A practical method for incorporation of Fe (III) in Titania matrix for photocatalytic applications

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Abstract
The unprecedented catalytic role of Iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O) has been explored in a top-down technique for the synthesis and Iron (III) doping of Titanium dioxide nanoparticles (TiO₂-NPs). In the experimental procedure, the chosen 1:1 ratio of Fe(NO₃)₃·9H₂O and TiO₂ bulk powder is allowed to work hydrothermally in top-down synthesis and Fe-doping of (TiO₂) nanoparticles. Field emission scanning electron microscopy (FESEM) shows the particle structure or morphology of the Fe-doped TiO₂-NPs. Raman and x-ray photoelectron spectroscopy (XPS) is used to study the composition and iron-content at the surface of the synthesized nanoparticles. X-ray diffraction (XRD) pattern has several peaks for α-Fe₂O₃ corresponds to Iron doping in the synthesized nanoparticles of (TiO₂). The current technique provides a practical method for maximum yield and high quality of Fe-doped TiO₂ nanoparticles for its potential photovoltaic and photocatalytic applications in modern technologies.

1. Introduction
Titanium dioxide (TiO₂) is an important low-cost multifunctional metal oxide with higher chemical and photochemical stability, excellent photocatalytic activity, nontoxicity, electrical, electronic, and optical properties for a range of potential applications in developing technologies [1–6].

Anatase, rutile, and brookite are the three well-known crystallographic forms of TiO₂. Anatase is usually found to be effective in photovoltaic and photocatalytic applications, whereas, rutile is used for optical and electronic applications due to its high dielectric constants [7]. A good ratio of rutile and anatase forms can give a catalyst with desired properties in a Titania matrix. On heating at higher temperatures (>1000 °C), anatase changes to rutile form [8]. TiO₂ has a wide band gap of 3.2 eV. As a result of this wide band gape, most of its optical application is restricted to only the ultraviolet (UV) region which resulted in further delays in its commercial uses [9, 10]. Plenty of efforts have been made to resolve this issue by increasing its absorption wavelength (λ > 400 nm) to have a wider absorption spectrum. The main solution sought to improve the absorption in the visible region is the doping of TiO₂ with different transition metals. Doping alters the chemical composition and modifies the electronic structure of TiO₂ which results in changing its optical properties. In this regard, doping of metal ions, including chromium, nickel, vanadium, zinc, and iron, has been considered by many researchers in the past [11–15].
Iron metal ions are found to be suitable for doping due to the similarity in size of ionic radii of both Fe$^{3+}$ and Ti$^{4+}$ (i.e. 0.64 Å and 0.68 Å respectively) [16, 17]. Adsorption of iron on the TiO$_2$ surface can improve the separation of free carriers by using it as an electron or hole trapper [18]. Besides, it can be easily integrated with the TiO$_2$ crystal lattice [16, 19]. A great advantage of incorporating Fe into TiO$_2$ lattice is its use in hydrogen production and photocatalysis due to an increase in the absorption of visible light and reduction in the energy gap of TiO$_2$ [20]. Photocatalysis is an advanced oxidation process that has been used in different water disinfection techniques for the removal of organic and inorganic contaminants. It can mineralize biological compounds into eco-friendly materials. Besides, it is cost-effective and energy-efficient [21]. Beside doping, reduction of size from bulk to nano can also significantly alters the absorption, emission, optical or photocatalytic properties of TiO$_2$ due to quantum confinement phenomena [22].

Keeping in view the advantages of reduced size Fe-doped TiO$_2$ structures, many techniques, or procedures (based on different experimental set-ups and precursors) have been developed. It includes the ‘spin coating method’ (in which the effect of iron doping has been observed in the as-deposited thin film of TiO$_2$ [23]), as well as the MOCVD [24, 25], and sol-gel technique [26]. Followed by the ‘mechanochemical ball milling method’ in which Fe-doped TiO$_2$ nanoparticles have been prepared by using a 1:5 ratio of TiO$_2$ powder and FeCl$_3$ as precursors [17]. Irrespective of complex and lengthy procedures, Fe-doped TiO$_2$ with atomic and mol percentage of Fe as, 0%–10% [27], 0.5%–5% [28], 0.3%–1% [2], 0.5%–2% [29], and 2% respectively [30] are available in the literature. In all these works the quantity of Fe-doped was so small that it was hardly detected in their XPS analysis and missed or undetected in XRD. The missed or undetected Fe in XRD analysis was theoretically justified by its almost similar ionic radii with Ti. The Fe$^{3+}$ ions were thus claimed to have replaced Ti$^{4+}$ ions in the titanium–lattice. It is believed that the incorporation of Fe$^{3+}$ ions into TiO$_2$ lattice weaken the neighboring oxygen atoms bonding and as a result oxygen atoms are readily released from the lattice causing an oxygen vacancy, hence more oxygen/H$_2$O/hydroxide ions can be adsorbed onto the surface of TiO$_2$ catalysts and this results in decreasing the conduction band electrons which lead to an increased photocatalytic activity of Fe-doped TiO$_2$ [31].

