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# The enhanced photocatalytic performance and first-principles computational insights of Ba doping-dependent TiO<sub>2</sub> quantum dots

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Degradation in the presence of visible light is essential for successfully removing dyes from industrial wastewater, which is pivotal for environmental and ecological safety. In recent years, photocatalysis has emerged as a prominent technology for wastewater treatment. This study aimed to improve the photocatalytic efficiency of synthesized TiO<sub>2</sub> quantum dots (QDs) under visible light by barium (Ba) doping. For this, different weight ratios (2% and 4%) of Ba-doped TiO<sub>2</sub> QDs were synthesized under ambient conditions via a simple and modified chemical co-precipitation approach. The QD crystal structure, functional groups, optical features, charge-carrier recombination, morphological properties, interlayer spacing, and presence of dopants were analyzed. The results showed that for 4% Ba-doped TiO<sub>2</sub>, the effective photocatalytic activity in the degradation process of methylene blue (MB) dye was 99.5% in an alkaline medium. Density functional theory analysis further corroborated that the band gap energy was reduced when Ba was doped into the TiO<sub>2</sub> lattice, implying a considerable redshift of the absorption edge due to in-gap states near the valence band.

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## 1. Introduction

Freshwater reservoirs are getting more drained and polluted due to their use in various industrial fields, notably garment industries. Freshwater supplies are constantly getting depleted due to population growth and extended droughts, and the world now faces a massive problem in fulfilling the expanding needs for potable water.<sup>1–4</sup> Approximately 750 million people on the planet are suffering from a shortage of clean water, and an increase in the supply of micropollutants in water has proven dangerous to the environment. Industries

including textiles, polycarbonate, paper printing, foodstuff, and chemicals are the primary water pollution sources.<sup>5–7</sup> Industrial dyes can cause major sicknesses in animals and humans, such as cancer, skin irritability, numerous respiratory ailments, allergies, and liver malfunctions.<sup>8</sup> It is reported that 15% of dyes are directly discharged into the environment. Some traditional approaches, including advanced oxidation processes,<sup>9</sup> adsorption,<sup>10</sup> flocculation and coagulation,<sup>11</sup> electrocoagulation,<sup>12</sup> and photocatalytic degradation,<sup>13</sup> are utilized in wastewater treatment. These methods have some flaws, such as inadequate removal and the formation of secondary contaminants. Besides these, photocatalytic activity (PCA) in the presence of metal oxide semiconductors is recognized as an effective approach for removing contaminants from wastewater.<sup>14</sup>

Many metal oxide semiconductors (Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MgO, and WO<sub>3</sub>) are widely used for photocatalytic dye degradation due to their excellent chemical stabilization, low toxicity, and broad band gap. Among them, titanium dioxide (TiO<sub>2</sub>) has versatile characteristics such as a large band gap, high physiochemical stability, zero toxicity, high oxidative power, inexpensiveness, effective bactericidal potential, and photocatalytic activity under UV light.<sup>15–17</sup> TiO<sub>2</sub> naturally exists in three crystalline phases: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic).<sup>18,19</sup> Among these, strong photocatalytic activity, chemical stability, and a negative charge-carrier potential are credited with making the anatase phase one of the most

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effective photocatalysts.<sup>20</sup> The physicochemical parameters, surface-to-volume ratio, grain size, geometry, crystallinity, and surface texture influence the photocatalytic activity.<sup>21,22</sup>

The development of new mixed metal oxides (MOs) for degrading various organic dyes by photocatalysis has been a major focus in recent years. As a result, doping TiO<sub>2</sub> with noble metals, rare-earth metals, and transition metals has been extensively studied to reduce the particle size and improve the photocatalytic and antibacterial properties of TiO<sub>2</sub>. Doping TiO<sub>2</sub> with the alkaline earth metal Ba alters the oxide's optical absorption characteristics, which may affect its antibacterial activity and PCA. By modifying the band gap energy, the Ba dopant may operate as an electron trap, inhibiting the recombination rate of e<sup>-</sup>/h<sup>+</sup> pairs. This enhances the antibacterial action and PCA by promoting the generation of reactive oxygen species.<sup>23</sup> According to Mills and Hoffmann's research, the photocatalytic efficiency of a nanocatalyst can be improved by doping the nanocatalyst with an appropriate substance.<sup>24</sup> However, few studies are reported in the literature regarding Ba-doped TiO<sub>2</sub> synthesized through different methodologies. In a recent study, up to 3% Ba-doped TiO<sub>2</sub> was synthesized using the sol-gel method at 80 °C for 5 hours. The product was calcined at 500 °C for 2 hours and a nanoparticle morphology was obtained. The acquired nanoparticles were utilized for the degradation of methylene blue (MB) dye for up to 150 minutes, and the calculated degradation percentage was insufficient.<sup>25</sup> In another study, up to 2% barium-doped TiO<sub>2</sub> was prepared using a mild hydrothermal method and placed in an oven at 100 °C for 12 hours to complete the chemical reaction. After drying the product at 50 °C, the nanocrystal morphology was determined and used for the degradation of acid red 18, a dye. The degradation efficiency was calculated to be 98.6% under acidic conditions for 90 minutes.<sup>26</sup> In this regard, pure TiO<sub>2</sub> and Ba-

doped TiO<sub>2</sub> in the anatase form are particularly interesting among the various photoactive MOs.

Herein, 2% and 4% Ba-doped TiO<sub>2</sub> were prepared with a simple co-precipitation technique and a QD morphology was achieved. We determined the maximum doping effect of Ba on TiO<sub>2</sub> using structural, optical, and morphological techniques and tested its ability to remove organic pollutants in different media from contaminated water. The obtained results showed maximum degradation in almost all media; however, the most promising results were in the basic medium and were found to be 99.5%. Furthermore, computational density functional theory was employed to investigate the Ba-doped TiO<sub>2</sub> systems. We show that the changes in the electronic structure of TiO<sub>2</sub> doped with Ba can be explained by combining experimental results with theoretical calculations.

## 2. Experimental section

### 2.1 Materials

Titanium(IV) butoxide (C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti), ethanol (C<sub>2</sub>H<sub>5</sub>OH), sodium hydroxide (NaOH), and barium chloride dehydrate (BaCl<sub>2</sub>·2H<sub>2</sub>O) were purchased from Sigma-Aldrich (Germany).

