Photocatalytic study of Ni-N-codoped TiO₂ nanoparticles under visible light irradiation

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Abstract
In present paper pure and Ni-N-codoped TiO₂ nanoparticles have been synthesized via sol gel technique. Crystal phase formation of as synthesized nanoparticles was determined from x-ray diffraction which confirms the existence of anatase phase of TiO₂. The average crystalline size was determined from x-ray diffraction and estimated from Transmission Electron Micrographs found to vary from 24.8 nm to 10.2 nm. The morphology was studied by Field Emission Scanning Electron Microscopy and reveals that the synthesized nanoparticles are highly crystalline, spherical and small agglomerated. It is observed that on doping the agglomeration decreases and is due to relative rates of growth process. The band gap energy was calculated from UV-visible absorption spectroscopy and found to be 3.12, 1.81, 1.69 and 1.53 eV respectively. The appearance of emission bands at 453, 470, 483 and 494 nm in Photoluminescence spectra could be arising from defect energy states caused by oxygen vacancies within the forbidden region of TiO₂. The structural formation of the synthesized nanoparticles is investigated from Fourier-transform-infrared and Energy dispersive x-ray spectroscopy measurements. Photocatalytic degradation efficiency of as synthesized nanoparticles against two different dyes (Congo red and Methyl orange) was investigated under visible light source of wavelength 420–520 nm and is found to increase with dopant concentration (x). It is observed that the increase in Photocatalytic degradation efficiency of synthesized nanoparticles is attributed to decrease in carrier recombination rate arises from the decrease in band gap energy. On the basis of these observations it is concluded that the increase in Photocatalytic activity is due to increase in surface area arises from the decrease in average crystalline size of the synthesized nanoparticles.

1. Introduction
In recent years the environment pollution and contamination of wastewater by different types of municipal and industrial wastes has become major problem for every country. In waste water these pollutants can be organic (such as dyes, pesticides, and pharmaceutical wastes) or inorganic (chlorides, alkalinity, nitrogen, phosphorus, sulfur, toxic inorganic compounds, heavy metals etc.) constituents. Organic pollutants are very harmful to the environment and human being. Researchers have drawn more attention towards the development of efficient techniques for the removal of organic and inorganic pollutants from environment and wastewater. Different techniques such as microorganism, adsorption, ion exchange technique etc have been used earlier. However uses of these methods are limited due to high cost, poor degradation efficiency and complicated technology. Photocatalysis is a promising chemical method, because of its simplicity, low cost, non toxicity and high photocatalytic degradation efficiency in visible light [1–5]. For waste water treatment, photocatalysis using semiconductor oxides e.g. TiO₂, ZnO, WO₃ is the promising environmentally friendly process, because it promotes the degradation of toxic and refractory organic pollutants [6, 7]. Among different semiconductor