Unlike the above, the key focus in the current work is to study the iron salts and explore its catalytic properties in the synthesis and Fe-doping of the as-synthesized TiO$_2$ nanoparticles. Iron is safe, inexpensive, environmental-friendly, and easily available metal (in the Earth as the second most abundant metal) [32]. Iron catalysts can efficiently catalyze many reactions like hydrolyzation, oxidation, cyclodaddition, hydrogenation, cross-coupling reaction, and isomerization, etc [33–36]. As a result, Iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) has been chosen as a catalyst to explore its unprecedented role in the synthesis of Fe-doped TiO$_2$ nanoparticles. In the first place, amorphous bulk powder of Fe(NO$_3$)$_3$·9H$_2$O and TiO$_2$ are chosen as precursors in a 1:1 ratio. The precursors are planned to hydrothermally work via a top-down approach in the synthesis of TiO$_2$ nanoparticles under the catalytic activity of Fe(NO$_3$)$_3$·9H$_2$O. At the second stage, the Fe from the decomposed Fe(NO$_3$)$_3$·9H$_2$O is allowed to be doped in TiO$_2$ lattice by replacing the host atom at the lattice sites.

2. Experimental details

Amorphous micron-size powder of Iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) and commercial TiO$_2$ (sigma–Aldrich) are homogeneously mixed in a 1:1 ratio (with a total weight of 1 gram). The mixture is then dissolved in 50 ml of de-ionized water and continuously stirred for 30 min. The dissolved mixture is taken into a Teflon-lined autoclave and allowed to hydrothermally react at 150 °C for 25 h. After that, the resulted product is first washed several times with deionized water and then with ethanol. Consequently, the product is put inside an oven for drying at 120 °C for 2 h. Afterward, the dried product is carefully ground to a fine powder in the alumina boat. Finally, the Fe-doped TiO$_2$ is obtained in the form of nanoparticles. The obtained product of Fe-doped TiO$_2$ nanoparticles is characterized to study its structure, morphology, or shape (via FESEM), elemental composition, and phase (via XPS, Raman, and XRD).

3. Results and discussion

Size reduction and Iron doping of TiO$_2$ have been performed in one time precursors previously used only in the Iron doping of TiO$_2$ nanoparticles [27]. In this regard, changes have been made in the precursor’s size, ratio, final temperature, and reaction duration. Final temperature has been set at 150 °C (instead of 200 °C) for a reaction duration of 25 h (instead of 24 h). In other words, the final temperature has been reduced by 50 °C, and the reaction duration has been increased by one hour. Most importantly, the micron size powder of Fe(NO$_3$)$_3$·9H$_2$O and TiO$_2$ is taken in a 1:1 ratio. The main objective was to check the unprecedented role of Fe(NO$_3$)$_3$·9H$_2$O as a catalyst in size reduction and Fe-doping. Initially, the catalytic role of Fe(NO$_3$)$_3$·9H$_2$O reduced TiO$_2$ from bulk to nano. The process does not stop all at once but continues till the reduced TiO$_2$ also
starts working as a catalyst and decomposes Fe(NO₃)₃·9H₂O at a higher temperature. Due to almost the same ionic radii of Fe³⁺ (0.64 Å) and Ti⁴⁺ (0.68 Å) [16], it is possible that some of Fe³⁺ from decomposed Fe(NO₃)₃·9H₂O may either replace some of the host Ti⁴⁺ in the TiO₂ lattice or otherwise stuck itself in the defects produced in the reduced TiO₂ and finally comes out in the form of Fe-doped TiO₂ nanoparticles.