### 2.2 Synthesis of Ba-doped TiO<sub>2</sub> quantum dots

To synthesize TiO<sub>2</sub>, titanium(IV) butoxide (20 mL) was dissolved in ethanol (50 mL) under vigorous stirring at 75 °C to form a solution. Later, 400 mL deionized water (DI water) and NaOH (0.5 M) were introduced dropwise to form a colloidal solution; the formation of precipitates started during the incorporation of the 0.5 M NaOH solution while maintaining the above-mentioned colloidal solution at pH ~ 10. Then, the colloidal solution was centrifuged for 6 minutes at 7500 rpm to achieve sedimentation, and the product was rinsed numerous times

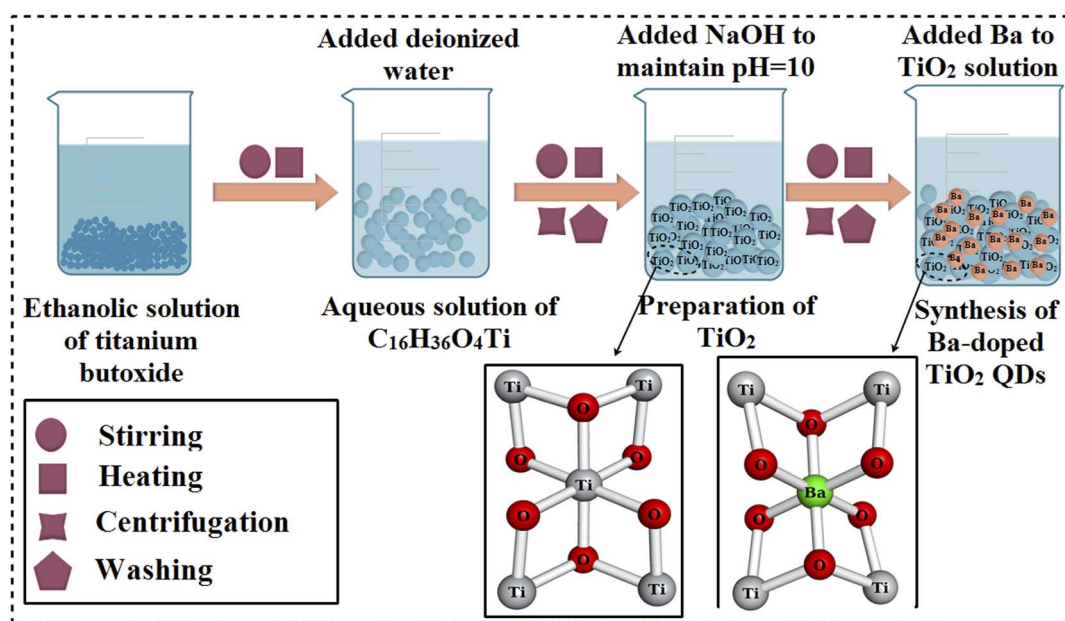


Fig. 1 Schematic diagram of the synthesized Ba-doped TiO<sub>2</sub> QDs.



with deionized (DI) water to eliminate impurities. The final product was dried at 500 °C to create anatase-phase TiO<sub>2</sub> fine powder using the co-precipitation technique. For the doping of Ba into TiO<sub>2</sub>, different concentrations of Ba (2 and 4 wt%) were incorporated in the colloidal solution of TiO<sub>2</sub> QDs, and the same procedure was adapted for the synthesis of doped QDs (Fig. 1).

### 2.3 Photocatalysis

The PCA of the TiO<sub>2</sub> and Ba-doped TiO<sub>2</sub> QDs under the influence of light ranging between 400 and 800 nm at room temperature was evaluated with UV-vis spectrophotometry. Initially, 5 mg of the nanocatalyst was dissolved in a 30 mL aqueous solution of MB while being vigorously stirred for 10 minutes in the absence of light. Then, the solution was exposed to the above-mentioned light for 2 hours, with 3 mL of the solution taken out every 30 minutes for UV-vis analysis to evaluate the MB dye degradation ( $\lambda_{\text{max}} = 665 \text{ nm}$ ). The percentage degradation efficiency was calculated using eqn (1).

$$\text{Degradation efficiency(\%)} = \left(1 - \frac{C_t}{C_0}\right) \times 100 \quad (1)$$

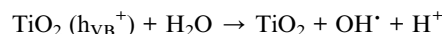
where  $C_0$  is the initial absorbance and  $C_t$  is the final absorbance of MB with respect to time.

**2.3.1 Reaction mechanism.** The structure of semiconductors plays a significant role in photocatalysis. The mechanism of TiO<sub>2</sub> as a photocatalyst is described below and depicted in Fig. 2.

(i) Photoexcitation: photocatalysis (PCA) begins with photoexcitation, which occurs when photons have energy equal to or greater than the band gap energy of the material ( $E_g$ ). These photons urge electrons in the VB to move towards the CB.

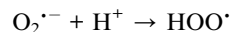
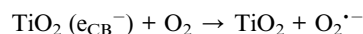


(ii) Water ionization: in order to form a hydroxyl radical (OH<sup>•</sup>), the positive holes (h<sup>+</sup>) can oxidize hydroxide ions or water molecules that have been adsorbed on the surface of TiO<sub>2</sub>.



At the photocatalyst surface, these OH<sup>•</sup> radicals act as oxidizing agents that strike adsorbed organic molecules that are very close to the catalyst surface and take part in mineralization to improve decontamination.

(iii) Ionosorption of oxygen: superoxide radicals (O<sub>2</sub><sup>•-</sup>) are formed when excited electrons react with oxygen. Protons and superoxide radical anions combine to generate hydroperoxyl radicals (HOO<sup>•</sup>).



O<sub>2</sub><sup>•-</sup> not only plays a part in more oxidation cycles but also prevents e<sup>-</sup>/h<sup>+</sup> recombination while keeping TiO<sub>2</sub> a neutral molecule.

(iv) Photosensitized oxidation: in conditions where catalysts are present, the excited state of MB can inject an electron into the conduction band. After this step, the dye is changed into a cationic radical, which subsequently degrades and produces compounds in accordance with the following reactions:

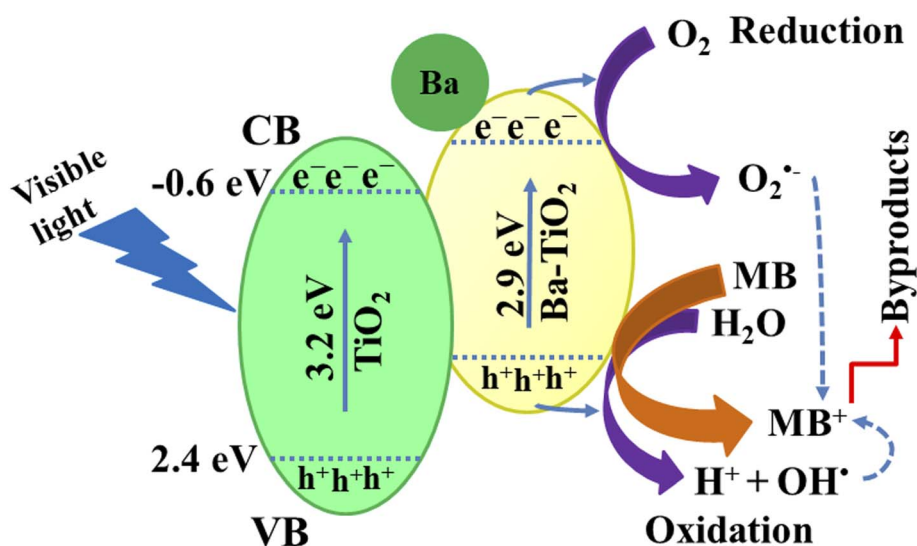
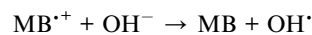
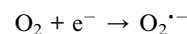
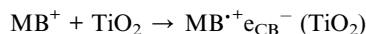


Fig. 2 Schematic photocatalytic mechanism of the Ba-doped TiO<sub>2</sub> QDs.





