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# Magnetic self-doped TiO<sub>2-x</sub>/Fe<sub>3</sub>O<sub>4</sub>@g-C solar-driven photocatalytic composite for water decontamination†

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Declining water resources and their contamination with chemicals risk the aquatic environment. Therefore, this work was devoted to designing a magnetically recyclable photocatalyst suitable for water treatment, namely, a TiO<sub>2-x</sub>/Fe<sub>3</sub>O<sub>4</sub>@g-C composite. Different preparation conditions were investigated together with the corresponding characteristics. The pure defective anatase TiO<sub>2-x</sub> phase of low band gap energy was detected through XRD and DRS analyses. Low charge recombination after the formation of defects was confirmed. The performances of the prepared photocatalysts in phenol degradation under solar light were evaluated, revealing the superior efficiency of TiO<sub>2-x</sub> prepared hydrothermally at 200 °C/24 h relative to intact TiO<sub>2</sub>. This best sample was incorporated with Fe<sub>3</sub>O<sub>4</sub>@g-C to facilitate its recovery and reuse. This successful combination was confirmed using XRD, Raman and XPS tools. TiO<sub>2-x</sub>/Fe<sub>3</sub>O<sub>4</sub>@g-C 2:1 formulation was found to be the most photoactive and could be reused up to five times without significant loss in its efficiency. Therefore, the precisely developed magnetic photocatalyst is promising for application in the water-treatment process.

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## 1. Introduction

To date, many photocatalysts have been investigated for the degradation of different pollutants.<sup>1</sup> Among them, TiO<sub>2</sub>, which was first discovered by Fujishima and Honda,<sup>2</sup> has attracted most of the attention owing to its excellent electronic and optical properties, electrochemical corrosion resistance, non-toxicity, good stability, low cost and abundant availability. However, the wide band-gap of TiO<sub>2</sub> ( $E_g \approx 3.2$  eV) limits its photo-response to UV-light only, which comprises only 5% of the solar energy.<sup>3</sup> Numerous efforts have been devoted to improving visible light activation, including incorporating quantum dots or co-catalysts, metal deposition and doping of metals/nonmetals, and heterojunction formation with another semiconductor with an unequal band structure.<sup>4,5,6</sup>

Another strategy is self-doping, which can tune the electronic structures and extend the photo-response range, thereby enhancing the photocatalytic activity of semiconductors without introducing any foreign elements.<sup>7</sup> The improved visible light harvesting of TiO<sub>2-x</sub> stems from the distortion of

TiO<sub>2</sub> crystals *via* oxygen vacancies (OVs) or Ti<sup>3+</sup>, which in turn causes the formation of new energy levels within the band gap.<sup>8</sup> For instance, self-doped TiO<sub>2-x</sub> was prepared through the introduction of OVs in the lattice structure, leading to a narrower band-gap and enhanced visible light absorption.<sup>8,9</sup> TiO<sub>2-x</sub> has been applied in water treatment under solar light. For instance, the TiO<sub>2-x</sub>/rGO nanocomposite has been implemented in the degradation of BPA and phenol, resulting in more than 90% removal efficiency.<sup>10</sup> Furthermore, Wu and his co-workers<sup>11</sup> used Ti<sup>3+</sup> self-doped TiO<sub>2</sub> nanoparticles as a photoanode for MB degradation and water splitting. The Ti<sup>3+</sup> self-doped TiO<sub>2</sub> nanoparticles showed intensive light absorption, fast photogenerated carrier transport and low recombination rate, thereby exhibiting improved photocatalytic (PC) and photoelectrocatalytic (PEC) activities of the final products compared with those of pure TiO<sub>2</sub>.

Generally, heterogeneous photocatalysts are practically applied either in an immobilized or slurry form. The immobilized form has a smaller surface area, but it is easy to be separated from water. In contrast, slurry photocatalysts have a higher surface area than immobilized ones, but they are difficult to be recovered from water. To overcome this paradox, magnetic nanoparticles can be incorporated into the powdered photocatalyst to provide an easy way to separate the photocatalyst from water using an external magnetic field without affecting the total surface area significantly.

Various methods have been employed for the synthesis of magnetic nanoparticles (MNPs) of various compositions and

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phases with distinct magnetic properties. Optimal performance is achieved when the MNPs have high saturation magnetization ( $M_s$ ) and stable magnetic and surface properties. Normally, MNPs possessing the strongest magnetic properties could be achieved using metals (Fe,  $M_s \sim 221 \text{ emu g}^{-1}$ )<sup>12</sup> or metal alloys (CoFe or CoNiFe,  $M_s \sim 245 \text{ emu g}^{-1}$ ).<sup>13</sup> Unfortunately, naked metal NPs have high chemical activity and are easily oxidized upon contact with air, generally leading to a loss of magnetism. This has promoted the widespread use of MNPs, such as iron(III) oxide ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ,  $M_s \sim \text{bulk } 92 \text{ emu g}^{-1}$ ).<sup>13</sup> The magnetic characteristics of  $\text{Fe}_3\text{O}_4$  nanoparticles enable their effortless recovery from water or wastewater using low magnetic fields or handheld magnets. This renders it a cost-effective and practical technique for treatment purposes owing to its benefits such as soft ferromagnetism, half-metallicity, minimal toxicity, and biocompatibility.<sup>14</sup>

However, high concentrations of ferrite lead to a considerable reduction in the semiconductor photocatalyst's efficiency. This is because spinel ferrites in this case act as recombination centres rather than trapping centres for electron/hole ( $e^-/h^+$ ) pairs. To overcome this problem, the prepared  $\text{Fe}_3\text{O}_4$  was covered by a barrier layer such as carbon (C) in different forms. For instance,  $\text{rGO-TiO}_2@Fe_3O_4$  was used for the degradation of chlorophenol under visible light with efficacy equal to 94%;<sup>15</sup>  $\text{TiO}_2/Fe_3O_4/\text{graphene oxide}$  was investigated for the removal of methylene blue (MB) under UV light (82%) and visible light (76%);<sup>16</sup> on the other hand, Hatefi, Younesi *et al.* applied  $\text{Fe}_3\text{O}_4/\text{TiO}_2$  with graphene quantum dots for the removal of MB under low-pressure mercury-vapor lamp and could achieve 86% removal efficiency.

An interesting type form of carbon is the glassy form. Glassy carbon (g-C) has high thermal resistance, extreme chemical stability, low density and great hardness compared with other carbons, which also exhibit excellent biological compatibility and high electrical conductivity.<sup>17</sup> The latter feature is expected to help in preventing the recombination of charge carriers, which would lead to better photocatalytic activity. Therefore, it is interesting to explore using glassy carbon as the barrier layer between self-doped  $\text{TiO}_2$  and  $\text{Fe}_3\text{O}_4$ .

To the best of our knowledge, the  $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4@g\text{-C}$  superparamagnetic photocatalytic composite has not yet been prepared. Therefore, we devote this work to optimizing the degree of defects of  $\text{TiO}_{2-x}$  by adjusting the hydrothermal conditions used for obtaining  $\text{TiO}_{2-x}$ , thus optimizing the ratio between  $\text{Fe}_3\text{O}_4@g\text{-C}$  and  $\text{TiO}_{2-x}$  to finally have the most active and easiest magnetically separable composite. The optimization process was based on the efficiency of phenol degradation as a model organic pollutant. According to the collected results, the designed composite is very efficient under solar irradiation and can be recovered and reused successfully several times without a noticeable drop in its activity.

## 2. Experimental methods

### 2.1 Preparation of the pristine and defective $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4@g\text{-C}$ composite

Firstly, pristine and defective  $\text{TiO}_2$  were prepared. In typical procedure, 1.8 mL of titanium(IV) isopropoxide (TTIP, ACROS

ORGANICS Co.) was added to 100 mL double distilled water (DDW) under slow stirring by a glass rod until the complete hydrolysis of TTIP. Then, the formed precipitate was washed with DDW. Subsequently, the precipitate was dissolved in 20 mL of 15%  $\text{H}_2\text{O}_2$  aqueous solution (El-Nasr Pharmaceutical Chemical Co.). Afterward, 85 mL DDW containing 1.82 g of L-ascorbic acid (Alpha Chemika Co.) was added to prevent the formation of a dense gel. The final mixture was transferred to a 150 mL Teflon-lined autoclave and heated for different times and temperatures. The formed precipitate was collected by centrifugation at 10 000 rpm for 10 min with consecutive washings by DDW and ethanol. Finally, the powder was dried at 70 °C for 6 h under vacuum.

$\text{Fe}_3\text{O}_4@g\text{-C}$  superparamagnetic nanoparticles were prepared as follows. Anhydrous  $\text{Fe}_3\text{Cl}$  and hexamethylenetetramine (HMTA) were dissolved in a solution of ethylene glycol and distilled water (DW) of equal volumes. The resulting solution was heated in a Teflon-lined autoclave at 110 °C for 6 h. After washing the precipitate with DW and ethanol, it was dried at 70 °C for 12 h in a vacuum oven. Then, the ground powder was calcinated at 650 °C for 1.5 h in Ar atmosphere.

Finally, the  $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4@g\text{-C}$  composites of different formulations were synthesized by suspending a definite amount of  $\text{Fe}_3\text{O}_4@g\text{-C}$  in 20 mL DDW for 15 min using an ultrasonic bath. After that, a certain amount of  $\text{TiO}_{2-x}$  was added to the  $\text{Fe}_3\text{O}_4@g\text{-C}$  suspension. The whole mixture was agitated in an ultrasonic bath for another 15 min. The well-dispersed mixture was frozen for one day, followed by freeze drying. The detailed procedure is schematically shown in Fig. 1.