The as-synthesized and Fe-doped TiO₂-NPs are first characterized via field emission scanning electron microscope (FESEM) to observe its apparent morphology. The obtained information about the structure or morphology of Fe-doped TiO₂-NPs can be observed in different magnifications in the FESEM micrograph shown in figures 1(a)–(d). In lower magnification (10 000×) FESEM micrograph shown in figure 1(a), all the Fe-doped TiO₂ seems like parts or building-blocks of salt rock. A double magnified (20 000×) micrograph in figure 1(b) identifies the smaller seeds like morphologies of the synthesized Fe-doped TiO₂-NPs. Most of the smaller size particles are closely packed alongside others at the bottom. The larger size particles are placed at the top and mostly seem isolated. It is an indication of the top-down approach followed during the synthesis and Fe-doping of TiO₂-NPs. Figure 1(c) shows the high magnification (40 000×) FESEM micrograph of the synthesized Fe-doped TiO₂ nanoparticles. Nanoparticles of different sizes (smaller and bigger) can be seen and observed in the current micrograph. The smaller the size of the particle, the more at the bottom it lies followed by a bit bigger and so on. Thus, the biggest particles in the sample are placed at the top followed by the smaller and smallest at the bottom. This observation further verifying the top-down approach followed during the synthesis and Fe-doping of TiO₂-NPs. A higher magnification (100 000×) micrograph shown in figure 1(d) further clarifies the difference between the bigger and smaller size particles (in the range of 10 to 100 nm) and their arrangement in the sample. The bigger particles at the top seem to be composed of a few smaller size particles or just started the division in smaller sizes as already predicted via a top-down approach.

Figure 2 shows the x-ray photoelectron spectroscopy (XPS) results for the elemental compositions of the synthesized Fe-doped TiO₂-NPs. The XPS survey with the peaks tagged for the corresponding elements for their binding energies is shown in figure 2(a). The survey shows not only the strong intensities O 1s and Ti 2p but also the Fe 2p peaks for the Fe-contents. These Fe 2p peaks were previously missing in the XPS surveys for Fe-doped TiO₂-NPs and were only shown via wide scanned or high-resolution XPS spectra [2, 37, 38]. This might either be due to the lower quantity use (10% or less) of Fe dopants or fewer resulted in Fe-doping of TiO₂. Figure 2(b) shows the high-resolution XPS Fe 2p spectra. The Fe 2p₃/₂ peak located at ~712 eV corresponding to binding
energy of Fe$^{3+}$ [37, 39]. It is possible as Fe(NO$_3$)$_3$·9H$_2$O has been used as a major content in the precursors. Besides, the Fe 2p spectra also have an asymmetric tail (tagged as Fe 2p$_{1/2}$) at a binding energy of $\sim$724 eV. The binding energy of this tail is different from that of bulk and is mainly assign to the surface structures [40, 41]. Similarly, figure 2(c) shows the high-resolution Ti 2p spectra. The Ti 2p$_{3/2}$ peak found at 458.8 eV and Ti 2p$_{1/2}$ at 464.7 eV corresponds to the binding energy of Ti$^{4+}$ (TiO$_2$) [37, 39, 42].

Figure 3 shows the Raman spectrum for un-doped (white color) and Fe-doped TiO$_2$ (creamish yellow color) nanoparticles. The reported Raman spectra (is displayed in figure 3) has several peaks at 144 (cm$^{-1}$), 395 (cm$^{-1}$), 519 (cm$^{-1}$), and 639 (cm$^{-1}$) [43, 44]. The peaks at 144 (cm$^{-1}$) and 639 (cm$^{-1}$) corresponds to the $E_g$ modes of vibration as a result of stretching of O-Ti-O in TiO$_2$. The peak at 395 (cm$^{-1}$) is assigned to $B_{1g}$ modes of vibration due to the symmetric bending of O-Ti-O. Similarly, the peak at 519 (cm$^{-1}$) is the overlapping of $A_{1g}$ and $B_{1g}$ modes correspond to antisymmetric and symmetric bending of O-Ti-O respectively [28]. The comparison of the current data for both un-doped and Fe-doped TiO$_2$, with the literature shows that there is no significant difference in Raman spectra of undoped and Fe-doped TiO$_2$. Except, a small broadening and decrease in the intensity of the Raman peaks have been observed for Fe-doped TiO$_2$ [28]. The decreased intensity and broadening of the Raman peaks also point to the reduced size (nano) of the material.
Figure 4 has the x-ray diffraction (XRD) pattern of the synthesized Fe-doped TiO$_2$. The displayed pattern has several peaks at different $2\theta$ values of 25.23, 27.47, 35.8, 37.78, 41.22, 48.10, 49.5, 54.11, 56.41, 62.7, 68.7, 70.4, and 75.03. According to 'JCPDS No. 21-1272', the peaks found at 25.23, 37.78, 48.10, 54.11, 56.41, 62.7, 68.7, 70.4, and 75.03 correspond to (101), (004), (200), (105), (211), (204), (116), (220) and (107) planes in anatase phase [28, 30, 45]. Like-wise, the XRD pattern also has a peak spotted at a $2\theta$ value of 27.47. This peak, according to 'JCPDS No. 21-1276' corresponds to (121) plane in the rutile phase [30]. In addition to TiO$_2$ phases, the XRD pattern has several more peaks at $2\theta$ = 33, 35.5, 40.9, and 49.3. All these peaks correspond to (104), (110), (113), and (024) planes in $\alpha$-Fe$_2$O$_3$ according to 'JCPDS No. 03-0800' [46]. By applying Debye–Scherrer’s equation we get the nominal average particle size of the manufactured (undoped and doped) TiO$_2$ nanostructured powder, which is 15 to 20 nm. The peaks are not observed in XRD of pure TiO$_2$. The detection of $\alpha$-Fe$_2$O$_3$ in the XRD pattern (of the doped sample) is because of a higher concentration (50%) of Fe$^{3+}$ content in the precursors. As equal ratios of the precursors are used, therefore, all Fe$^{3+}$ ions cannot replace Ti$^{4+}$ ions or adjust as impurities at the interstitial positions. As a result, some of the Fe contents developed in iron oxides ($\alpha$-Fe$_2$O$_3$) on the TiO$_2$ surface.