When the catalyst absorbs visible light holes in the valence band (VB), electrons are produced in the conduction band (CB). In this way, electron–hole pairs are generated and initiate the redox reaction on the TiO<sub>2</sub> surface. OH<sup>•</sup> radicals are produced whenever the holes ( $h_{\text{VB}}^+$ ) interact with an adsorbed hydroxyl group. In contrast, the reaction of electrons ( $e_{\text{CB}}^-$ ) with oxygen produces the superoxide anion radical O<sub>2</sub><sup>•-</sup>. The degradation of MB occurs due to a collaborative effort of OH<sup>•</sup> and O<sub>2</sub><sup>•-</sup> radicals. Lastly, the oxidation of organic molecules produces CO<sub>2</sub> and H<sub>2</sub>O.<sup>27</sup>

### 3. Results and discussion

XRD was employed to examine the crystalline structure and crystallite size of undoped and doped TiO<sub>2</sub> in the range of 15°–65° (Fig. 3a). The identified TiO<sub>2</sub> pattern is consistent with JCPDS card no. 00-021-1272, revealing that the peaks coincide with the anatase phase of TiO<sub>2</sub>. The tetragonal structure was validated by the diffraction peaks detected at  $2\theta = 25.28^\circ$ ,  $37.80^\circ$ ,  $48.05^\circ$ ,  $53.89^\circ$ , and  $62.69^\circ$ , which synced with the (101), (004), (200), (105), and (204) planes, respectively.<sup>28</sup> Additionally, the presence of barium titanium oxide (Ba<sub>2</sub>O<sub>20</sub>TiO<sub>9</sub>) was observed at  $20.0^\circ$ ,  $27.4^\circ$ ,  $28.6^\circ$ , and  $44.92^\circ$ , with the *hkl* values of (013), (141), (220) and (303), respectively, which matched well with JCPDS card no: 00-040-0405. Upon Ba doping, intense TiO<sub>2</sub> peaks were found and peak shifting was observed towards higher angles, which indicates an improvement in crystallinity. The crystalline sizes of the synthesized dopant-free and doped TiO<sub>2</sub> were computed using the Debye–Scherer formula.

Subsequently, SAED patterns were recorded to explore the highly crystalline nature of the pristine and Ba-doped TiO<sub>2</sub>, as depicted in Fig. 3c–e. The XRD results validate the tetragonal crystalline structure of TiO<sub>2</sub> by indexing the images with the diffraction planes (101), (004), (105), (200), and (204).

FTIR analysis was applied for the functional group identification of the doped TiO<sub>2</sub> samples. Wavenumbers ranging from 4000 to 500 cm<sup>-1</sup> were used to record the spectra (Fig. 3b). The Ti–O–Ti bridging stretching and Ti–O stretching modes were observed at the bands at 527 and 628 cm<sup>-1</sup>, respectively.<sup>29</sup> Bands appeared at 1640 cm<sup>-1</sup> and 3200–3400 cm<sup>-1</sup>, corresponding to the hydroxyl group (OH) bending and stretching vibrations caused by the presence of H<sub>2</sub>O molecules in the TiO<sub>2</sub> catalyst.<sup>30</sup> Band ranges at 2150–2360 cm<sup>-1</sup> were revealed with higher doping concentrations of Ba, ascribed to the physical adsorption of CO<sub>2</sub> and CO.<sup>31</sup> The spreading of the adsorption region over 950–400 cm<sup>-1</sup> upon Ba doping was attributed to the characteristic M–O bond oscillations (where M = Ti and Ba). Shifting in the band position suggests that Ba<sup>2+</sup> ions were successfully doped into TiO<sub>2</sub>.<sup>32</sup>

The optical properties of TiO<sub>2</sub> are widely known to be highly dependent on the material type (*e.g.*, single-crystal, powder) along with the fabrication methods. The absorbance spectra of undoped and barium-doped TiO<sub>2</sub> were measured by UV-vis spectrophotometry. The absorption peak identified for the as-prepared TiO<sub>2</sub> at ~350 nm is attributed to electron transfer from the 2p to 3d region of the VB of O<sup>2-</sup> to the CB of Ti<sup>3+</sup>.<sup>33</sup> In the absorption spectra, a redshift is observed with Ba (2%, 4%) doping, resulting in decreased band gap energy (*E<sub>g</sub>*). Tauc transformation was used to calculate *E<sub>g</sub>*, as displayed in Fig. 4b. The estimated *E<sub>g</sub>* was 3.25 eV for TiO<sub>2</sub>,<sup>33</sup> and *E<sub>g</sub>* was reduced with a low and high doping concentration of Ba (3.16 eV and

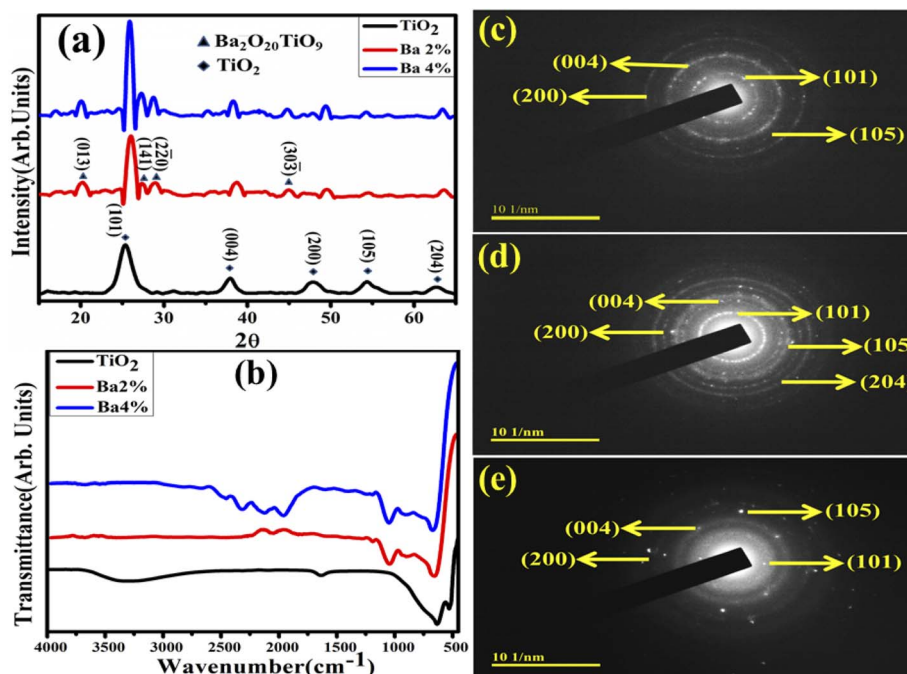


Fig. 3 (a) X-ray diffraction patterns, (b) FTIR spectra and (c–e) SAED patterns of pure and Ba (2%, 4%)-doped TiO<sub>2</sub> QDs.