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metal oxides, TiO₂ is considered to be an excellent and superior photo catalyst because of its low cost, excellent stability, environmental friendly, superior oxidation ability, high specific surface area in nano size material, high photocatalytic activity in visible light and appropriate ability to initiate a variety of organic reactions [8]. Various methods such as sol–gel [9], Hydrothermal process [10], Chemical Vapor Deposition [11], Pulsed laser deposition [12], wet impregnation [13], Electrochemical coating [14], Ion-assisted Sputtering [15] etc have been used to synthesized pure and doped TiO₂ nanoparticles. Out of these methods, sol–gel technique can be considered as the most effective technique for the production of TiO₂ nanomaterials. It is a simple and low cost synthesis process and offers many advantages such as high purity, high crystalline, homogeneity and flexibility of the growing spherical TiO₂ nanoparticles [16–18]. However, the wide applications of TiO₂ as photo catalyst are limited due to its two significant drawbacks. The first drawback is the wide band gap (3.2 eV) TiO₂ anatase phase that shows limited photo catalytic response under ultraviolet irradiation as only 3%–5% of the solar irradiation reaching the Earth’s surface as Ultraviolet and 39% as visible light. The second drawback is the fast recombination of electron-hole pair [7]. In recent years new techniques have been developed by researchers to extend the Photocatalytic response of TiO₂ nanoparticles from ultraviolet to the visible light region without the decrease in photocatalytic activity [19]. Doping with transition metals/non metals creates new energy states within forbidden gap of TiO₂ and enhances the light absorption properties [20]. Using sol-gel technique stable TiO₂/rectorite nanoparticles have been synthesized and dried in air at 50 °C, 70 °C and 120 °C. The dried sample at 70 °C termed as TR-70 leads to large surface area resulting in higher photocatalytic activity under UV light irradiation [21]. The TiO₂-rectorite composites was prepared at low temperature by sol-gel technique, without further calcinations the prepared nanocomposites showed a high photocatalytic activity for degradation of organic pollutant under UV irradiation [22]. Under different heat treatment condition mixed crystal phase’s anatase-brookite and anatase-rutile of TiO₂/kaolinite mesoporous nano composite were fabricated by using facile method at low temperature. Due to large specific surface area of anatase-brookite mesoporous nano composites and decrease in charge carrier recombination rate the photocatalytic activity in degradation of organic molecules under UV irradiation was evaluated much higher compared to other crystal phases of TiO₂ [23]. It has been reported that electrodes of TiO₂ nanorod-clusters loaded on carbon aerogel (TiO₂ NRC/CA) and graphite (TiO₂ NRC/graphite) were synthesize by hydrothermal process. The TiO₂ NRC/CA electrode exhibits excellent photocatalytic activity for degradation of PNA under visible light due to its large surface area compared to other electrode [24]. TiO₂/sepilite nano-composites were prepared by simple sol-gel technique. The as prepared samples showed efficient photocatalytic activity for degradation of ARG and 3-NP under UV light [25]. Stable β–Bi₂O₃/TiO₂-NT’s were synthesized by pulse electro deposition method. The decrease in band gap energy and enhance in surface area leads to increase in photocatalytic activity under visible light for the removal of CBZ in aqueous solution [26]. The effects of nickel and nitrogen doping on the Photocatalytic activity of TiO₂ have been investigated by several authors [27–31]. In the present work we have planned to synthesize pure and nickel/nitrogen co-doped TiO₂ nanoparticles via sol-gel technique. The following techniques such as x-ray diffraction (XRD), Energy-dispersive x-ray Spectroscopy (EDXS), Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), Fourier-transform infrared Spectroscopy (FTIR), UV-Visible absorption and Photoluminescence spectroscopy have been used to characterize and study the Photocatalytic activity of synthesized nanoparticles. The Photocatalytic degradation efficiency of synthesized nanoparticles against two different dyes (methyl orange and congo red) was investigated under visible light source.

2. Experimental details

2.1. Materials
Titanium (IV) Isopropoxide (Ti(OCH(CH₃)₂)₄) and Nickel Chloride (NiCl₂ · 6H₂O) used as source material for Titanium and Nickel respectively were purchased from Merck Chemical Reagent Co. Ltd. All materials used for synthesis of nanoparticles were of Analytical reagent grade 99.9% pure. Deionized (DI) water was used throughout the experiment for the preparation different solutions.

2.2. Synthesis of pure and nickel/nitrogen co-doped TiO₂ nanoparticles
Pure and nickel/nitrogen co-doped TiO₂; NiₓN₀₉₅T₁₀.₉₅₋ₓO₂; x = 0.04, 0.08 & 0.12 mol% nanoparticles were synthesized by sol gel technique. In the first step, 13 ml solution of titanium tetra isopropoxide was added drop wise into 50 ml methanol in a round bottom beaker kept in dark under constant magnetic stirring for one hour. In the second step 0.5 gm of nickel and 0.15 gm of urea were dissolved in small amount of DI water and then 0.8 ml concentrated HNO₃ was added slowly. The highly viscous sol gel was obtained on mixing and stirring both solutions for 5 h. The as obtained gel was washed several times with DI water and then dried at 100 °C in hot air oven for 24 h to evaporate water and organic residues. The dry gel was annealed at 400 °C for 4 h in a
muffle furnace to obtain dark green nickel/nitrogen codoped TiO$_2$ nanoparticles. The other molar compositions of co-doped TiO$_2$ nanoparticles were also prepared by the same procedure. The systematic experimental procedure for the synthesis of 0.04 mole% nickel/nitrogen codoped TiO$_2$ nanoparticles is presented in figure 1.