### 2.2 Characterization of the prepared materials

Crystalline phases in the prepared materials were identified using X-ray diffraction (XRD) patterns, which were collected using an PANalytical X'Pert Pro diffractometer (the Netherlands) with  $\text{CuK}\alpha$  source ( $\lambda = 1.5406 \text{ \AA}$ ). The crystallized phases were identified by comparing the collected patterns with standard ASTM cards. The magnetization hysteresis loop was measured by a Riken Denshi BH-55 vibrating sample magnetometer (VSM) at room temperature. The band-gap was calculated from the UV-vis diffuse reflectance spectra (DRS) measured using a JASCO V730 spectrophotometer (Japan) equipped with diffuse reflectance accessories. Raman spectra were obtained using a Witec Alpha300 R confocal Raman microscope with 532 nm excitation wavelength at a power of 1 mW. The defects were identified using a BRUKER EMX EPR Spectrometer. The morphology was examined under a high-resolution transmission electron microscope (HR-TEM, JEOL TEM-2100, Japan). The recombination of electron and hole was identified using a spectrofluorometer (Edinburgh Instruments, FS5). X-ray photoelectron spectra (XPS) were collected using a Surface Science instrument X-probe, X-ray000 400  $\mu\text{m}$  – FG ON.

### 2.3 Evaluation of the photocatalytic performance

The photocatalytic activities of the prepared materials were evaluated using phenol as a model organic pollutant under



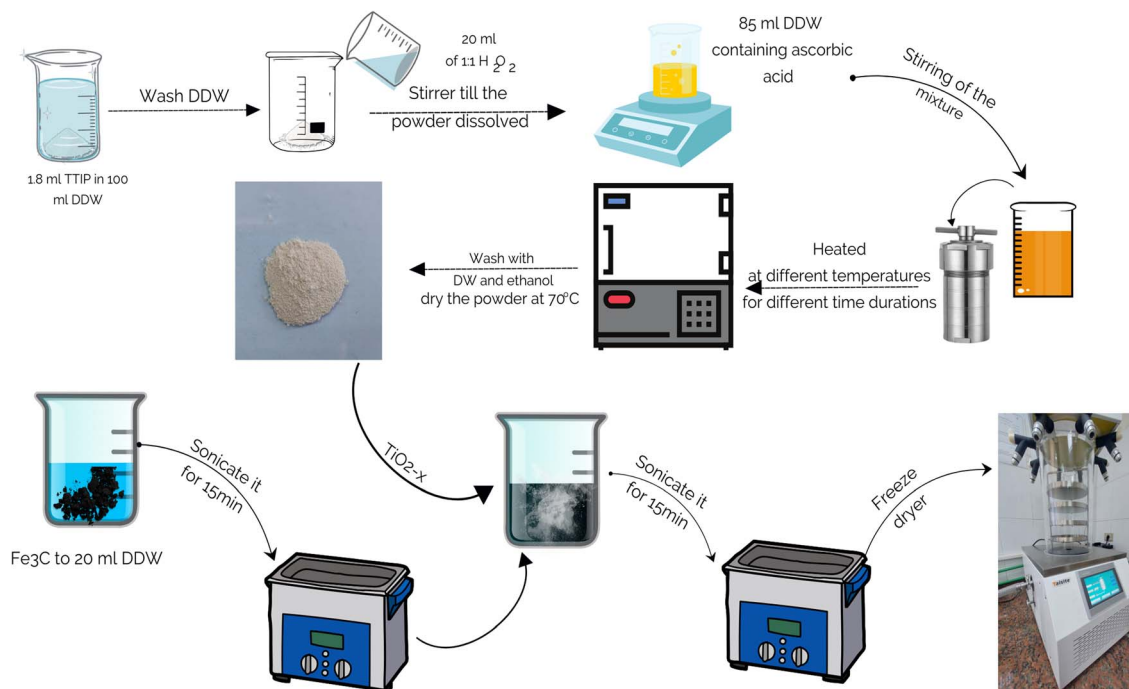


Fig. 1 Schematic preparation scheme of  $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4@\text{g-C}$ .

solar light in a batch system. A solar simulator (UVA CUBE 400, Dr Hönle AG UV Technology, Germany) equipped with a halogenide high-pressure lamp (model: SOL 500) was used for the photocatalytic experiments. This lamp emits radiation that simulates natural sunlight ( $1000 \text{ W m}^{-2}$ ) in a downward direction. 100 mL of phenol solution was mixed with an appropriate amount of the photocatalyst and irradiated using the solar simulator. At certain times, the samples were collected, filtered, and stored for analysis. An analogous procedure was applied for the reusability test, but the experiment was conducted for 7 h to ensure cleaning of the photocatalyst surface. Later, the photocatalyst was collected using an external magnetic field. The

collected powder was washed with DW and ethanol before using in the next experiment.

Phenol concentrations were analysed using a high-performance liquid chromatograph (HPLC, Agilent 1260, USA) based on the following conditions: 60 : 40 water and acetonitrile as isocratic eluent, 25 °C column temperature, and detection at 280 nm wavelength.

## 3. Results and discussion

### 3.1 Optimization of the pure photocatalyst

**3.1.1. Characteristics of the pristine and defective  $\text{TiO}_2$ .** X-ray diffraction (XRD) was used to investigate the effect of

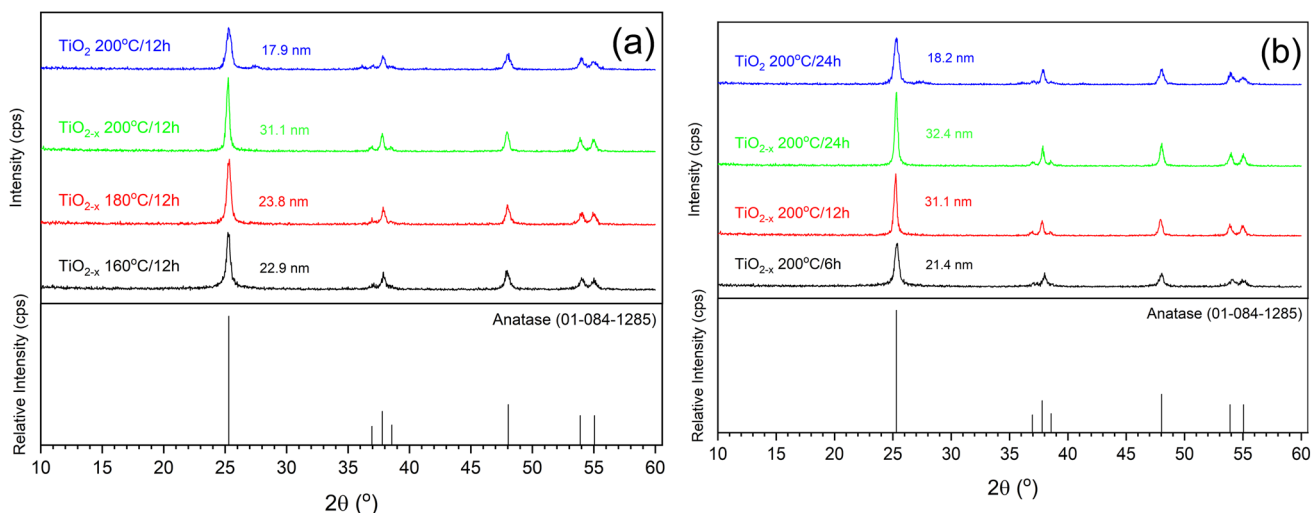


Fig. 2 XRD patterns of pure and defective  $\text{TiO}_2$  samples prepared at different (a) temperatures and (b) times.



hydrothermal conditions on the crystal structure of the as-prepared samples, as presented in Fig. 2. Generally, all the prepared materials exhibited diffraction peaks matching the (101), (103), (004), (112), (200), (105), (211) planes of anatase TiO<sub>2</sub> (ICDD no. 01-084-1285), without any additional diffraction peaks related to other phases, thus indicating the high purity of the prepared samples. According to the data in Fig. 2a, increasing the hydrothermal temperature resulted in an enhanced crystallinity of TiO<sub>2-x</sub>, as evidenced by the increasing peaks intensities and decreasing full-width half maxima of the peaks. Thus, 200 °C was chosen as the optimum temperature and was utilized to study the effect of the hydrothermal time. The patterns in Fig. 2b illustrate the growth of TiO<sub>2-x</sub> crystals with the time of the hydrothermal process. On comparing the crystallite sizes calculated using Scherrer equation,<sup>18</sup> it was found that both time and temperature of the hydrothermal process have a similar effect on the crystallinity of the produced material. The effect of ascorbic acid on the crystallinity could be

explored by comparing the XRD patterns of the samples prepared in the presence or absence of ascorbic acid under the same hydrothermal conditions (*i.e.*, pristine and defective TiO<sub>2-x</sub>). The addition of ascorbic acid enhanced the crystal size. Therefore, it can be deduced that the addition of ascorbic acid led to the formation of large defected crystals, as shown in TEM images. The same phenomenon was previously reported in the defective TiO<sub>2</sub> prepared using the same reducing agent.<sup>19,20</sup> It is worth mentioning that the hydrothermal time did not significantly affect the crystallinity of the pristine TiO<sub>2</sub> samples prepared in 12 h and 24 h (17.9 and 18.2 nm, respectively). This further highlights the effect of ascorbic acid on the crystallinity of titania crystals under different hydrothermal conditions.