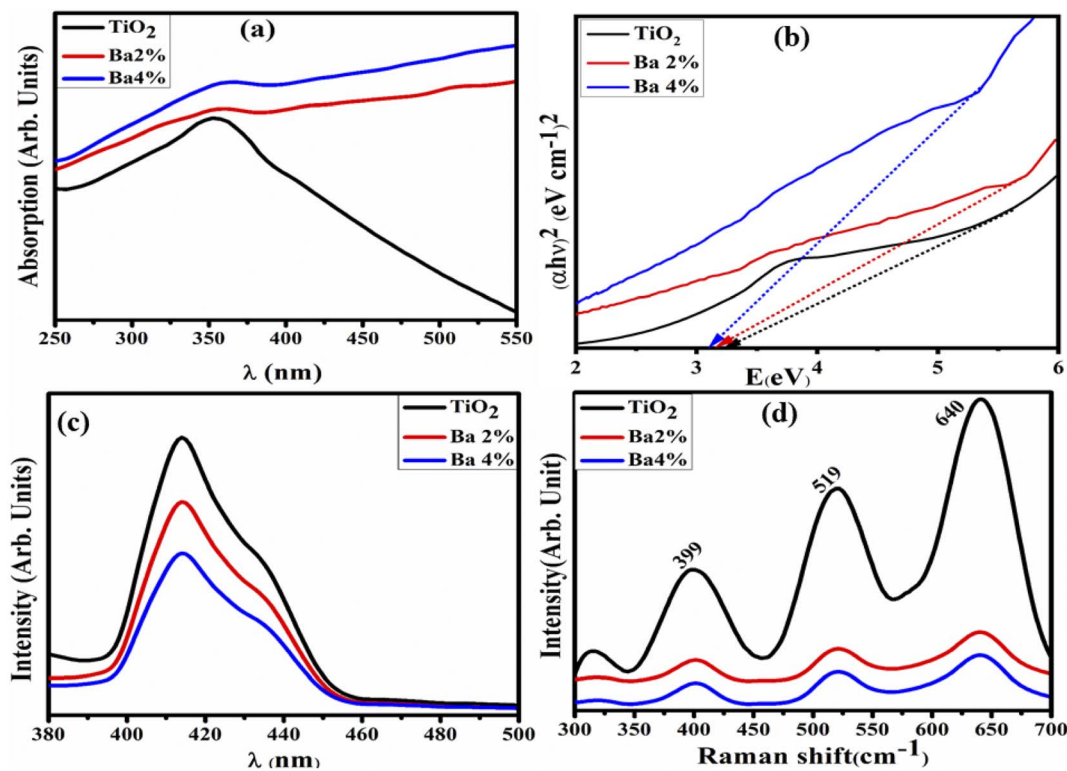


Fig. 4 (a) Absorbance spectra, (b)  $E_g$  by Tauc plot, (c) photoluminescence spectra and (d) Raman spectra of the  $\text{TiO}_2$  and Ba (2%, 4%)-doped  $\text{TiO}_2$  QDs.

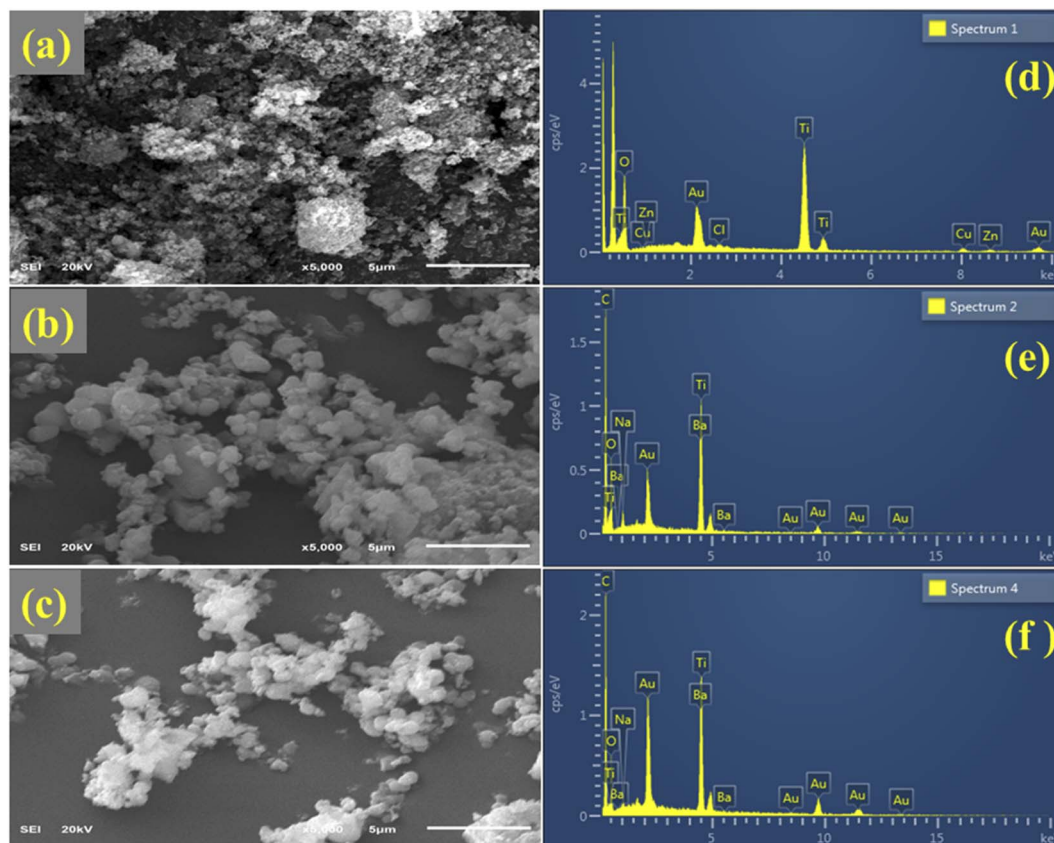


Fig. 5 (a–c) FESEM images and (d–f) EDS analysis of pure and Ba (2%, 4%)-doped  $\text{TiO}_2$ .



3.12 eV, respectively). The reduction in the band energy gap can be attributed to the increasing crystallite size, as demonstrated by the XRD measurements.

PL spectroscopy was used to assess the  $e^-h^+$  recombination rate, recorded between 380 and 500 nm at an excitation wavelength of 350 nm (Fig. 4c). The  $\text{TiO}_2$  peak intensity observed at 414 nm demonstrated the high recombination rate of  $e^-h^+$  pairs, which influences the  $\text{TiO}_2$  photocatalytic performance significantly. Furthermore, the peak intensity was reduced, which indicates a lower charge recombination rate upon doping and thus higher photocatalytic activity.<sup>34,35</sup> These emission transitions have been credited to unilaterally charged oxygen vacancies in  $\text{TiO}_2$  and arise when a photogenerated  $h^+$  mixes with an  $e^-$  taking up oxygen vacancies.<sup>36</sup> When the concentration of Ba increases, the peak intensity reduces as higher concentrations restrict the inter-nuclear space, and the emission intensity begins to flow towards the energy-killing domains.<sup>37–40</sup> Raman spectroscopy was used to investigate the lattice strain, phase transformations, lattice dynamics, and local symmetry of the samples.<sup>41,42</sup>