Figure 1. Systematic presentation of synthesis process (So-gel technique).

Figure 2. X-ray diffraction pattern of pure and co-doped TiO$_2$ (Ni$_x$N$_{0.05}$Ti$_{0.95-x}$O$_2$; $x = 0.04, 0.08$ & $0.12$ mol%) nanoparticles.
2.3. Characterization of synthesized nanoparticles

The single phase formation of synthesized nanoparticles was verified from x-ray diffraction pattern recorded at room temperature using Cu-Kα radiation of wavelength \( \lambda = 1.5406 \text{ Å} \). The surface morphology of synthesized nanoparticles was studied by using Zeiss Evo 40 analytical Scanning Electron Microscope (SEM). The elemental composition of as synthesized nanoparticles was estimated using an energy dispersive x-ray spectrometer (EDXS) attached to the SEM. The TEM images were recorded using Hitachi (H-7500) microscope at an accelerating voltage of 200 kV. The optical band gap energy was calculated from UV-visible absorption spectra recorded at room temperature using Perkin Elmer UV-visible spectrophotometer in spectral range 200–800 nm. The structural formation was studied by FTIR transmission spectra recorded at room temperature using Perkin-Elmer FTIR spectrophotometer in the spectral range 400–4000 cm\(^{-1}\). The appearance of surface states was studied from Photoluminescence spectra recorded at room temperature in wavelength region 400–600 nm. The photocatalytic activity of synthesized nanoparticles was investigated under visible light source (Phosphorus coated mercury vapour lamp equipped with visible filter) in the wavelength region 420–520 nm.

![Figure 3](image-url)

**Figure 3.** (a) FESEM image of pure TiO\(_2\) nanoparticles at resolution of 200 nm (b) FESEM image of co-doped TiO\(_2\) (Ni\(_{x}\)N\(_{0.05}\)Ti\(_{0.95-x}\)O\(_2\); \( x = 0.04 \text{ mol}\%) nanoparticles at resolution of 200 nm (c) FESEM image of co-doped TiO\(_2\) (Ni\(_{x}\)N\(_{0.05}\)Ti\(_{0.95-x}\)O\(_2\); \( x = 0.08 \text{ mol}\%) nanoparticles at resolution of 200 nm (d) FESEM image of co-doped TiO\(_2\) (Ni\(_{x}\)N\(_{0.05}\)Ti\(_{0.95-x}\)O\(_2\); \( x = 0.12 \text{ mol}\%) nanoparticles at resolution of 200 nm.

**Table 1.** X-ray diffraction parameter, crystalline size, band gap energy of pure and co-doped TiO\(_2\) (Ni\(_{x}\)N\(_{0.05}\)Ti\(_{0.95-x}\)O\(_2\); \( x = 0.04, 0.08 \& 0.12 \text{ mol}\%) nanoparticles.

| Sample matrix | Diffracted angle 2\(\theta\) (degree) | Crystalline size (nm) from XRD | Crystalline size (nm) from TEM | Band gap (\(E_g\)) eV |
|---------------|-------------------------------|-------------------------------|-------------------------------|-----------------------------|
| Ni\(_{0.05}\)Ti\(_{0.95-x}\)O\(_2\) | 25.37 | 24.8 | 25 | 3.12 |
| \( x = 0.04 \text{ mol}\% \) | 25.43 | 15.3 | — | 1.81 |
| \( x = 0.08 \text{ mol}\% \) | 25.43 | 12.5 | — | 1.69 |
| \( x = 0.12 \text{ mol}\% \) | 25.43 | 10.2 | 10 | 1.53 |

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3. Results and discussion

3.1. X-ray diffraction analysis

The recorded x-ray diffraction pattern of synthesized nanoparticles is displayed in figure 2. All observed peaks in diffraction pattern are assigned to crystal planes of TiO$_2$ anatase phase and perfectly match with JCPDS file No. 84-1285. No additional peak was observed in diffraction pattern indicate that the dopant cations are well incorporated into TiO$_2$ lattice. The average crystalline size ($D$) of as synthesized nanoparticles was determined from the FWHM of (101) peak of x-ray diffraction pattern by using Debye–Scherrer’s formula [32]

$$D = \frac{K \lambda}{\beta \cos \theta}$$

(1)

Where $K$ is the constant which depends on the shape of the crystal and in spherical shape its value is 0.9. $\lambda$ is the wavelength of incident x-rays radiation, $\theta$ is the x-rays diffraction angle and $\beta$ is the full width at half maximum (FWHM) of (101) peak. The determined values of average crystalline size found to be 24.8 nm for pure and 15.3, 12.5 and 10.2 nm for the $x = 0.04$, 0.08 and 0.12 mole% co-doped samples and are listed in table 1.