The UV-vis diffuse reflectance (DRS) technique was used to evaluate the optical properties of the prepared samples. The absorption coefficients were calculated from the DRS spectra using the Kubelka-Munk equation,<sup>21</sup>  $\alpha = K/S = (1 - R)^2/2R$ , where  $K$  is the absorption coefficient,  $S$  is the scattering

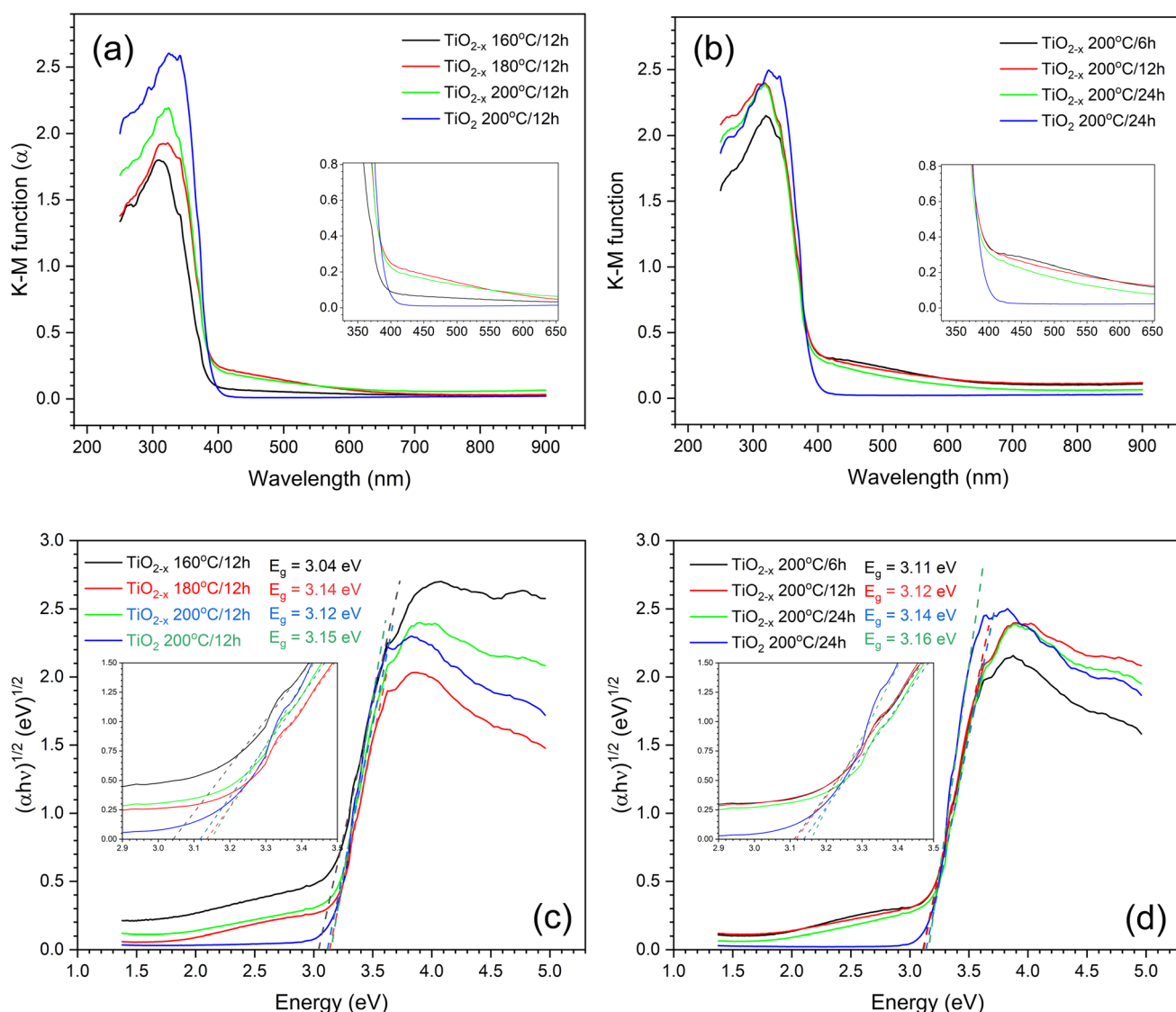


Fig. 3 (a and b) Transformations of the UV-vis DRS spectra, and (c and d) Tauc plot of TiO<sub>2</sub> prepared under different hydrothermal conditions.



coefficient, and  $R$  is the reflectance obtained from DRS. The calculated spectra are shown in Fig. 3a and b. Increasing the hydrothermal reaction time caused an increase in the absorptivity of the prepared samples either in UV or visible light range, which may be due to either the enhanced crystallinity of the samples, as previously observed by the XRD results, or the formation of more defects. Unfortunately, it was difficult to segregate the effects of grain size and self-doping under the studied conditions. The same obstacles were previously reported.<sup>22</sup> However, comparing the  $\text{TiO}_2$  and  $\text{TiO}_{2-x}$  prepared under the same conditions (*i.e.*, 200 °C/12 h) revealed that  $\text{TiO}_{2-x}$  exhibited better absorption in the visible light range, which can be due to the presence of defects that form a shallow donor level below the conduction band, thus narrowing the band gap.<sup>22</sup> This level originates from the Ti dangling bonds associated with the shortage of oxygen atoms.<sup>23</sup> Since  $\text{TiO}_{2-x}$  (200 °C) displayed the best absorption in both UV and visible light ranges, it was used to assess the variation in DRS with the hydrothermal time at this temperature, as shown in Fig. 3b. It is evident that the absorption of  $\text{TiO}_{2-x}$  samples slightly decreases with increasing time of hydrothermal treatment; nevertheless, all  $\text{TiO}_{2-x}$  still possess better absorption in the visible light region than the  $\text{TiO}_2$  sample. The Tauc plots presented in Fig. 3c and d support the shrinkage in the band-gap when using ascorbic acid under the investigated conditions. However, the calculated band-gaps do not follow the same order observed in the absorption spectra. This might be due to the incorrectness of the band-gap calculation using Tauc plots in the case of doped semiconductors, as previously reported.<sup>21</sup> To sum up, temperature plays a major role in governing the optical properties of the defective  $\text{TiO}_{2-x}$  rather than the time of the hydrothermal process.

PL spectra were measured to assess the recombination of the photogenerated electron-hole pairs. A lower fluorescence intensity implies the limited recombination of electrons and holes, which is beneficial to the photocatalytic performance because of the high number of free charges available for the photocatalytic reaction.<sup>24</sup> Fig. S1† shows the recorded PL spectra of  $\text{TiO}_2$  and  $\text{TiO}_{2-x}$  prepared under different hydrothermal conditions. Samples prepared using ascorbic acid (*i.e.*,  $\text{TiO}_{2-x}$ ) at any of the studied hydrothermal temperatures showed quenched PL intensities, as illustrated in Fig. S1a.† Specifically,  $\text{TiO}_{2-x}$  200 °C/12 h showed the lowest PL intensity, indicating that this sample possesses the lowest charge recombination and possibly the best photocatalytic performance. The study of the effect of hydrothermal time, presented in Fig. S1b,† shows that short hydrothermal time led to low PL intensity, while a longer time (*i.e.*, 24 h) resulted in a slightly higher PL intensity. However, it should be mentioned that the pristine  $\text{TiO}_2$ , prepared in the absence of ascorbic acid, still possesses the highest PL intensity, indicating the formation of new sublevels in the samples prepared using ascorbic acid due to the formed defects. Therefore, it can be deduced that although ascorbic acid enhanced the growth of  $\text{TiO}_2$  crystals, according to the XRD results, it caused a deformation of the formed crystals, as evidenced by the low PL intensities of the samples prepared in the presence of ascorbic acid.

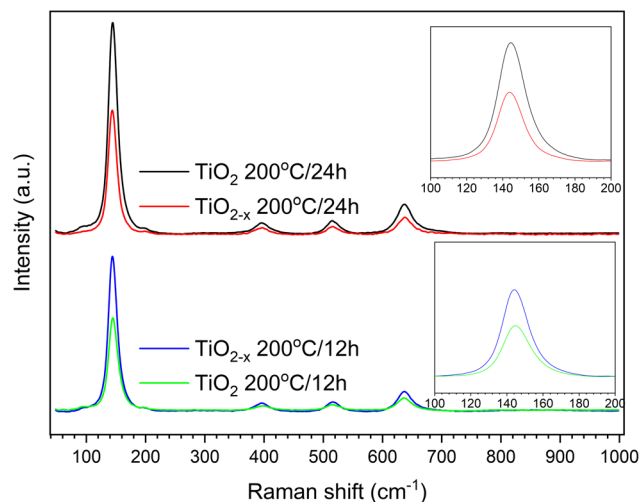


Fig. 4 Raman spectra of  $\text{TiO}_2$  and  $\text{TiO}_{2-x}$  prepared at 200 °C in 12 h and 24 h.

Another important analytical tool to determine the crystalline phases and any defects in them is Raman spectroscopy. As shown in Fig. 4, similar peaks appearing at 144  $\text{cm}^{-1}$ , 396  $\text{cm}^{-1}$ , 516  $\text{cm}^{-1}$  and 636  $\text{cm}^{-1}$  were observed in all the samples. These peaks can be assigned specifically to the  $E_g$ ,  $B_{1g}$ ,  $A_{1g}$ , and  $E_g$  vibrational modes in the anatase  $\text{TiO}_2$  crystal, as reported out by Wang *et al.*,<sup>25</sup> indicating the good purity of the prepared samples. This is consistent with the XRD results shown above. A deep investigation of the Raman spectra of the  $\text{TiO}_{2-x}$  samples indicated a lower peak intensity with a small shift toward a lower wavenumber relative to the pristine  $\text{TiO}_2$  sample that was hydrothermally treated for 24 h (insets of Fig. 4). This refers to the presence of surface disorder, as reported by Gu, Pan *et al.*,<sup>26</sup> enclosing localized defects that originated from the formation of  $\text{Ti}^{3+}$  (ref. 27) or oxygen vacancies (*i.e.*, Ti–Ov–Ti bonds).<sup>28</sup> On the contrary, the peaks of pristine  $\text{TiO}_2$  prepared in 12 h appeared at almost the same position as those of the corresponding defected sample  $\text{TiO}_{2-x}$  but with higher intensities. This shows that ascorbic acid enhanced the crystallization in a shorter time of hydrothermal treatment rather than the formation of defects in the growing crystals. This speculation is also supported by the measured crystallite sizes shown in Fig. 2 (*i.e.*, 31.1 nm and 17.9 nm for  $\text{TiO}_{2-x}$  200 °C/12 h and  $\text{TiO}_2$  200 °C/12 h, respectively). Therefore, it can be deduced that the role of ascorbic acid varies according to the hydrothermal time; it mainly supports the crystal growth during a short hydrothermal time, then deforms the formed crystals on increasing the hydrothermal time.