Fig. 4d presents the Raman spectra of doped  $\text{TiO}_2$  between 300 and 700  $\text{cm}^{-1}$ . The peaks appearing at 399, 519, and 640  $\text{cm}^{-1}$  for the samples are attributed to distinct LO vibration modes, demonstrating the improved crystallinity of  $\text{TiO}_2$  with Ba (2%, 4%) doping, having minimum interlayer stress and defect density.<sup>43</sup> All the samples exhibited high bands at 399,

519, and 640  $\text{cm}^{-1}$ , which most certainly correlate to the permissible Raman modes  $B_{1g}$ ,  $B_{1g}$ , and  $E_g$ , respectively, with the space group  $D_{4h}$ .<sup>19,44</sup>

The surface morphology and chemical composition of the synthesized QDs were confirmed by FESEM and EDS spectroscopy, as shown in Fig. 5. Aggregated quantum dots (QDs) of different sizes appear (Fig. 5a). Upon Ba doping, small-scale agglomeration was observed (Fig. 5b). A layer of Ba is formed as the concentration increases, and the QDs are dispersed (Fig. 5c). The EDS spectra for the  $\text{TiO}_2$  QDs are presented in Fig. 5d–f. Prominent peaks of Ti with O reveal the successful preparation of  $\text{TiO}_2$  QDs. The presence of Ba in the spectra confirms the successful incorporation of dopants, whereas the peaks of Cu and C are attributed to the Cu grid and carbon tape used to mount the samples, respectively (Fig. 5e and f). Furthermore, Au, Zn, and Cl peaks emerged, which were assigned to the coating of gold sprayed over the sample and some contamination. Additionally, a peak of Na was found in each prepared sample, ascribed to the use of NaOH to maintain the pH of the solutions.

The morphology, size, and shape of the  $\text{TiO}_2$  and Ba (2%, 4%)-doped  $\text{TiO}_2$  QDs were examined using TEM, as illustrated in Fig. 6a–c. Spherical-shaped small-size QDs ranging from 6 to 9 nm are observed, as shown in Fig. 6a. On doping with Ba, the synthesized QDs appeared to be loosely bound with the  $\text{TiO}_2$  QDs (Fig. 6b). By increasing the dopant concentration, the QDs

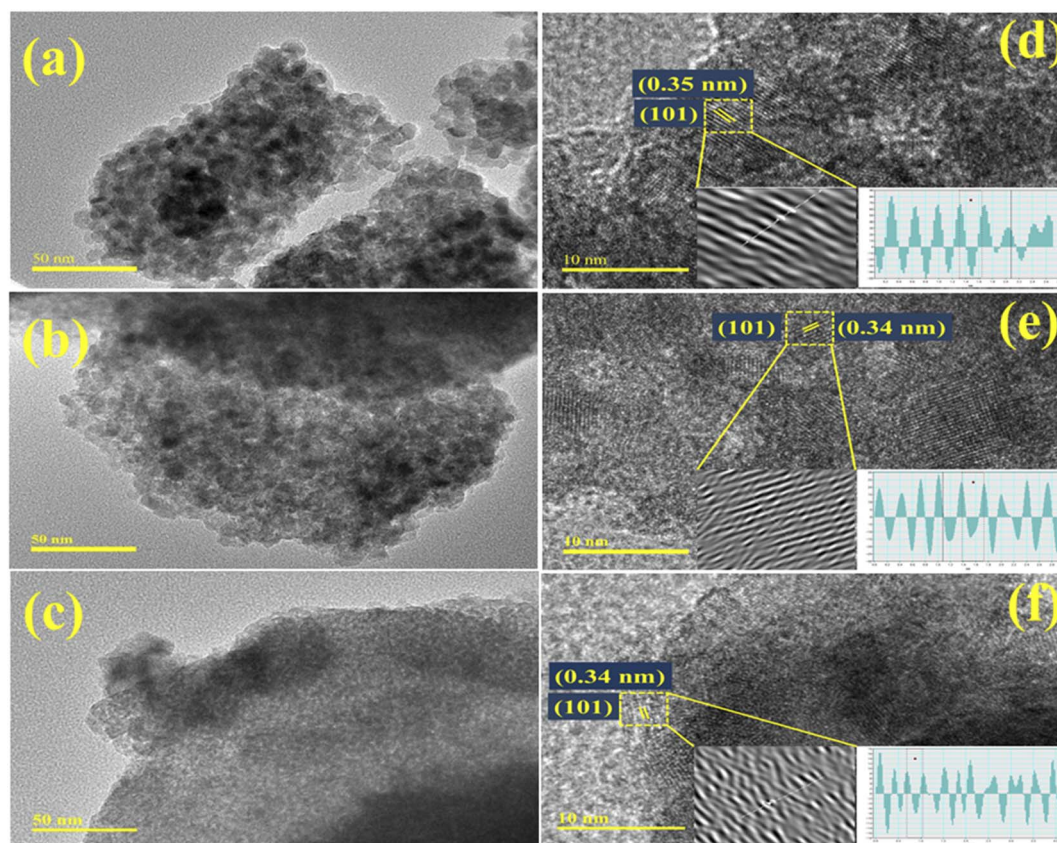


Fig. 6 (a–c) TEM images of pure and Ba (2%, 4%)-doped  $\text{TiO}_2$ ; (d–f) interlayer  $d$ -spacing HRTEM images of undoped and Ba-doped  $\text{TiO}_2$ .



