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SHORT COMMUNICATION

Photocatalytic treatment of oil and grease spills in wastewater using coated N-doped TiO_2 polyscales under sunlight as an alternative driving energy

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Abstract To enhance the overall efficiency of oil and grease removal in wastewater coated N-doped TiO_2 photocatalytic polyscales were fabricated through sol–gel technique. The materials fabricated were characterized using powder X-ray diffraction, Fourier transmission infrared spectroscopy, scanning electron microscopy, and UV–Vis spectroscopy. In order to enhance degradation efficiency of organic pollutant under natural sun light, shifting of absorption range of TiO_2 to visible spectrum, various modifications such as surface modification and size optimization were carried out by doping of nitrogen under sol–gel processes. To ease recovery of suspended catalysts from aqueous media, the coated N-doped TiO_2 were prepared by decorating photocatalytic particles onto suitable substrates. N-doped TiO_2 polyscales with desired functionalities were coated onto the spherical supporting substrates using a binding agent. The photocatalytic treatment studies clearly indicated the considerable level of the oil and grease and other organic pollutants removal from wastewater (up to 85–90 % ± 2) using coated N-doped TiO_2 under natural sunlight as an alternative driving energy source. Removal of oil and grease along with other organic pollutants in wastewater using coated N-doped TiO_2 polyscales is a versatile, economical, and environmental friendly technique due to the ease of handling and recovery, utilization of natural sunlight which is renewable energy source.

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Keywords Photocatalyst · Wastewater · Sol–gel · TiO_2 · Oil and grease · Coating · Natural sunlight

Introduction

Nowadays water treatment is expensive, and new technology is needed for the sustainable reclamation and reuse of polluted water and wastewater (Zekker et al. 2012, 2013, 2014, 2015a, b; Rodrigo et al. 2016; Ergo et al. 2014; Sadler et al. 1994). Due to drastic modernization and urbanizations, the use of petroleum oil and grease products for its energy need at industrial and anthropogenic activities has been increased drastically which led oil and grease pollution in water bodies (Hassan 1989; Rosario et al. 2003; Agota et al. 2012; Olumide et al. 2011; Zekker et al. 2012, 2014). Oil and grease is pollution caused by many sources such as accidental oil spills, leaks, industrial discharges, automobile discharge, and sewage, during chronic and careless usage of oil and oil products (Hassan 1989; Rosario et al. 2003). Some of the accidental incidents with tankers and leakage clearly demonstrated that oil contamination in an environmentally or economically sensitive area which could cause irreparable damage (Hassan 1989; Rosario et al. 2003; Agota et al. 2012; Olumide et al. 2011). It is estimated that 1.7 to 8.8 million metric tons of oil and grease contaminants are released into the world's water bodies every year (National academy of sciences 1985; Cooney 1984), of which >90 % is directly related to human activities (O'Brien and Peter 1976). It is also estimated that about 30 % of the oil and grease enters freshwater systems (Cooney 1984; Gennaro 2004; Brubaker 1993; Stolzenbach et al. 1977) and they could also affect the water quality by forming a layer of floating film, which causes a decrease in the gas exchange of the air and water

body (Lepo et al. 2003; Adeola et al. 2012; Willard et al. 1995; Savita and Suchi 2007). Oil and grease pollution in fresh water bodies are very common, with >5000 oil spills taking place each year in the inland water of continental India (Savita and Suchi 2007; Laszlo et al. 2015). Such pollution can also affect aquatic life as well as human activities in the area of fisheries by damaging fishing boats, fishing gear, and floating fishing equipment (Savita and Suchi 2007). Unfortunately, conventional water treatment techniques are unable to remove oil and grease contamination completely and those techniques have some drawbacks such as time-consuming, costly, and long processes (Laszlo et al. 2015; Syed 2015; Kulik et al. 2007; Suresh Kumar et al. 1996; Zekker et al. 2016). Photocatalytic oxidation is the process in which oil and grease oxidize into carbon dioxide, water, and salts by a catalyst using light as driving energies without producing any residues. Catalyst-assisted advanced oxidation processes (AOPs) form hydroxyl radicals in aqueous media, and hydroxyl radicals are highly reactive with high oxidation potential ($E^0 = 2.8$ V) and nonselective substances to degrade petroleum hydrocarbon compounds (Pera-Titus et al. 2004; Andreozzi et al. 1999), and this is able to react with all types of oil contaminants. Titanium dioxide (TiO_2) is wildly used photocatalyst in AOPs due to its chemical stability, wide availability, and potential interest as photocatalyst with bandgap energy of $\sim$3.3 eV. Visible light responsive TiO_2 by doped metals or nonmetal ions into TiO_2 system can explain bandgap energy tunings for the visible ranges that emphasize the utilization of natural sunlight as an alternative driving energy. There are various advantages in modification of TiO_2 by doping with nitrogen such as narrowing of bandgap tuning toward absorbing visible light, enhanced impurity energy levels, and mitigating the recombination processes (Asahi et al. 2001; Irie et al. 2003; Ihara et al. 2003; Mehmet et al. 2014a, b; Vinod et al. 2015). Also, immobilization of photocatalytic particles on the surface of suitable supporting materials is the best choice for instance when compared to slurry form, because a much faster reaction rate is achieved by individual particles without aggregation. In addition, easy recovery of the photocatalysts reduces the operation cost of treatment and increases the degradation efficiency of contaminants by easy illumination to the light sources (Shivaraju et al. 2010a, b, Shivaraju 2011).