In order to support the previous speculation, the morphology of  $\text{TiO}_2$  200 °C/12 h,  $\text{TiO}_2$  200 °C/24 h,  $\text{TiO}_{2-x}$  200 °C/12 h and  $\text{TiO}_{2-x}$  200 °C/24 h was imaged under TEM, as shown in Fig. 5. Generally, all samples are composed of nanoparticles (*i.e.*, particle size < 100 nm). For short hydrothermal time,  $\text{TiO}_2$  200 °C/12 h shows mostly ~22 nm cuboid particles, as depicted in Fig. 5a. However, the TEM image for  $\text{TiO}_{2-x}$  200 °C/12 h in Fig. 5b illustrated that adding ascorbic acid deformed the crystals during their growth, leading to the formation of



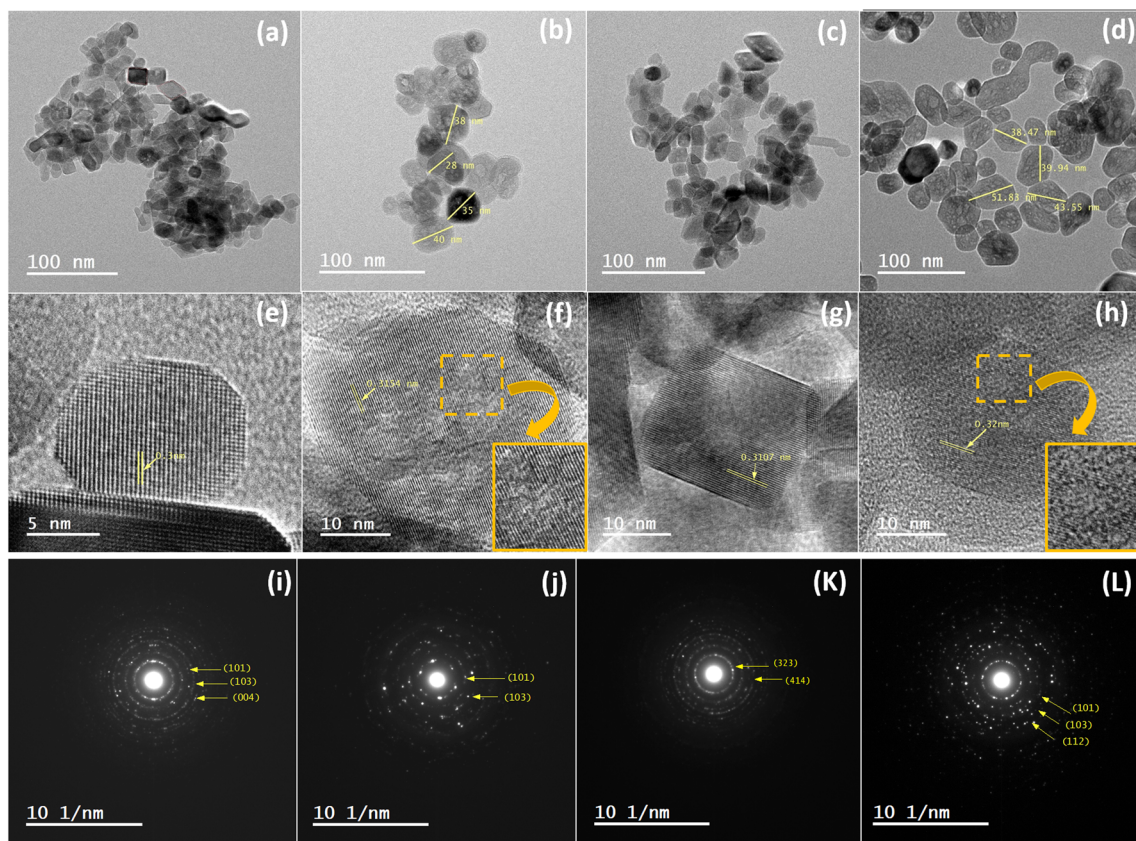


Fig. 5 TEM images of  $\text{TiO}_2$  and  $\text{TiO}_{2-x}$  samples: (a, e and i)  $\text{TiO}_2$  200 °C/12 h, (b, f and j)  $\text{TiO}_{2-x}$  200 °C/12 h, (c, g and k)  $\text{TiO}_2$  200 °C/24 h and (d, h and l)  $\text{TiO}_{2-x}$  200 °C/24 h.

irregular nanoparticles. Furthermore, ascorbic acid increased the particle size to  $\sim 35$  nm, which is nearly 1.6 times that of the pristine  $\text{TiO}_2$  200 °C/12 h sample. The  $\text{TiO}_2$  200 °C/24 h sample prepared at a longer hydrothermal time (24 h) constitutes a well-defined cuboid of 22 nm size, which is nearly the same as  $\text{TiO}_2$  200 °C/12 h (Fig. 5c). This observation is in line with the XRD

analyses shown in Fig. 2. The TEM image of the  $\text{TiO}_{2-x}$  200 °C/24 h sample in Fig. 5d also shows a larger deformed nanoparticle, with an average size of  $\sim 44$  nm, than its control sample (*i.e.*,  $\text{TiO}_2$  200 °C/24 h) and the defected sample prepared at a shorter hydrothermal time (*i.e.*,  $\text{TiO}_{2-x}$  200 °C/12 h). The increase in the particle size may be due to the ascorbic acid

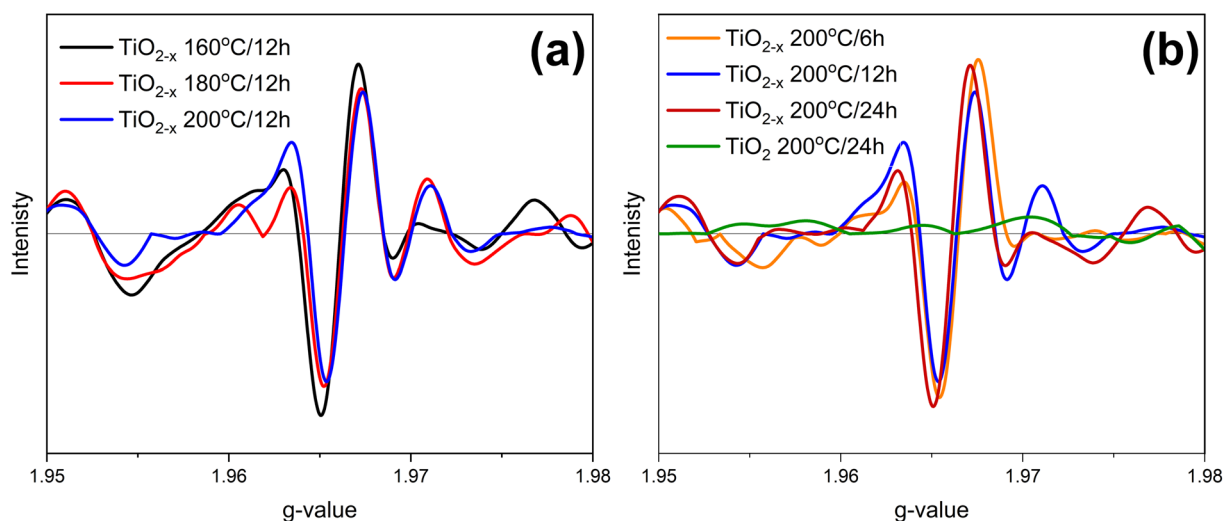


Fig. 6 EPR spectra of the prepared samples; effects of (a) temperature and (b) time.

effect and elongated hydrothermal time. It is worth mentioning that the measured particle sizes are consistent with the sizes calculated from the XRD patterns.

Fig. 5e–h shows the lattice spacing of  $\text{TiO}_2$  200 °C/12 h,  $\text{TiO}_{2-x}$  200 °C/12 h,  $\text{TiO}_2$  200 °C/24 h, and  $\text{TiO}_{2-x}$  200 °C/24 h samples with values of 0.3, 0.315, 0.3107 and 0.32 nm, respectively, corresponding to the interplanar crystal spacing of the (101) plane. Generally, the selected area electron diffractions of the whole samples show strong dotted-rings diffraction pattern, referring to the polycrystalline nature of these samples. The identified planes from the SAED pattern were (101), (103) and (004) in case of  $\text{TiO}_2$  200 °C/12 h, (101) and (103) in case of  $\text{TiO}_{2-x}$  200 °C/12 h, (101) and (112) in case of  $\text{TiO}_2$  200 °C/24 h, and (101), (103) and (112) in case of  $\text{TiO}_{2-x}$  200 °C/24 h. All of these planes are characteristic for the anatase crystals, indicating the high purity of the prepared samples.

EPR spectroscopy was used to identify the defect type, *i.e.*,  $\text{Ti}^{3+}$  or oxygen vacancies, in the prepared samples. The collected EPR spectra are elucidated in Fig. 6.  $\text{TiO}_2$  200 °C/24 h shows an insignificant EPR signal due to the diamagnetic nature of  $\text{TiO}_2$ . On the other hand, all the prepared samples exhibited a strong signal at  $g \sim 1.966$ , revealing the presence of  $\text{Ti}^{3+}$ , as previously reported by Zhang *et al.*<sup>29</sup> However, it was difficult to determine which sample has more defects because the differences in the signal intensities are insignificant. Therefore, it can be concluded that  $\text{Ti}^{3+}$  is the major defect caused by ascorbic acid. This result is consistent with the previously reported research.<sup>30</sup>

XPS technique was used to shed light on the components, chemical states of the elements, and nature of the defects in the prepared materials. The high-resolution XPS spectra of the detected elements are presented in Fig. 7. According to the full-scan data presented in Fig. 7a, three elements, namely, carbon,