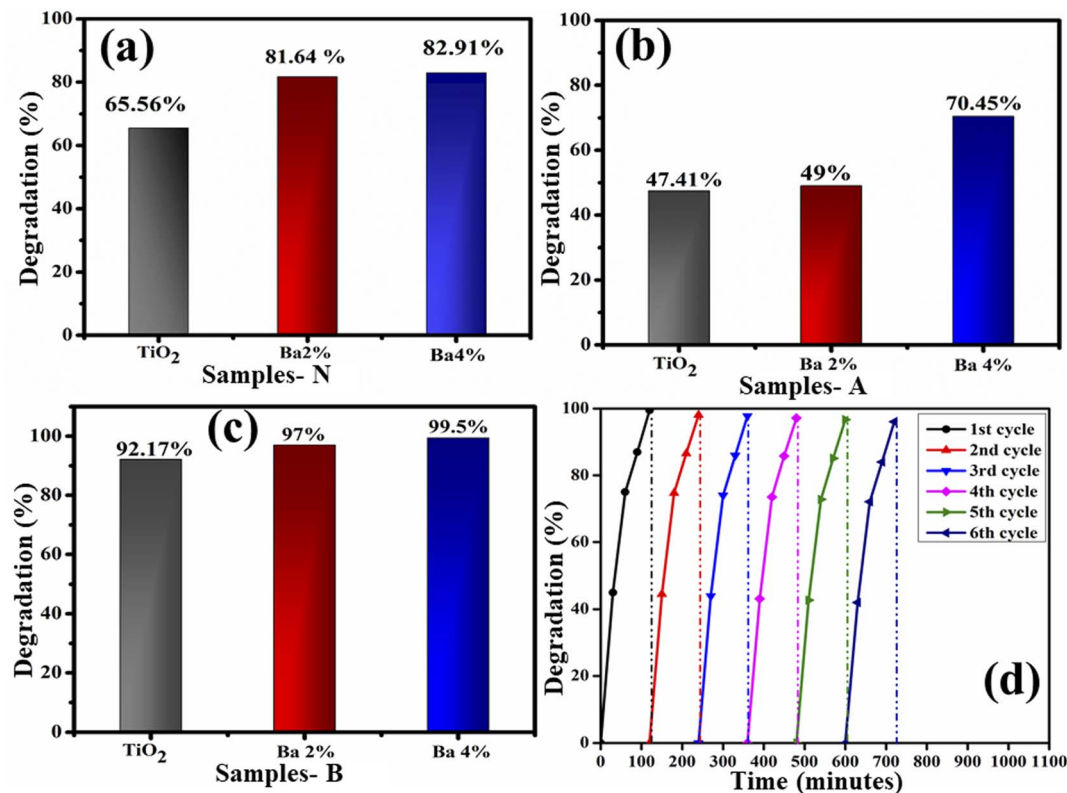


Fig. 7 Photocatalytic degradation of  $\text{TiO}_2$  and Ba (2% 4%)-doped  $\text{TiO}_2$  in (a) neutral, (b) acidic and (c) basic media and (d) the photocatalytic degradation of MB by 4% Ba-doped  $\text{TiO}_2$ .

Table 1 Comparison of the present work with the reported literature

Photocatalysts	Pollutants	Time	Degradation	References
$\text{CeO}_2$ -doped $\text{TiO}_2$	Rhodamine B	8 h	99.89%	50
$\text{TiO}_2$ -TMAOH	MB	20 min	80%	51
$\text{TiO}_2$ thin-films	MB	240 min	92%	52
$\text{TiO}_2$ /PVA	MB	120 min	98.43%	53
$\text{TiO}_2$ /PAAm	MB	5 h	95.00%	54
Ba-doped $\text{TiO}_2$	MB	120 min	99.5%	Present study

seem to become overlapped and highly aggregated, which may result in their decreased size (Fig. 6c). Moreover, HRTEM was utilized to determine the interlayer  $d$ -spacing, as shown in Fig. 6d–f. The interlayer  $d$ -spacing of  $\text{TiO}_2$  and Ba (2%, 4%)-doped  $\text{TiO}_2$  were estimated to be 0.35, 0.34, and 0.34 nm, respectively, assigned to the (101) plane for doped and undoped  $\text{TiO}_2$ , and well agreed with the XRD results. The above optical, structural, and morphological characterizations for doped  $\text{TiO}_2$  indicate that the Ba-doped  $\text{TiO}_2$  lattice has an anatase phase with a tetragonal crystalline structure, as confirmed by SAED. The addition of Ba increased the absorption and introduced a redshift as the crystallite size increased, which could capture a wide range of wavelengths. The morphological study confirmed the formation of QDs with agglomeration upon doping.

To determine the PCA of the prepared nanocatalyst, UV-vis spectrophotometry was used (Fig. 7). The degradation

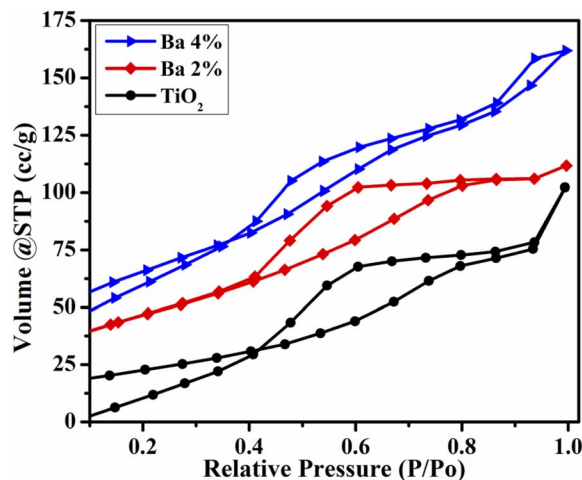


Fig. 8  $\text{N}_2$  adsorption–desorption isotherms.



efficiency was calculated against acidic, basic and neutral media. In a neutral medium (pH 7), the percentage degradation was estimated to be 65.56%, 81.84%, and 82.91% for dopant-free and doped TiO<sub>2</sub>, respectively, as presented in Fig. 7a. The solution pH influences the photocatalytic mechanism, which may affect the adsorption of the dye on the photocatalyst surface. MB, as a positively charged dye, degrades slowly at lower pH; as a result, the degradation efficiency is enhanced on increasing the pH. Moreover, in an acidic medium (pH 4), the

measured degradation results are 47.41%, 49%, and 70.41% for the doped and undoped TiO<sub>2</sub>, respectively, as demonstrated in Fig. 7b. From the results in the acidic medium, the degradation of MB seems to be ineffective compared to that in the neutral medium, attributed to the positively charged surfaces of the catalysts, which tend to resist the adsorption of the cationic adsorption species. Furthermore, in a basic medium (pH 12), the prepared nanocatalyst exhibits efficient dye degradation results of 92.17%, 97%, and 99.5% for TiO<sub>2</sub> and Ba (2%, 4%)-doped TiO<sub>2</sub>, respectively, as illustrated in Fig. 7c. Increased electrostatic interaction between the positively charged dye and the negatively charged catalyst in the basic dye solution causes the surface charges to become negative, which facilitates dye degradation.<sup>45–47</sup> Generally, the PCA is influenced by the surface area of the nanocatalyst, as a large surface area provides more active sites, increases the number of redox reactions on the nanocatalyst surface and results in the degradation of MB.<sup>48,49</sup> The results show that the MB dye degrades maximally when treated with Ba-doped TiO<sub>2</sub> rather than with the TiO<sub>2</sub> QDs. For the Ba-doped TiO<sub>2</sub> photocatalysts, the possible charge separation mechanism is described as follows. Charge pairs are formed when visible light interacts with the TiO<sub>2</sub> QDs, and electrons in the charge pairs move from the valence band (VB) to the conduction band (CB), leaving a hole in the VB. Most of these electron–hole pairs tend to recombine and lower the

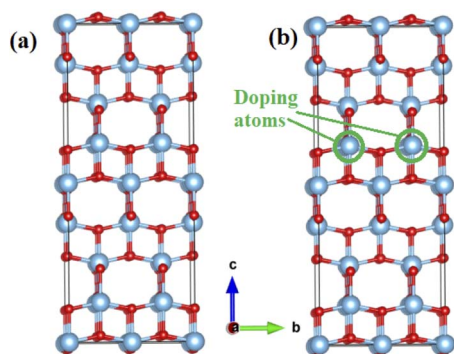


Fig. 9 Computational model (a  $2 \times 2 \times 2$  supercell) for the anatase (a) TiO<sub>2</sub> and (b) Ba-doped TiO<sub>2</sub>.

