The fit of kinetic curves showed that the pseudo  $n^{\text{th}}$  order model was adequate to model the experimental results. Furthermore, compared to pristine SrTiO<sub>3</sub>, all of the prepared SrTiO<sub>3</sub>/rGO nanocomposites had higher photocatalytic activity under UV-visible light irradiation, which could be attributed to graphene's photosensitizer role in the SrTiO<sub>3</sub>/rGO composites and the formation of p-n heterojunctions between p-type rGO and n-type SrTiO<sub>3</sub> nanocubes, as well as the localized surface plasmon resonance caused by Ag nanoparticles. The findings show that

incorporation of graphene into SrTiO<sub>3</sub>/rGO nanocubes and their decoration Ag particles increased visible light absorption and considerably improved photogenerated carrier separation. The photocatalytic performance of the sample SrTiO<sub>3</sub>/rGO<sub>20%</sub> @Ag<sub>4%</sub> in the MB degradation was the best of all the photocatalysts tested, with activity reaching 94% under UV-visible light after 40 minutes of irradiation. On the basis of these findings, a photocatalytic reaction mechanism can be proposed. In this mechanism, the rGO acts as photosensitizer for wide band gap of SrTiO<sub>3</sub> semiconductor and the metal band states that are firmly buried into the states of the semiconductor forms Schottky barrier at the metal–semiconductor interface.

## Declarations

-**Ethical Approval:** Not applicable

-**Consent to Participate:** Not applicable

-**Consent to Publish:** Not applicable

-**Authors Contributions:**

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by GUEDIRI Mohamed Khalil, CHEBLI Derradji and BOURZAMI Riadh. The first draft of the manuscript was written by CHEBLI Derradji, BOUGUETTOUCHA Abdallah and AMRANE Abdeltif and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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-**Competing Interests:** The authors declare that they have no competing interests

-**Availability of data and materials:** Not applicable

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