3.2. Field emission scanning electron microscopy analysis

To study the surface morphology, the images of synthesized samples were recorded under Field Emission Scanning Electron Microscope and are displayed in figures 3(a)–(d). The SEM images reveal that the synthesized nanoparticles are highly crystalline, spherical and small agglomerated. On addition of dopant concentration ($x$) the agglomeration decreases and is due to relative rates of growth process [33].
3.3. Energy dispersive x-ray spectroscopy analysis

The elemental composition of synthesized nanoparticles was determined from the energy dispersive x-ray spectroscopy spectrums as shown in figures 4(a)–(d). The peak appearance of Ti, O, Ni and N in appropriate intensity and weight percentage confirm the formation of single phase TiO$_2$ nano crystallites. The peak intensity ratio associated with Ti and O approximately is estimated as 1:2. The absence of impurity peak in observed spectra suggests the stable phase formation of TiO$_2$ nanoparticles.

Figure 5. (a): Transmission Electron Microscopic image of pure TiO$_2$ nanoparticles (b): Transmission Electron Microscopic image of co-doped TiO$_2$ (Ni$_{0.05}$Ni$_{0.95-x}$O$_2$; $x = 0.12$ mol%) nanoparticles.
3.4. TEM analysis
The Transmission Electron Micrographs of synthesized nanoparticles are displayed in figures 5(a) and (b). It is clearly observed figure 5(a) that the synthesized pure TiO₂ nanoparticles are agglomerated in nature. On doping the agglomeration of nanoparticles decreases and is due to replacement of TiO₂ by nickel and nitrogen dopant that leads to decrease in cation vacancies, which in turn decrease the crystalline size. The nanoparticles synthesized from higher doping concentration \( x = 0.12 \text{ mol}\% \) are discrete and somewhat more spherical as shown in figure 5(b). The average crystalline sizes estimated from TEM images are well correlated with x-ray diffraction measurements.

3.5. Photoluminescence spectroscopy analyses
The photoluminescence spectra of synthesized nanoparticles are displayed in figure 6. The excitation wavelengths at which it has maximum intensity can be determined from photoluminescence spectra [34]. The emission peaks observed at 453, 470, 483 and 494 nm of higher wavelengths compared to the band edge emission of wavelength (340 nm) in photoluminescence spectra are due to the quasi-free recombination at the various absorption band edges. The combinations of these states are called the surface state emissions. These surface states are localized within the forbidden energy gap and trapped the excited state electrons leads to higher wavelength emissions as observed in photoluminescence spectra of synthesized nanoparticles under study. The electron and holes are trapped by oxygen vacancies and surface hydroxyl groups; therefore contribute to the visible luminescence in these synthesized nanoparticles.

![Figure 6. Photoluminescence spectra of pure and co-doped TiO₂(NiₓN₀.05Ti₀.₉₅₋ₓO₂; \( x = 0.04, 0.08 \& 0.12 \text{ mol}\% \)) nanoparticles.](image)

| Sample matrix | Photocatalytic degradation efficiency (%) of two different dyes after 120 min of visible light exposure |
|---------------|---------------------------------------------------------------------------------------------------------|
| \( \text{Ni}_x\text{N}_{0.05}\text{Ti}_{0.95-x}\text{O}_2 \) | Methyl orange (MO) | Congo red (CR) |
| Pure TiO₂     | 10           | 12 |
| \( x = 0.04 \text{ mol}\% \)   | 38          | 49 |
| \( x = 0.08 \text{ mol}\% \)   | 61          | 62 |
| \( x = 0.12 \text{ mol}\% \)   | 79          | 82 |
3.6. UV-visible absorption spectroscopic analysis