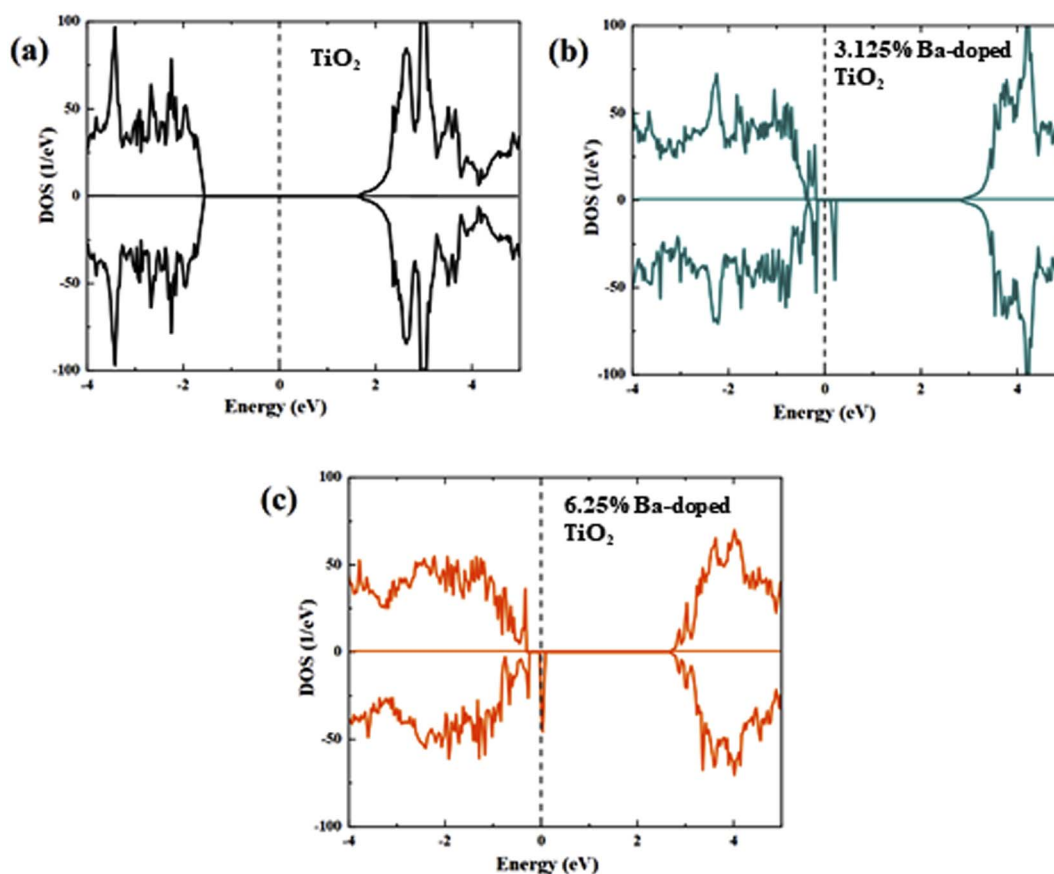


Fig. 10 Calculated total of (a) pure, (b) 3.125% Ba- and (c) 6.25% Ba-doped TiO<sub>2</sub> using the DFT-1/2 method. The Fermi level is represented by the red vertical dashed line.



degradation capability of TiO<sub>2</sub>. Incorporating metal ions (Ba) into the TiO<sub>2</sub> lattice as electron traps inhibits the recombination of charge pairs, resulting in increased photocatalytic activity. The separation of charges and the transport of these charges play a significant role in enhancing the photocatalytic activity.<sup>25</sup> In this regard, 4% Ba-doped TiO<sub>2</sub> shows the maximum results in all the media for MB degradation, attributed to the lower recombination rate as evidenced from the PL spectra (Fig. 4c). 4% Ba-doped TiO<sub>2</sub> has lower charge recombination that results in enhanced photocatalytic degradation. Additionally, recycling experiments were used to examine the photostability of TiO<sub>2</sub> doped with 4% barium, as presented in Fig. 7d. Even after being subjected to six separate cycles of the photocatalytic degradation of MB by visible light, the high-concentration Ba-doped TiO<sub>2</sub> QDs exhibited a high level of stability and maintained an exceptional level of activity. A literature comparison with the current study is provided in Table 1.

The BET surface area and pore size of the as-prepared TiO<sub>2</sub> and Ba-doped TiO<sub>2</sub> samples were investigated using BET analysis. The N<sub>2</sub> adsorption-desorption isotherms of all the samples are shown in Fig. 8. The adsorption-desorption isotherm of TiO<sub>2</sub> and Ba-doped TiO<sub>2</sub> matched the characteristics of a traditional type IV curve that had an H4 hysteresis loop (Fig. 8). A mesoporous structure was found in both the undoped and doped TiO<sub>2</sub> QDs. In addition, the BET surface areas of the

prepared QDs increased gradually to 119.183, 132.846, and 138.5 m<sup>2</sup> g<sup>-1</sup> for TiO<sub>2</sub> and Ba (2%, 4%)-doped TiO<sub>2</sub>, respectively. The average pore size was calculated to be 3.6, 4.5, and 10.8 nm for dopant-free and doped TiO<sub>2</sub>, respectively. It can be observed that the incorporation of Ba increased the surface area, which is beneficial for enhanced photocatalytic activity.

### 3.2 Electronic calculations

The electronic structures and optical characteristics were investigated by comprehensive first-principles calculation with the DFT method using the QuantumATK software package.<sup>55</sup> In our calculation, the exchange and correlation potential were dealt with by functionals at both the Perdew–Burke–Ernzerhof (PBE)<sup>56</sup> and DFT-1/2 method levels.<sup>57,58</sup> The Brillouin region was represented by a Monkhorst–Pack special *k*-point grid (5 × 5 × 1 for geometric optimization and 10 × 10 × 4 for electronic structure calculation). The basis set was set to the norm-conserving PseudoDojo<sup>59</sup>-medium with a mesh cut-off energy of 125 Ha. The force tolerance was set to 0.01 eV Å<sup>-1</sup> for geometric optimization.

The crystalline atomic structure of anatase TiO<sub>2</sub> was modeled by a 2 × 2 × 2 supercell containing 32 Ti atoms and 64 O atoms, as illustrated in Fig. 9a. The calculated lattice constants for TiO<sub>2</sub> (*a* = *b* = 3.782 Å and *c* = 9.552 Å) are very close to the experimental data (*a* = *b* = 3.7842 Å, *c* = 9.5146 Å).<sup>60</sup>