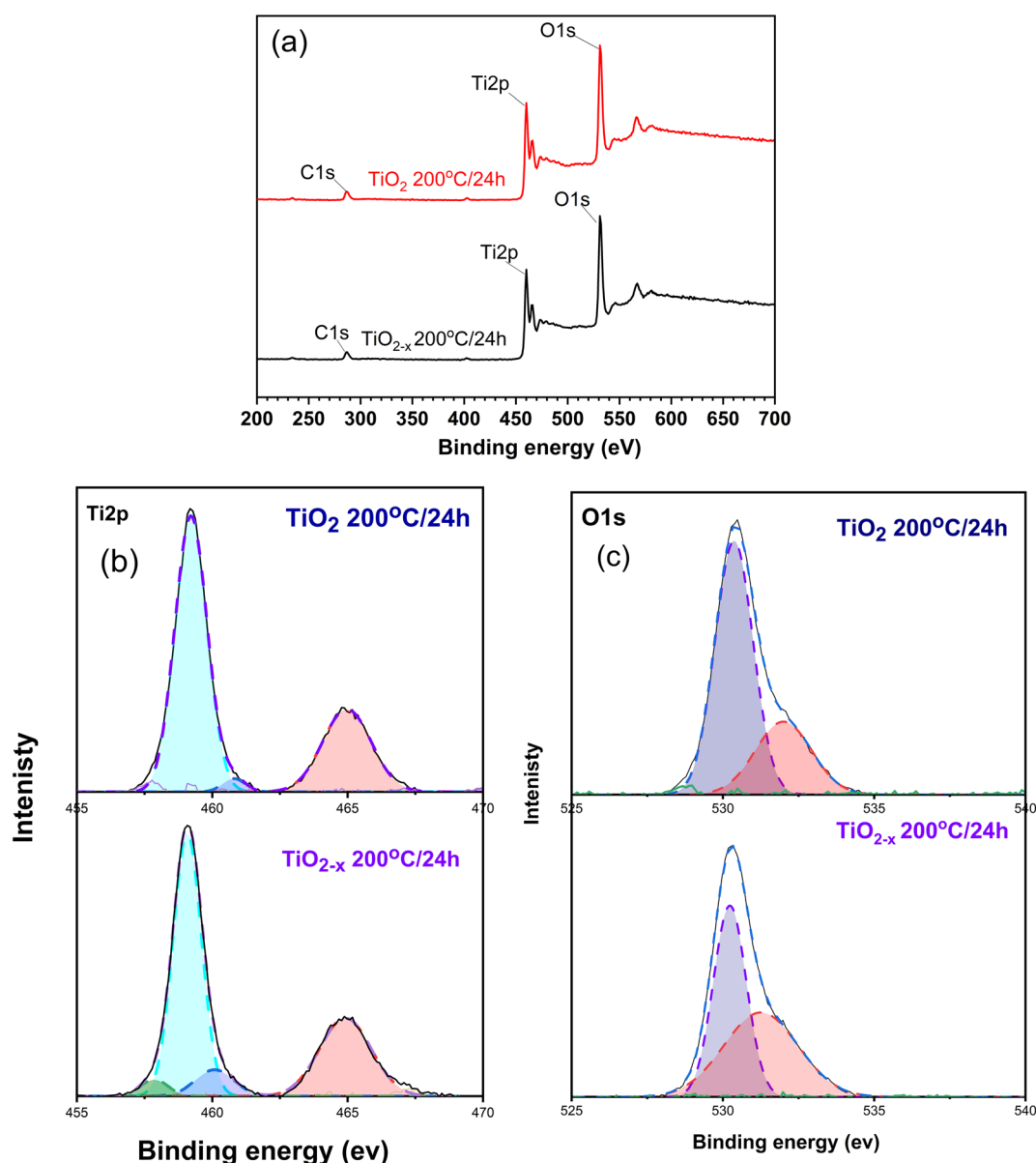


Fig. 7 XPS spectra of the prepared samples; (a) full scan and (b and c) deconvoluted spectra of Ti and O elements.





oxygen, and titanium, could be recognized in the spectra of all the samples. The peak of carbon (*i.e.*, C 1s) at 284.6 eV is probably due to the contamination by atmospheric carbon during sample preparation.<sup>31</sup>

Fig. 7b displays the Ti 2p peaks of the intact and defective TiO<sub>2</sub> prepared at 200 °C for 24 h under the hydrothermal conditions. The intact sample (*i.e.*, TiO<sub>2</sub>) showed two peaks at 459.19 and 464.89 eV corresponding to the Ti<sup>4+</sup> 2p<sub>3/2</sub> and Ti<sup>4+</sup> 2p<sub>1/2</sub> states, respectively.<sup>32</sup> These peaks were shifted to lower binding energies in the defective sample (TiO<sub>2-x</sub>), *i.e.*, 459.09 and 464.74 eV, respectively. This suggests the formation of Ti<sup>3+</sup> defects in this sample. Deconvoluting the two major peaks revealed the presence of a peak at 460.8 eV corresponding to Ti<sup>3+</sup> in Ti<sub>2</sub>O<sub>3</sub>. This indicates that both TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub> are formed in the prepared samples but with different intensities; in TiO<sub>2-x</sub> 200 °C/24 h, the peak intensity is more than TiO<sub>2</sub> 200 °C/24 h by 4 times, indicating the presence of more defects. Deconvoluting the peak at 459.09 eV in case of the TiO<sub>2-x</sub> 200 °C/24 h sample showed a new peak at 457.7 eV, which confirms the formation of Ti<sup>3+</sup>.<sup>33</sup>

The high resolution XPS spectrum of O 1s in Fig. 7c depicts two peaks centred at 530.36 and 531.2 eV for the TiO<sub>2</sub> 200 °C/24 h sample. These peaks are representative for the Ti–O–Ti and surface –OH species, respectively, as previously reported.<sup>34</sup> On the other hand, the shift of the peak at 530.2 eV in TiO<sub>2-x</sub> 200 °C/24 h originates from the formation of the oxygen vacancy near the Ti<sup>3+</sup>, according to ref. 32. Furthermore, the increase in the peak at 531.2 eV indicates the formation of oxygen vacancy, as mentioned by ref. 35.

**3.1.2. Performance of the pristine and defective TiO<sub>2</sub>.** In the beginning, the photocatalytic performances of the pure pristine and defective TiO<sub>2</sub> (TiO<sub>2-x</sub>) prepared under different hydrothermal conditions (temperature = 160, 180, and 200 °C; time = 6, 12, and 24 h) were assessed in terms of the removal of phenol under solar light. Generally, the non-linear fitting of the collected data, with the coefficient of determination (*R*<sup>2</sup>) ranging from 0.884 to 0.998 and chi-square (*χ*<sup>2</sup>) values between

1.53 × 10<sup>-4</sup> and 1.18 × 10<sup>-2</sup>, revealed good adherence to the first-order kinetics, as shown in Fig. 8a. The calculated first-order rate constants for each material were compared in Fig. 8b in order to assess the effect of preparation conditions on the photocatalytic process. It has been shown that increasing the hydrothermal time enhanced the activity in general. Similarly, the increased hydrothermal temperature had a positive effect on the photocatalytic activity. These observations are in line with the enhanced crystallinity and optical properties, as referred previously. Interestingly, the defected TiO<sub>2-x</sub> showed a significantly improved photocatalytic activity relative to pristine TiO<sub>2</sub> because it consists of large deformed particles, which resulted in better charge separation, as evidenced by TEM and PL analyses shown above. Based on the findings in Fig. 8b, it is evident that the degradation rate of phenol is higher using TiO<sub>2-x</sub> 200 °C/24 h compared to TiO<sub>2-x</sub> 200 °C/12 h. This might be attributed to the formation of massive defects in TiO<sub>2-x</sub> 200 °C/12 h,<sup>36</sup> which might hinder the formation of a reasonable number of charge carriers. On the other hand, when it comes to TiO<sub>2-x</sub> 200 °C/24 h, the increase in the hydrothermal time helped in the formation of larger crystal size, which played a crucial role in the enhanced degradation of phenol.

## 3.2 Optimization of the magnetic composite

**3.2.1. Characteristics of the magnetic composite.** Based on the characteristics and performance of the pristine and defective TiO<sub>2</sub>, it was obvious that the TiO<sub>2-x</sub> sample prepared under the hydrothermal conditions at 200 °C/24 h exhibits the best performance. Thus, it was decided to merge this sample in different ratios with the magnetic component Fe<sub>3</sub>O<sub>4</sub>. The XRD patterns of the pure magnetic component and the prepared composites are illustrated in Fig. S2.† The pure magnetic component pattern shows diffraction peaks at 2θ = 30.31°, 35.6°, 43.3°, 53.7° and 57.13°, which can be ascribed to the (311), (220), (400), (422), and (511) diffraction planes, respectively, for the magnetite (Fe<sub>3</sub>O<sub>4</sub>) phase (ICDD no. 01-088-0315).

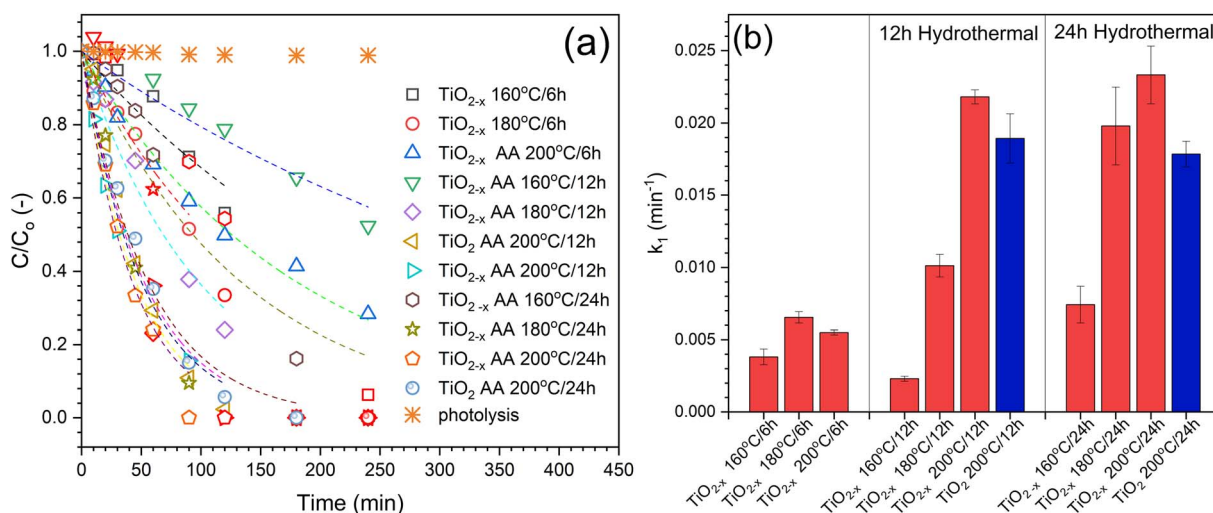


Fig. 8 Photocatalytic degradation of phenol using pristine and defective TiO<sub>2</sub> prepared at different hydrothermal conditions. (a) Experimental data with 1st order kinetics fitting, and (b) comparison of the calculated rate constants [100 mg per L catalyst, 10 mg per L phenol, and natural pH].