The UV-Visible absorption spectra of synthesized nanoparticles are shown in figure 7(a). The absorption edge of pure TiO$_2$ nanoparticles correspond to band gap energy 3.12 eV is slightly shifted towards higher wave length region on addition of dopant correspond to red shift clearly indicates the reduction in optical band gap energy \[28, 35\]. The optical band gap energy of synthesized nanoparticles was determined from Tauc’s plot (figure 7 (b)) using relation \[36, 37\].

\[
\alpha h\nu = B(h\nu - E_g)^r
\]

where $\alpha$ & $h\nu$ are the absorption coefficient and incident photon energy respectively, $E_g$ is the optical band gap energy, $B$ is the proportionality constant called band tailing parameter and $r$ is the index of inter band transition. In the present calculation we have used $r = 2$, because TiO$_2$ has an indirect transition. The determined values of optical band gap energy to be 3.12, 1.81, 1.69 and 1.53 eV respectively and are listed in table 2. In present synthesized nanoparticles on increase in nickel concentration ($x$) the optical band gap decreases and is due to the
replacement of TiO₂ by nickel dopant suggest that the synthesized nanoparticles are suitable for photocatalytic degradation under visible light.

### 3.7. Fourier transforms infrared spectroscopy analysis

The FTIR transmission spectra of synthesized nanoparticles show six peaks at 502.37, 615.95, 1404.58, 1624.5, 2345.17 and 3421.73 cm⁻¹ respectively as shown in figure 8. It was reported that the broad band lies in the region 400 to 1000 cm⁻¹ assigned to Ti–O and Ti–O–Ti bridging modes [21]. In case of pure TiO₂ synthesized sample the broad band observed at 502.37 cm⁻¹ is assigned to banding vibration of Ti–O bond in TiO₂ lattice of anatase phase. On addition of dopant this absorption band is shifted to higher wave number 615.95 cm⁻¹ ascribed to Ti–O bond is the characteristics of anatase titania [24, 38]. The standard FTIR spectra of TiO₂ reveals that the absorption band appear at 502.37 cm⁻¹ should be ascribed to vibration of Ti–O bond in TiO₂ lattice indicates that the organic legend was completely lost during annealing of sample at 400 °C [21]. The absorption band
observed at 1404.58 cm$^{-1}$ is assigned to Ni-TiO$_2$ nanoparticles on increasing nickel concentration this band becomes more intense which indicates that the dopant are properly entered into TiO$_2$ network [39]. The absorption bands appears at 1404.58, 1624.5 & 34.21.73 cm$^{-1}$ in present spectra confirms the stable anatase phase of TiO$_2$ nanoparticles [21]. The absorption bands observed at 1624.5, 2345.17 and 3421.73 cm$^{-1}$ are assigned to O–H stretching vibration of hydroxyl or water groups and these are persistent in all the synthesized samples [40].

Figure 10. (a): Photocatalytic degradation efficiency (%) of pure and co-doped TiO$_2$(Ni$_x$N$_{0.05}$Ti$_{0.95-x}$O$_2$, $x = 0.04, 0.08$ & 0.12 mol%) nanoparticles against Congo red dye under visible light (b): Photocatalytic degradation efficiency (%) of pure and co-doped TiO$_2$(Ni$_x$N$_{0.05}$Ti$_{0.95-x}$O$_2$, $x = 0.04, 0.08$ & 0.12 mol%) nanoparticles against Methyl orange dye under visible light.
3.8. Photocatalytic degradation activity