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The XRD characterization results confirm the first-ever practical method for the incorporation of Fe (III) in the Titania matrix. The cleared Fe(III) contents found in the synthesized Fe-doped TiO₂ nanoparticles can effectively be utilized for tailoring the wide band gap of TiO₂. This will further improve its optical properties for a range of potential applications beyond the ultraviolet (UV) region. The increased Fe (III) contents found in TiO₂ lattice will be of great importance in the hydrogen production as well as photocatalysis due to an increase in the absorption of visible light and reduction in the energy gap. The photocatalytic efficiency could be enhanced due to the oxygen defects, crystallite size and synergic effect of the specific surface area.

Optical properties of the Fe-doped TiO₂-NPs were observed by performing a UV–Vis absorption spectroscopic study. It can be observed from figure 5 shows that Fe-doped TiO₂-NPs exhibited a broad absorption peak below 400 nm, which corresponds to the typical absorption of TiO₂. This peak can be attributed to the electronic excitation in the anatase phase of the TiO₂ from a lower to a higher energy level. Furthermore, the change in color of the sample from white (pure TiO₂) to creamish yellow (Fe-doped TiO₂) was due to the incorporation of dopant metal and increase in absorption towards visible light [47].

The photocatalytic activity of Iron doped and Undoped Titanium dioxide is studied by using photocatalytic degradation of methyl orange as shown in figure 6. The Sample doped with Iron has higher photocatalytic activity than pure TiO₂. The maximum degradation activity of 61% and 40% (in 2 h) is observed in the Fe-doped and undoped samples respectively. The increase in photocatalytic activity due to Fe-doping in TiO₂ is according to the available literature [48]. However, in some cases after iron doping, the author did not observe any change [49]. The Fe adsorbed on the surface of doped TiO₂-NPs serves as an electron or holes trapper, which in other words, increases the separation of free carriers [18]. This is due to the reduction of Fe⁴⁺ to Fe²⁺ through the capture of photoelectron and oxidation of Fe²⁺ to Fe³⁺ by the O₂ molecules in the medium. In the presence of a small amount of Fe³⁺, the electrons or holes separation increases which consequently results in improved photocatalytic activity. However, when a large amount of Fe³⁺ is doped, the distance between the trappers is narrowed dramatically and Fe³⁺ turns into recombination centers [50].

Meanwhile, since the energy level for Fe⁴⁺/Fe³⁺ is higher than the valence band energy of undoped TiO₂, Fe³⁺ ions will act as a hole trap. By trapping electrons, Fe⁴⁺ ions can be reduced to Fe³⁺ ions, whereas surface hydroxyl groups turn into hydroxyl radicals as shown in figure 7. The ability of Fe³⁺ ions to scavenge electrons and holes is the major aspect that we believe helps to explain the higher photocatalytic activity observed in our Fe-doped TiO₂ samples. As the crystallite size is reduced, surface-to-volume ratio of the particle’s rises; as a result, photo-generated electron/hole pairs can migrate to the surface through a short pathway, and the e⁻/h⁺ volume recombination rate should decrease, resulting in increased photocatalytic activity.

4. Conclusions

Several techniques with a range of Iron salts or compounds have been claimed for Iron doping of TiO₂-NPs. However, none of the techniques was able to show the Iron contents in the synthesized doped samples by characterization techniques like XRD, etc. Thus, most of the previous works were only restricted to theoretically justification based on similarities in ionic radii. Unlike previous, Iron (III) nitrate nonahydrate is found to be an
effective catalyst in catalytic size reduction of TiO₂ (from bulk to nano) and its Iron doping. The unprecedented catalytic role of Iron (III) nitrate nonahydrate has successfully been verified through XPS, Raman, and most prominently by the XRD technique. The current technique has been found to result in a maximum yield of Fe-doped TiO₂-NPs sufficient enough to be used in its photovoltaic and photocatalytic applications.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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