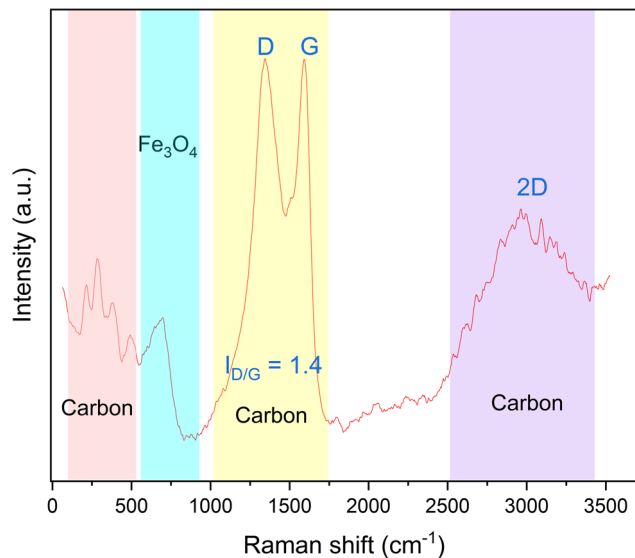


Fig. 9 Raman spectra of the prepared magnetic component.

All the composite samples displayed the peaks of the  $\text{Fe}_3\text{O}_4$  phase along with the peaks relevant to the  $\text{TiO}_2$  anatase phase (ICDD no. 01-084-1285). This suggests the successful formation of the magnetic photoactive composites. It is worth mentioning that the difference in the peak intensities between  $\text{Fe}_3\text{O}_4$  and  $\text{TiO}_2$  were varied according to the mixing ratio between the two components. This is another evidence of the effective binding between the two components because magnetic recovery was done during the washing of the prepared composites.

Although XRD analysis suggested the formation of the  $\text{Fe}_3\text{O}_4$  phase, it is possible to have maghemite ( $\text{Fe}_2\text{O}_3$ ) also in our sample since the two phases, *i.e.*,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ , possess superimposed XRD peaks. Raman spectroscopy has been widely used to differentiate the iron oxides, especially magnetite and maghemite. The representative Raman spectrum of the synthesized magnetic material is presented in Fig. 9. The broadband at  $688\text{ cm}^{-1}$  can be assigned to the  $\text{A}_{1g}$  transition of magnetite.<sup>37</sup> According to Chen *et al.*,<sup>38</sup> the two strong peaks at  $1345\text{ cm}^{-1}$  and  $1593\text{ cm}^{-1}$  refer to the D and G modes of

graphitic carbon, respectively, and the ratio between the area under the peak of those peaks (*i.e.*,  $I_{D/G}$ ) is used as a measurement of the relative degree of disorder in the carbonaceous materials.  $I_{D/G}$  was found to be 1.4, which is higher than unity, indicating the presence of a substantial graphitization degree and a high  $\text{sp}^2$  content in the formed carbon.<sup>17,39</sup> Moreover, there are low frequency bands in the range of  $200\text{--}500\text{ cm}^{-1}$ , which correspond to P1, P2, P3 and P4, whose peaks appear in case of glassy carbon, as mentioned by Jurkiewicz and co-workers.<sup>17</sup> Additionally, there is an overtone broad peak at  $2500\text{--}3450\text{ cm}^{-1}$ . The deconvolution of this peak showed two bands at approximately  $2670\text{ cm}^{-1}$  and  $3000\text{ cm}^{-1}$  corresponding to the 2D bands in glassy carbon.<sup>40</sup> To sum up, the magnetic component prepared in this study consists of  $\text{Fe}_3\text{O}_4$  with glassy carbon.

The morphology of the pure magnetic component and the prepared composites were visualized in the TEM images depicted in Fig. 10. From Fig. 10a, it can be seen that the magnetic component is composed of irregular nanoparticles with an average size of  $\sim 13.5\text{ nm}$ , covered with a glassy carbon sheet. The lattice spacing of the observed nanoparticles is  $1.859\text{ nm}$ , which is corresponding to the interplanar crystal spacing of the (331) plane of  $\text{Fe}_3\text{O}_4$ . These observations demonstrate that the prepared magnetic component is  $\text{Fe}_3\text{O}_4@g\text{-C}$ . The inset selected area electron diffraction (SAED) image shows blurry dotted rings, indicating the polycrystalline nature of this samples. The successful formation of the  $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4@g\text{-C}$  composite was confirmed according to the images in Fig. 10b and c. In these images, both  $\text{Fe}_3\text{O}_4@g\text{-C}$  and  $\text{TiO}_{2-x}$  crystals could be clearly recognized, and their abundance is relatively consistent with the added amounts. Furthermore, the inset images of SAED in Fig. 10b and c belonging to the  $\text{TiO}_{2-x}$  crystals showed very strong diffraction patterns due to the good crystallinity of  $\text{TiO}_{2-x}$ , unlike the vague SAED of  $\text{Fe}_3\text{O}_4@g\text{-C}$ . This disparity arises from the carbon cover on  $\text{Fe}_3\text{O}_4$ , whereas the  $\text{TiO}_{2-x}$  crystals are naked.

The magnetic properties of the prepared materials were assessed using VSM analysis, as shown in Fig. 11. The  $\text{Fe}_3\text{O}_4@g\text{-C}$  sample showed the desired superparamagnetic behaviour, *i.e.*, of  $55\text{ emu g}^{-1}$  magnetization saturation ( $M_s$ ) with low

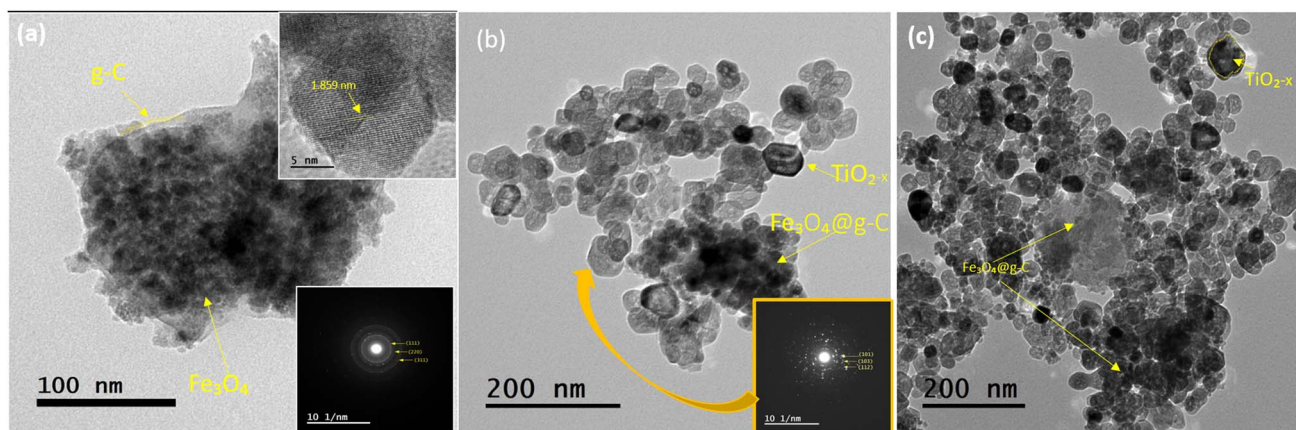


Fig. 10 TEM images of (a)  $\text{Fe}_3\text{O}_4@g\text{-C}$  and (b)  $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4@g\text{-C}$  200 °C/24 h 1 : 1 and (c)  $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4@g\text{-C}$  200 °C/24 h 4 : 1.



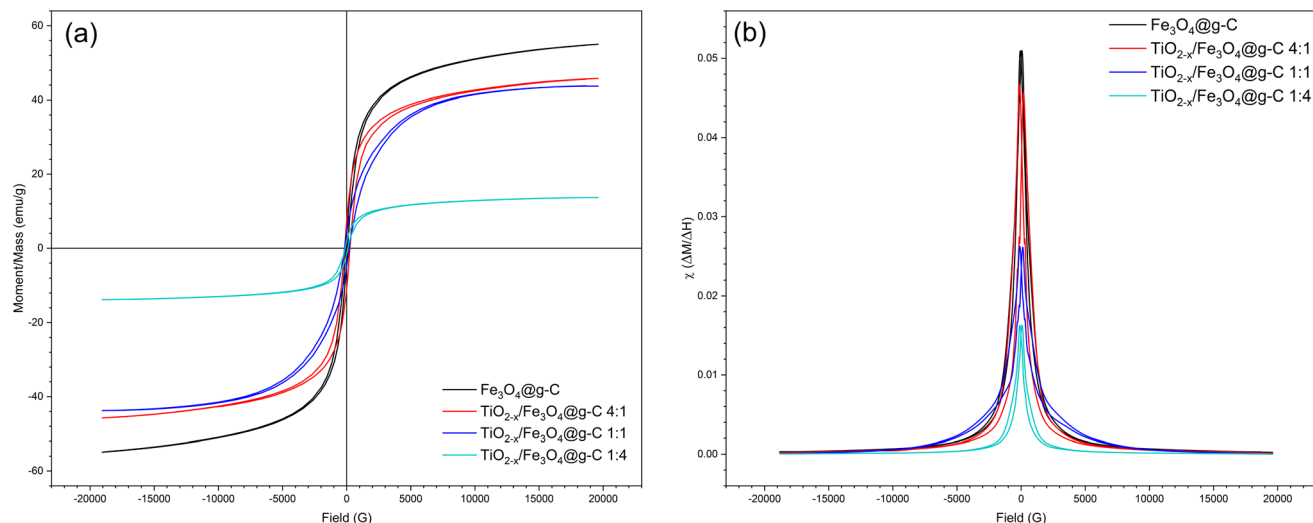


Fig. 11 (a) VSM hysteresis loops and (b) magnetic susceptibility of the pure  $\text{Fe}_3\text{O}_4$ @g-C and  $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4$ @g-C composite of different ratios.

coercivity ( $H_c$ ) and retentivity ( $M_r$ ) (Fig. 11a). As expected, the sample with more  $\text{Fe}_3\text{O}_4$ @g-C content showed high saturation magnetization ( $M_s$ ), whereas the samples containing more  $\text{TiO}_{2-x}$  content showed low saturation magnetization ( $M_s$ ). However, all the samples possess superparamagnetic behaviour, enabling fast magnetization under the effect of an external magnetic field and good dispersion in its absence.