Hence, the aim of this study was to enhance photocatalytic degradation of oily wastewater using N-doped TiO_2 polyscales under natural sunlight illumination as an alternative driving energy. In addition, effective recovery of suspended photocatalytic particles from aqueous media using suitable supporting materials which reduces the operation cost and enhances the illumination efficiency. Supported N-doped TiO_2 polyscales could be attributed in the continuous utilization and ease recovery of photocatalyst after treatment of oily wastewater which emphasizes the sustainable route of wastewater treatment.

Materials and methods

Preparation of photocatalytic materials

N-doped TiO_2 polyscale was prepared through sol–gel method using 10 ml of titanium tetra isopropoxide (TTIP) and a mixture of deionized water (25 ml) and alcohol (25 ml) under continuous mixing on a magnetic stirrer at ambient temperature. A small amount of ammonia was added into the mixture as a dopant (N) source, and then, it was kept for completion of the reaction along with continuous stirring (1500 rpm) for 5 h. The product was kept for aging for 24 h without any disturbance. Finally, the mixture was dried at 50 °C for 24 h in a dust-free hot air oven. Impurities were removed from the obtained product by continuous washing with double-distilled water and then dried at room temperature. The resultant product was calcinated in a muffle furnace at 450 °C for 2 h using a silica vessel with airtight lid. Coating N-doped TiO_2 particles onto the substrate was accomplished using fevicol as an effective binding agent. Later, the fabrication was continued by rapid mixing 2–3 drops of binder with 5 g of porous spherical ceramic beads (1–2 mm in size) and suddenly decorated by daubing approximately 1 g of N-doped TiO_2 polyscale. The prepared N-doped TiO_2 polyscale was dried under dust-free environment at room temperature. The same procedure was followed for the preparation of coated N-doped TiO_2 polyscale using thermocol beads (3–4 mm in size) as the supporting substrates.

Characterization of coated N-doped TiO_2 polyscales

The prepared N-doped TiO_2 polyscales were characterized using different analytical techniques to study the obtained features such as absorption band shift, crystallinity, structural elucidation, surface morphology, and photocatalytic activities. The analytical techniques like UV–Visible spectroscopy (Shimadzu UV-2100), Powder X-ray diffraction (XRD) (Rigaku Smart lab), Fourier transform infrared spectroscopy (FTIR) (Shimadzu-8400S), and Scanning electron microscopy (SEM) (JEOL USA JSM-6390LV) were used to characterize coated N-doped TiO_2 polyscales. Stability of decorated photocatalytic particles onto the substrate in an aqueous medium was studied by weight loss experiments under different speeds.