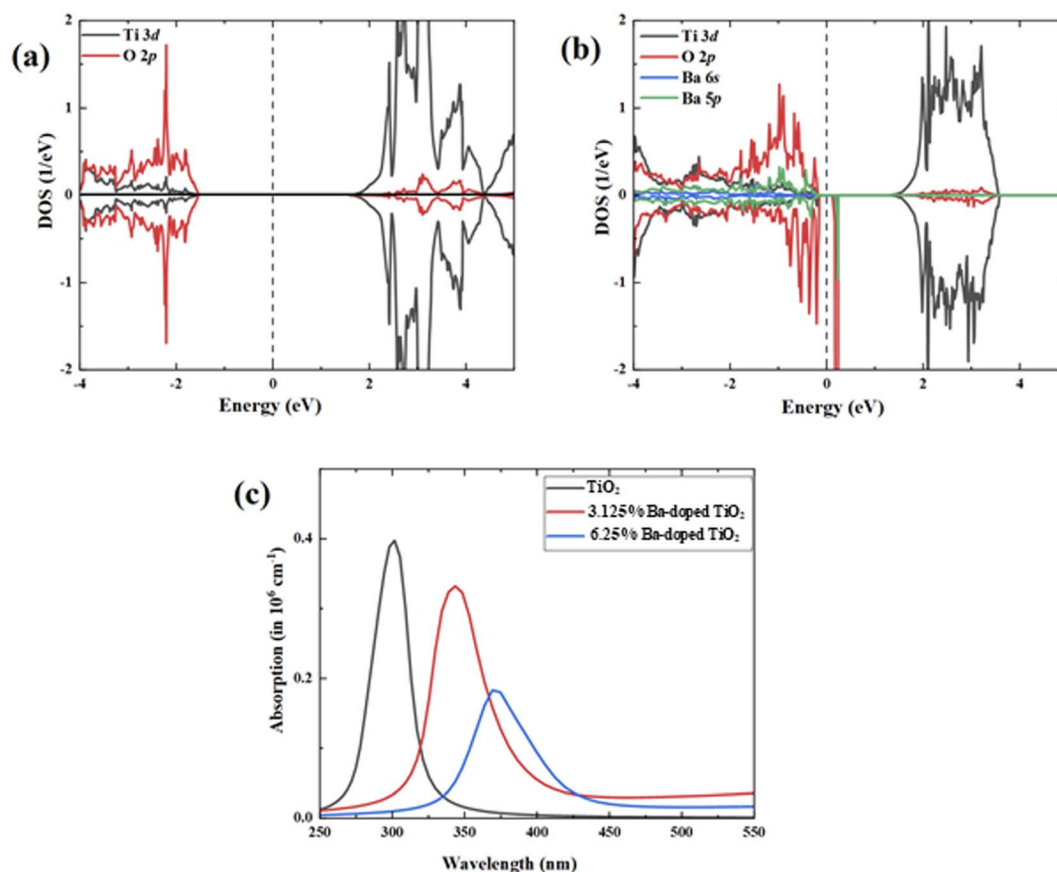


Fig. 11 PDOS of (a) pristine TiO<sub>2</sub> and (b) 3.125% Ba-doped TiO<sub>2</sub> and (c) the optical absorption spectra.



The Ba-doped structures were prepared by substituting one and two Ti atoms with one and two Ba atoms, affording doping concentrations of 3.125% (1/32) and 6.25% (2/32), respectively (Fig. 9b). When Ba impurities were introduced into the TiO<sub>2</sub> structure, the *a*- and *c*-lattice values (*a* = *b* = 3.790 Å, *c* = 9.766 Å and, *a* = *b* = 3.778 Å, *c* = 10.013 Å for 3.125% and 6.25% Ba-doped TiO<sub>2</sub>, respectively) were slightly higher than those in the pristine material. The hexagonal lattice deformation due to Ba-doping causes this difference.

The electronic densities of states of the undoped and doped systems were calculated to analyze the effect of Ba doping into the TiO<sub>2</sub> lattice from the perspective of the electronic structures (Fig. 10). The calculated pristine TiO<sub>2</sub> band gap was found to be 3.17 eV based on the GGA-1/2 method, which is very close to our measured experimental value and previously reported results.<sup>61–65</sup> The analysis of the partial DOS of pure TiO<sub>2</sub> (Fig. 11a) shows that the upper valence region is mostly dominated by O 2p states, while the lower conduction region is mainly due to the Ti 3d character. Doping Ba at Ti sites modified the electronic structure by generating a slightly asymmetric DOS near the valence band, as illustrated in Fig. 11b. It is observed that in-gap states appear in the band gap, especially in the peak in the DOS of the minority spin close to the upper part of the valence band. It can also be seen that the edge of the valence band advances closer to the Fermi level, indicating an increase in charge-carrier concentration and a modest reduction in the band gap.

The obtained band gap values are found to be 3.07 eV and 3.002 eV for 3.125% Ba- and 6.25% Ba-doped TiO<sub>2</sub>, respectively. Additionally, the band gap values are shown to slightly decrease with further increase in Ba concentration. The same behavior was observed in our experimental measurements.

Moreover, the states that appear in the band gap can help to stimulate valence electrons to the conduction band, boosting the visible light absorption, which is beneficial to improving the optical absorption efficiency. The in-gap states may lower the threshold for photoexcitation, decrease the energy needed for electron transitions, and thereby broaden the optical absorption spectrum without altering the energy of the electrons or holes. This result gives a good explanation of the redshift. The features of the PDOS of Ba-doped TiO<sub>2</sub> systems show that the Ba 5p states are coupled with O 2p, while partially appearing in the band gap. The absorption spectra of the pristine and Ba-doped TiO<sub>2</sub> were computed and are illustrated in Fig. 11c. The absorption spectrum analysis displays that the pristine TiO<sub>2</sub> only absorbed photons in the ultraviolet range with no photo-absorption activity in visible light. In the case of the Ba-doped TiO<sub>2</sub> configurations, there is a considerable redshift of the absorption edge owing to the presence of an in-gap near the valence band, which makes it simpler for electrons to be driven to the conduction band.

## 4. Conclusion

The co-precipitation technique was employed to synthesize TiO<sub>2</sub> and Ba (2%, 4%)-doped TiO<sub>2</sub> quantum dots. The XRD patterns revealed a tetragonal structure and anatase phase with a highly

crystalline nature of TiO<sub>2</sub>, as confirmed by SAED. The FTIR spectra present a band at 670 cm<sup>-1</sup> attributed to the Ti–O–Ti bond after preparing Ba-doped TiO<sub>2</sub>. The absorbance increased with an increasing amount of Ba accompanied by a redshift and decrease in the band gap energy. PL measurement showed a higher electron recombination rate as the intensity increased upon doping relative to the doped TiO<sub>2</sub>. The strongest Raman signal of TiO<sub>2</sub> at 640 cm<sup>-1</sup> was indexed to the E<sub>g</sub> vibrational mode utilizing Raman spectroscopy. Moreover, TEM images confirmed the QD formation and the *d*-spacing (0.34–0.35 nm) was evaluated using the Gatan software, comparable with the XRD measurements. Additionally, the dye degradation efficiency of the prepared nanocatalysts was examined against MB using different media. Among these, the most effective dye removal efficiency was observed in the basic medium. To investigate the influence of Ba doping on the TiO<sub>2</sub> lattice from the viewpoint of the electronic structures, the electronic densities of states of the undoped and doped TiO<sub>2</sub> systems were computed. With increasing the Ba concentration, the band gap values appear to slightly decrease. According to the absorption spectrum study, pristine TiO<sub>2</sub> solely absorbed photons in the ultraviolet region, with no photo-absorption activity in visible light. The existence of an in-gap in the valence band in the Ba-doped TiO<sub>2</sub> configurations causes a significant redshift of the absorption edge, making it easier for electrons to be pushed to the conduction band. Lastly, the TiO<sub>2</sub> and Ba (2%, 4%)-doped TiO<sub>2</sub> QDs were found to be more effective against MB dye removal (99.5% in basic medium).

## Conflicts of interest

There are no conflicts to declare.

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