The Photo-catalysis is a well known photochemical reaction accelerated in the presence of a catalyst. The process of photo-catalytic activity of synthesized nanoparticles can be clearly explained on the basis of energy band diagram as presented in figure 9. Under visible light source an electron cannot be excited from valance band to conduction band in case of TiO_2 (band gap 3.21 eV). The addition of nickel and nitrogen dopant into TiO_2 lattice creates impurity levels of Ni 3d below the Ti 3d conduction band and N 2p above the O 2p valence band causes to decrease the band gap of TiO_2 as a result the transfer of electrons takes place from valance band to conduction band [41, 42]. Electron-hole pairs will form if the semiconductor material is illuminated with incident photon of energy equal to or greater than the band gap energy. These separated charge carriers may migrate to the catalyst surface and participate in redox reactions with different absorbed species e.g. in conduction band electrons will generate superoxide radical anion (O_2−) with oxygen and in valence band holes may react with surface bound H_2O or OH− to produce hydroxyl radical (OH·). These highly reactive species are responsible for the degradation of organic dyes [43]. In the present study the addition of dopant in TiO_2 lattice leads to the formation of impurity level in the forbidden region and decreases the band gap as a result the optical absorption shifts to the visible light region [21]. To study the Photocatalytic degradation efficiency of synthesized nanoparticles against both dyes (methyl orange and congo red), first 100 ml solution of concentration 10−5 mol liter−1 of both dyes was prepared in different beakers and then 0.05 gm of each pure and 0.04, 0.08 and 0.12 mol% co-doped TiO_2 nanoparticles were added separately in different beaker having prepared solution of dyes stirred regularly and then kept in dark for 30 min so that adsorption/desorption equilibrium to be setup. The photocatalytic dissolved solutions of dyes were subjected to visible light source under constant stirring. From each beaker 3 ml solution was sampled after every 20 min. The as obtained solution were centrifuged, filtered and finally analyzed on Perkin Lambda 20 UV-spectrophotometer to study the degradation efficiency. The photocatalytic degradation efficiency ‘η′ was determined from the relation

\[
\eta = \frac{C_0 - C}{C_0} \times 100
\]

Where C_0 is the initial concentration of photocatalytic dissolved solution of dye before exposure to visible light source and C is the concentration of photocatalytic dissolved solution of dye after exposure to visible light source at any time t.

The observed values of photocatalytic degradation efficiency (%) for both dyes are listed in table 2. The photocatalytic activity of synthesized nanoparticles can be expressed as photocatalytic degradation efficiency (%) as function of time (minutes) and is plotted in figures 10(a) and (b). It is well established that the co-doping in TiO_2 nanoparticles could leads to higher surface area that effectively enhance the photocatalytic activity under visible light irradiation [44, 45]. The pure TiO_2 synthesized nanoparticles show significant photocatalytic activity due to its suitable band gap and surface area for visible light adsorption. On increasing dopant concentration there is enhance in photocatalytic activity attributed to decrease in carrier recombination rate arises from decrease in energy band gap of synthesized nanoparticles. It has been reported that photocatalytic activity mainly depends upon large surface area and light adsorption capability [46–48]. In present synthesized nanoparticles on increasing dopant concentration particle size decreases leads to increase in surface area. The large surface area creates more active sites on the surface of catalyst secondly the decrease in band gap energy increases the light adsorption capability. The interaction between TiO_2 nanoparticles and dopant could suppress the growth of synthesized nanoparticles and reduce the carriers’ recombination rates [49]. It was reported that the nickel doped TiO_2 nanoparticles synthesized by different techniques shows similar results and enhance in the photocatalytic activity under visible light irradiation [36, 50]. It is obvious that on doping the Photocatalytic activity is improved due to increase in specific surface area arises from the decrease in average crystalline size and narrow band gap of the synthesized nanoparticles.

4. Conclusion

Pure and Ni-N-codoped TiO_2 nanoparticles have been synthesized by sol-gel technique. The crystalline phase formation and average crystalline size was determined from x-ray diffraction data which confirms the existence of anatase phase. The crystalline size of each sample calculated from x-ray diffraction and estimated from TEM image is well correlated. The Field Emission Scanning Electron Microscopy images reveals that synthesized nanoparticles are highly crystalline, spherical and small agglomerated. The optical band gap energy is found to decrease with increase in dopant concentration (x). The Photoluminescence spectra confirm the formation of defect energy states caused by oxygen vacancies within the forbidden region. The structural formation is verified by Fourier-transform-infrared and Energy dispersive x-ray spectroscopy measurements. The photocatalytic activity of as synthesized nanoparticles against both dyes was studied under visible light source of wavelength 420–520 nm. It is observed that the photocatalytic activity of synthesized nanoparticles is increases with co-
doping and is attributed to decrease in carrier recombination rate arises from the narrow band gap energy. On the basis of these observations it is concluded that the increase in Photocatalytic activity is due to increase in surface area arises from the decrease in average crystalline size and narrow band gap of the synthesized nanoparticles.

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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