Photocatalytic degradation study

The photocatalytic activity of coated N-doped TiO_2 polyscales was determined using brilliant green dye-$C_{27}H_{34}N_2O_4S$ (Himedia, laboratory grade) in the aqueous medium. About 50 ml of diluted dye solution was taken in a 100-ml reaction vessel, and a known amount of coated N-doped TiO_2 polyscales was added into the dye solution under continuous stirring (150 rpm/m) using magnetic stirrer. The whole setup of the reaction vessel was kept under the visible light source (100 W tungsten bulbs) as an energy source for 6-h irradiation time. Initial and final concentration of dye solution was measured by spectrometric technique at $\lambda_{max} = 420$ nm and standard calibration curve. The schematic of photocatalytic degradation experimental setup is shown in Fig. 1. The experimental setup constituted with 100 ml quartz vessel provided with lid and content of the vessel was stirred by means of a magnetic stirrer (Remi, India). Decreased concentration of dye solution (C) confirms the breakdown of dye molecules under the photocatalytic activities of coated N-doped TiO_2 polyscales. The photocatalytic degradation efficiency was calculated using Eq. 1.

$$\text{Photocatalytic degradation rate } (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

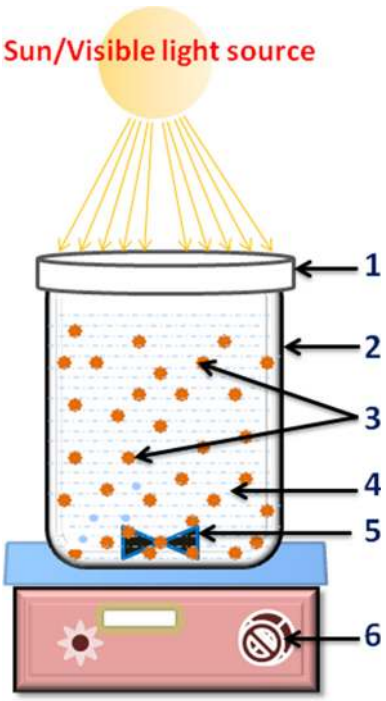

Fig. 1 Schematic of photocatalytic degradation experimental setup under visible light illumination: Silica lid-1; Reaction vessel-2; N-doped TiO_2 coated beads; Wastewater-4; Teflon-coated stirrer bar-5; Stirrer speed controller-6

where C_i is the dye initial concentration and C_f is the dye final concentration. Estimation of the photocatalytic degradation of oil and grease using coated N-doped TiO_2 polyscales was carried out under natural sunlight illumination. During the photocatalytic experiments under natural sunlight, exposure value of sunlight luminance was recorded frequently using lux light meter (Equinox EQ-1301). During the degradation study, approximately 1 g of coated N-doped TiO_2 polyscales was added into a 200 ml of model aqueous solution containing only 25 mg/l oil and grease in the reaction vessel. The irradiation time was varied from 6 to 24 h, and a blank experiment was also carried out without adding coated N-doped TiO_2 polyscales. Quantitative estimation of initial and final concentration of oil and grease in aqueous media was carried out by partition gravimetric method (APHA, AWWA, and WEF 2015). Photocatalytic degradation rate (%) was calculated using Eq. 2.

$$\text{Photocatalytic degradation rate of oil and grease } (\%) = \frac{OG_i - OG_f}{OG_i} \times 100 \quad (2)$$

where OG_i is initial weight of oil and grease and OG_f is the final weight of oil and grease.

Photocatalytic degradation of oil and grease in the real-time wastewater was determined using coated N-doped TiO_2 polyscales. The real-time wastewater sample was collected from the outlet of large-scale automobile service stations in Mysore City, India. The experiments were carried out by following above-mentioned procedure for 24-h irradiation time under natural sunlight. In addition to oil and grease removal potential, the chemical oxygen demand (COD) removal efficiency was also considered as an important parameter to determine the degradation efficiency of N-doped TiO_2 polyscales in the real-time wastewater. Determination of initial (10,400 mg/l) and final COD in the wastewater was carried out by standard analytical method (APHA, AWWA, and WEF 2015), and COD was analyzed 1-h intervals. The removal rate of COD by coated N-doped TiO_2 polyscales was calculated using Eq. 3.

$$\text{Photocatalytic removal rate of COD } (\%) = \frac{COD_i - COD_f}{COD_i} \times 100 \quad (3)$$

where COD_i and COD_f are initial and final CODs, respectively.

Results and discussion

The coated polyscales were prepared using N-doped TiO_2 particles; thermocol and ceramic beads were used as potential supporting substrates, which are less dense,

spherical in shape, and porous in nature. Among thermocol and ceramic beads, ceramic beads (<0.89 g/cm^3 density) were comparatively highly porous in nature than thermocol beads (< 0.67 g/cm^3 density) and vice versa in case of density. Photocatalytic degradation efficiency of coated N-doped TiO_2 polyscales was tested by the treatment of oil and grease in aqueous medium under natural sunlight illumination as a driving energy source.