Another evidence of the good magnetic behaviours of the prepared samples were deduced from their magnetic susceptibility ( $\chi$ ), as shown in Fig. 11b, since  $\chi$  is a measure of the response of a material to an applied magnetic field. The calculated  $\chi$  values for the prepared samples fall within the range  $>10^{-2}$  to  $\sim 10^5$ , which is characteristic of superparamagnetic materials, as reported by Frennea-Robin and Marchalot (2022).<sup>41</sup> As shown in Fig. 11b, the  $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4$ @g-C 4:1 sample exhibited  $\chi$  close to that of  $\text{Fe}_3\text{O}_4$ @g-C due to the high content of  $\text{Fe}_3\text{O}_4$  in this sample. Though the higher  $\text{TiO}_{2-x}$  content (four times) decreases the  $\chi$  value because of the increasing amount of non-magnetic component in the composite, this sample exhibits good susceptibility to an external magnetic field. To sum up, the prepared composites showed excellent magnetic properties, qualifying their application as magnetically recoverable photocatalysts.

The chemical composition and binding energies of the  $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4$ @g-C composite was examined by XPS. Full scan revealed the presence of Fe, O, Ti and C elements in this sample, as evidenced by the appearance of peaks at 713.26, 531.83, 460.09 and 286.5 eV corresponding to the Fe 2p, O 1s, Ti 2p, and C 1s energy states, respectively, as shown in Fig. 12a.

In the Ti 2p spectra illustrated in Fig. 12b, the sample revealed two peaks of  $\text{Ti}^{4+}$  2p<sub>3/2</sub> and  $\text{Ti}^{4+}$  2p<sub>1/2</sub> at 459.22 and 464.81 eV, respectively. As discussed above in the corresponding pure  $\text{TiO}_{2-x}$  sample, the Ti 2p peaks shifted to a lower binding energy relative to the pristine  $\text{TiO}_2$ , demonstrating the formation of  $\text{Ti}^{3+}$  ions. The deconvolution of the peak at 459.22 eV demonstrated a peak at 457.7 eV, which further confirms the

presence of the  $\text{Ti}^{3+}$  defect. The peak at 460 eV is also an indication of  $\text{Ti}^{3+}$ . The increase in this peak intensity compared to  $\text{TiO}_{2-x}$  is attributed to the formation of new bonds between Fe–O–Ti and Ti–O–C.<sup>32</sup> Thereby, the method used for synthesising the magnetic composite, *i.e.*,  $\text{Fe}_3\text{O}_4$ @g-C/ $\text{TiO}_{2-x}$ , did not affect the defect in the  $\text{TiO}_2$  crystals, and it is expected not to affect the photocatalytic activity.

The O 1s spectrum in Fig. 12c resulted in three peaks: the broad band centred at 530.28 eV that can be assigned to Ti–O, Fe–O and Fe–O–Ti bonds,<sup>42</sup> the peak at 533.29 eV can be attributed to the surface C–O bond,<sup>43</sup> and the peak at 531 eV is due to the formation of Fe–O–C.<sup>43</sup> The formation of Fe–O–C bonds is evidence of the strong binding between  $\text{Fe}_3\text{O}_4$ @g-C and  $\text{TiO}_{2-x}$  in the composite, which guarantee the stability of the composite during the treatment and reuse processes.

Fig. 12d depicts the characteristic peaks of Fe 2p at 711.03 and 724.13 eV, which can be assigned to the spin–orbit peaks of Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub>, which is in good agreement with the previously published literature.<sup>42</sup> Two satellite signals of the Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> peaks were observed at the same time, which can be attributed to the oxidation states of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in  $\text{Fe}_3\text{O}_4$  nanoparticles.<sup>44</sup>

The high-resolution C 1s spectrum in Fig. 12e was deconvoluted into four peaks. The peaks at 284.8 and 286.1 eV can be ascribed to C=C and C–C, respectively, which is an indication of the graphitic structure of glassy carbon, and the peak at 290 eV is ascribed to the presence of the carboxylate carbon.<sup>39</sup> There is another peak at 289.1 eV, which is due to the formation of the Ti–O–C bond.<sup>45</sup> The formation of the Ti–O–C bond is another evidence of the strong linkage inside the composite  $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4$ @g-C.

### 3.3 Performance of $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4$ @g-C

The different composite formulations were investigated for the photocatalytic degradation of phenol in order to determine the



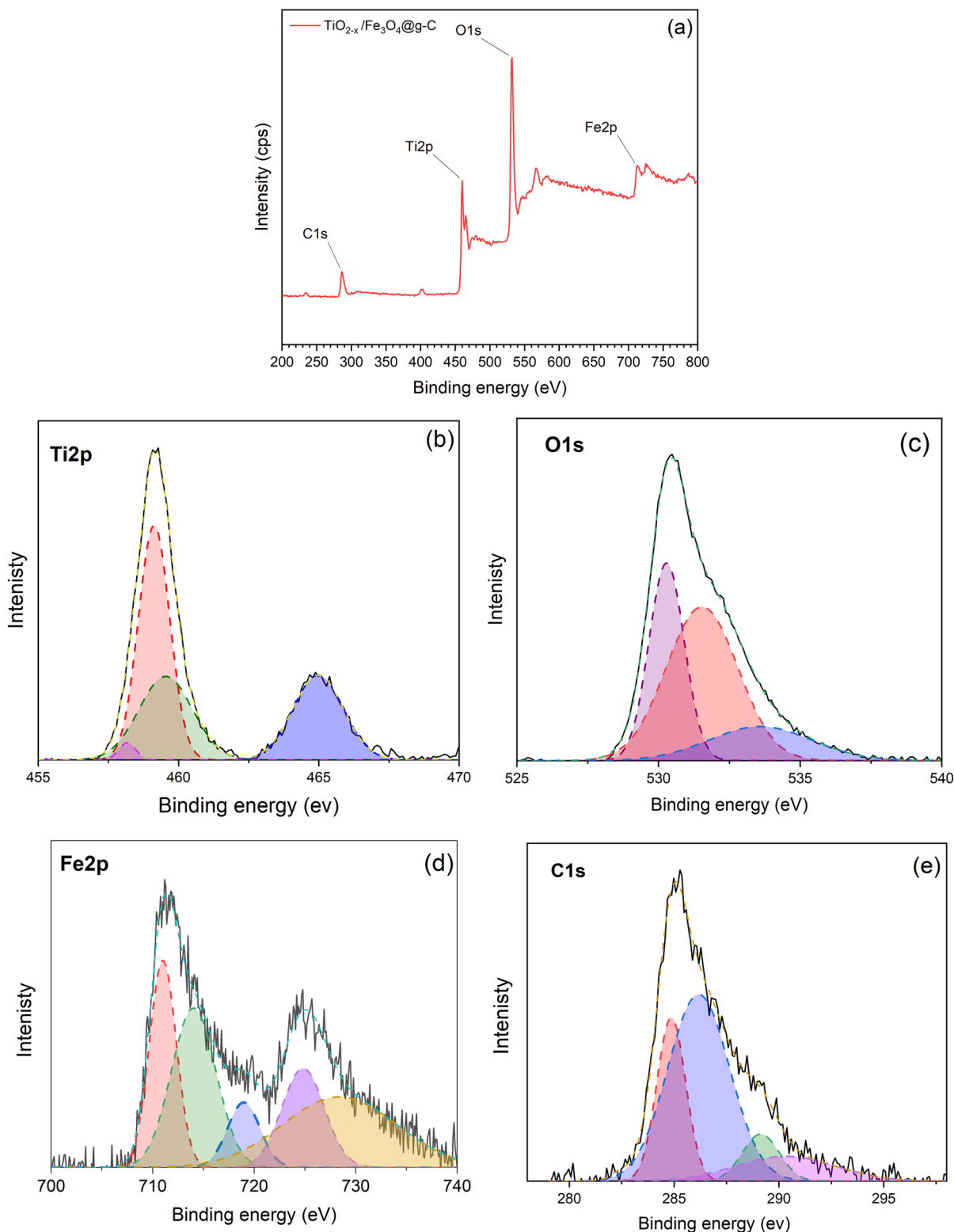


Fig. 12 XPS spectra of the  $\text{TiO}_{2-x}/\text{Fe}_3\text{O}_4/\text{g-C}$  1:1 composite; (a) full scan spectrum, (b) Ti 2p, (c) O 1s, (d) Fe 2p and (e) C 1s spectra.

best formulation. The time-dependent photocatalytic data is illustrated in Fig. 13a. Generally, the photocatalytic processes using the prepared samples followed the first-order kinetics. However, these observations are not accurate because the

prepared composites contain different amounts of the photoactive component, *i.e.*,  $\text{TiO}_{2-x}$ . Therefore, the  $\text{TiO}_{2-x}$  content in each composite sample was determined using the ICP technique (Fig. 13c) in order to calculate the activity precisely. There



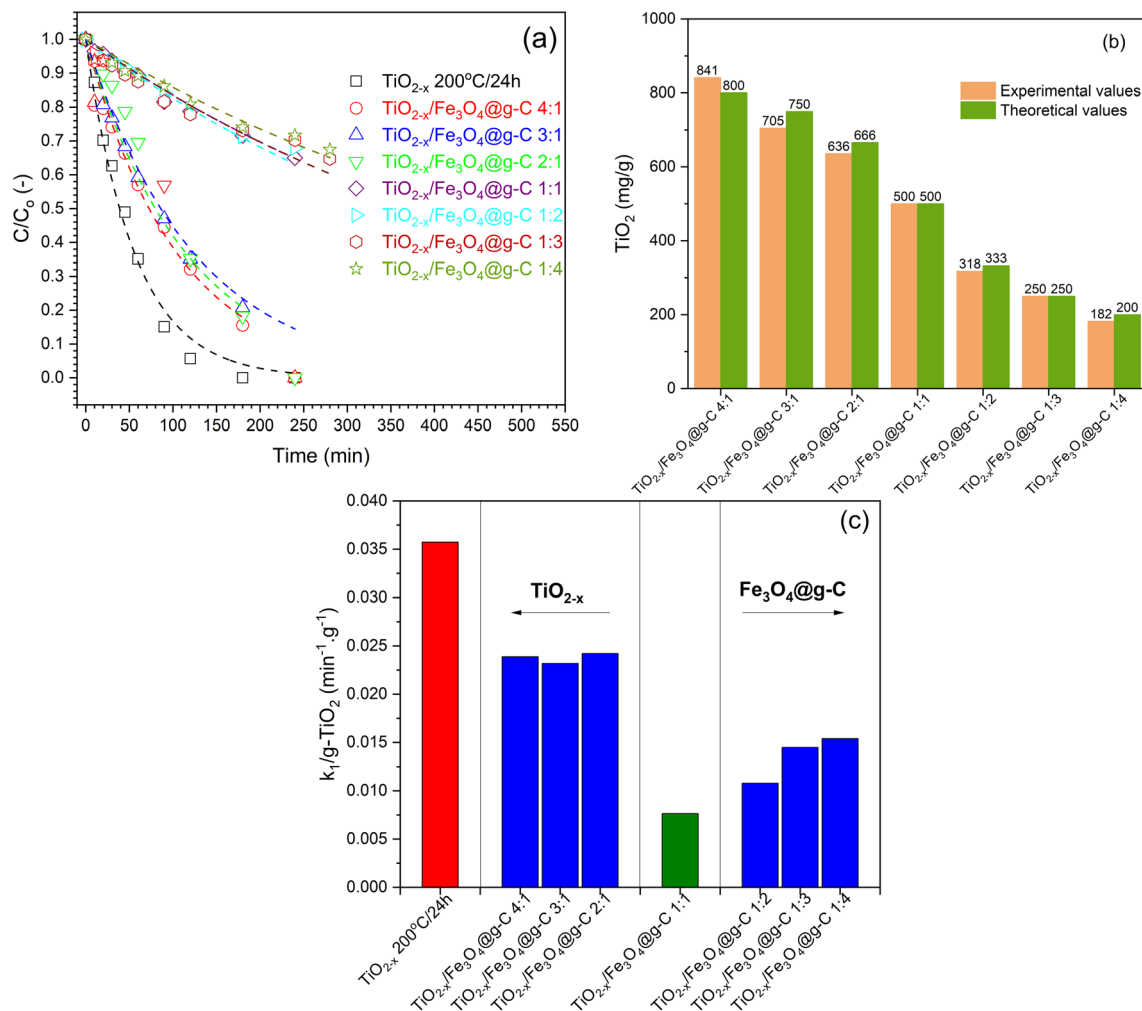


Fig. 13 (a) Experimental data of phenol photocatalytic degradation with 1st order kinetics fitting, (b) ICP analysis of TiO<sub>2</sub> content in the prepared samples, (c) corrected rate constants based on the TiO<sub>2</sub> content.

was no significant difference between the experimental and calculated values of the TiO<sub>2-x</sub> amount, indicating the efficiency of the method used to obtain the TiO<sub>2-x</sub>:Fe<sub>3</sub>O<sub>4</sub>@g-C composite. After correcting the obtained  $k_1$  values based on the TiO<sub>2-x</sub> amount in each sample, the calculated first-order rate constants ( $k_1$ ) are compared in Fig. 13c to compare the activities of the prepared samples. It has been realized that the higher ratio of TiO<sub>2-x</sub> led to better activity, which is more logical due to the addition of more photoactive sites to the system. In addition, the higher ratio of TiO<sub>2-x</sub> allowed the contact of TiO<sub>2-x</sub> with the glassy carbon in Fe<sub>3</sub>O<sub>4</sub>@g-C, which is responsible for the efficient separation of the photo-generated charges in TiO<sub>2-x</sub>, as previously reported.<sup>17</sup> On the contrary, increasing the TiO<sub>2-x</sub>:Fe<sub>3</sub>O<sub>4</sub>@g-C more than 1:1 did not enhance the photocatalytic process because the excess Fe<sub>3</sub>O<sub>4</sub>@g-C will not be in contact with TiO<sub>2-x</sub>. Therefore, the TiO<sub>2-x</sub>:Fe<sub>3</sub>O<sub>4</sub>@g-C composites of 1:2 and 4:1 ratios are the formulations that result in the best photocatalytic activity.

Phenol photodegradation using TiO<sub>2-x</sub>/Fe<sub>3</sub>O<sub>4</sub>@g-C as the catalyst is schematically illustrated in Fig. 14. The characterization results above revealed the formation of defects in the

catalyst due to the increase in the hydrothermal condition. As a result, the trap state energy levels are formed within the band-gap of TiO<sub>2-x</sub>. The presence of the defects is known to strengthen the absorption in both UV and visible light regions. In addition, Ti<sup>3+</sup> can act also as hole traps to suppress the recombination with the electron. In addition, the presence of glassy carbon helps in decreasing the charge carriers recombination,<sup>17</sup> leading to overall improved photocatalytic activity towards the phenol degradation.<sup>46</sup> On the other hand, the applicability of the Langmuir-Hinshelwood (L-H) model to the photodegradation results (see Fig. S3†) suggests the adsorption of phenol on the photocatalyst surface before being decomposed photocatalytically. Finally, the formed radicals react with the adsorbed phenol on the surface and degrade it.

The ultimate goal of synthesizing a magnetically recoverable photocatalyst is to reuse it several times. Thus, the two best formulations were used in photocatalytic phenol removal several times. The photocatalysts were recovered magnetically and then introduced in the next experiment. Fig. 15 shows the variation in the phenol removal efficiency from one experiment to another. The efficiency decreased after the second





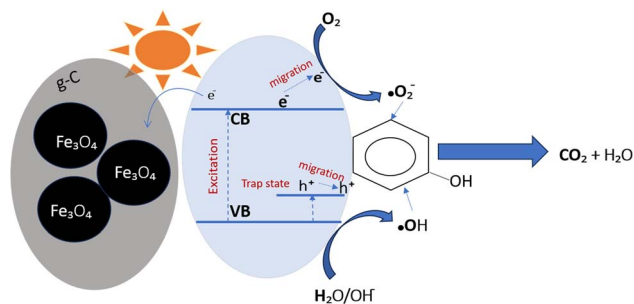


Fig. 14 Photocatalytic mechanism.

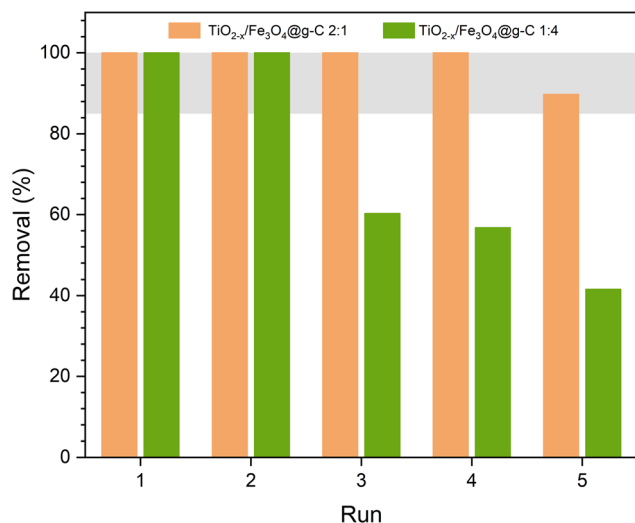


Fig. 15 Reusability of the best samples.

experiment when using the TiO<sub>2-x</sub>:Fe<sub>3</sub>O<sub>4</sub>@g-C 1:4 composite. According to Fig. 13a, the rate of phenol degradation in this case is low, leading to the incomplete degradation of phenol within 4 h. In order to ensure that phenol was completely degraded, the reusability test was extended to 7 h. Although this duration was efficient for complete phenol degradation, it caused an accumulation of the formed by-product on the catalyst surface even after washing the catalyst with DW and ethanol. Overall, the removal percentage decreased from one run to the next. On the contrary, the TiO<sub>2-x</sub>:Fe<sub>3</sub>O<sub>4</sub>@g-C 2:1 composite showed an excellent stable performance, revealing the stability of the composite. As its rate of degradation was high according to Fig. 13a, it caused the complete degradation of phenol in 4 h, making 7 h enough to degrade all the by-products and clean the catalyst surface.

## 4. Conclusion

Defective TiO<sub>2-x</sub> was successfully prepared under different temperature and time conditions following a hydrothermal method. The formation of the anatase phase was demonstrated in the prepared samples. The formation of the defects was also confirmed. TiO<sub>2-x</sub> 200 °C/12 h and TiO<sub>2-x</sub> 200 °C/24 h samples showed a significant degree of defects; however, in case of

TiO<sub>2-x</sub> 200 °C/12 h, the formation of massive defects negatively affects its performance. On the other hand, TiO<sub>2-x</sub> 200 °C/24 h showed the better removal of phenol. This could be attributed to the formation of defects and enhanced crystal growth that occurred on increasing the hydrothermal time. The defective composite TiO<sub>2-x</sub>/Fe<sub>3</sub>O<sub>4</sub>@g-C 200 °C/24 h was successfully prepared. The formation of chemical bonding between the two components was revealed by XPS analysis. Setting the ratio between Fe<sub>3</sub>O<sub>4</sub>@g-C and TiO<sub>2-x</sub> at 1:2 and 4:1 resulted in the best photocatalytic performance. However, the reusability test shows more degradation stability of the 1:2 ratio even after 5 runs.

## Data availability

All data generated or analysed during this study are included in this article.

## Conflicts of interest

There are no conflicts to declare.

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