Characteristics of coated N-doped TiO_2 polyscales

Coated N-doped TiO_2 polyscales were synthesized through sol–gel technique, and as-prepared polyscales were characterized using suitable analytical techniques. The optical and band shifting characteristics of coated N-doped TiO_2 polyscales were investigated using UV–Visible spectrophotometer, and the results were compared with pure TiO_2 particles. The UV–Visible absorption spectrum of coated N-doped TiO_2 polyscales and pure TiO_2 particles are depicted in Fig. 2. The spectrum of coated N-doped TiO_2 polyscales and TiO_2 particles exhibited a strong absorption band between 360–400 and 387 nm that is near UV region, respectively. Coated N-doped TiO_2 polyscale showed two absorption edges at 386 and 397.8 nm that are in the range of visible spectra. The optical absorption edges of coated N-doped TiO_2 polyscales showed considerably shifted edges near the visible region when compared to pure TiO_2. The shift in the absorption edge to smaller photon energy implies a decreased energy level in the conduction band, and a consequent narrowing of the bandgap (Asahi et al. 2001; Irie et al. 2003; Ihara et al. 2003). This shifting in their absorption edge near the visible region clearly implies band tuning coated N-doped TiO_2 polyscales using sol–gel technique. Coated N-doped TiO_2 polyscales showed a consequent narrowing of the bandgap from 3.22 eV to 3.20 and 3.12 eV; it induces the apparent activation of coated N-doped TiO_2 polyscales under natural sunlight illumination that consists with 90 and 10 % of visible and UV light, respectively. Powder X-ray diffraction pattern was recorded over a 2θ range of 10–80 with a speed of 3° per minutes using a nickel-filtered Cu Ka radiation source. In Fig. 3, spectra (a) and (b) indicated the powder X-ray diffraction pattern of pure TiO_2 and coated N-doped TiO_2 polyscales, respectively, which are dominantly indexed to JCPDS files 84–1285 (Emerson et al. 2015; Gomathi Devi and Kavitha 2014; Shivaraju et al. 2010a, b). The XRD pattern of coated N-doped TiO_2 polyscales confirmed the anatase phase and characteristic peak of anatase is sharp and clearly observed particularly at 2θ of 25.2. The XRD pattern of coated N-doped TiO_2 polyscales indicated increased peak intensity that induces well-crystalline phase when compared to pure TiO_2. Well-crystalline phase of coated N-doped TiO_2 polyscales is apparently stable and enhances the photocatalytic activities (Gomathi Devi and Kavitha 2014).

Figure 4 shows the FTIR spectrum of coated N-doped TiO_2 polyscales, and it indicates the stretching vibration of O–H bond from hydroxyl at 3417.24 cm^{-1}. FTIR peak at 1639.3 cm^{-1} indicates the O–H bending of molecularly physisorbed water, and the C=O stretching mode of vibration is observed at 1570 cm^{-1}. For a linear molecule such as absorbed CO or CO2, stretching mode of vibration is observed at 2340 to 2380 cm^{-1} and the molecule remains linear throughout the vibration. Nonlinear molecules usually have three different moments of inertia. In this case, the vibration rotation spectrum can be very

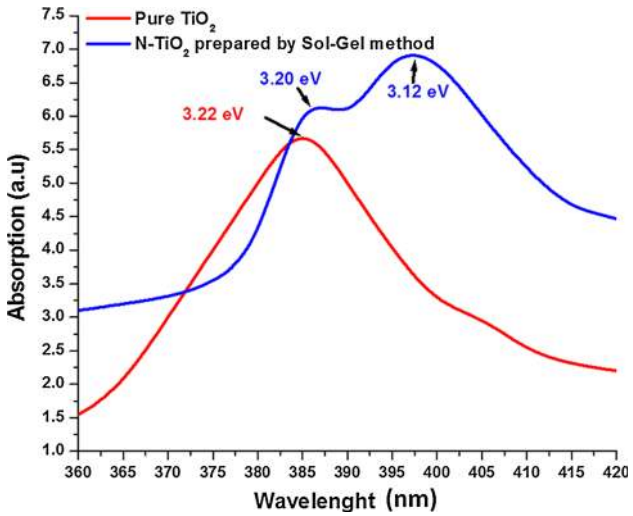

Fig. 2 UV–Visible spectra of N-doped TiO_2 polyscales and pure TiO_2 particles

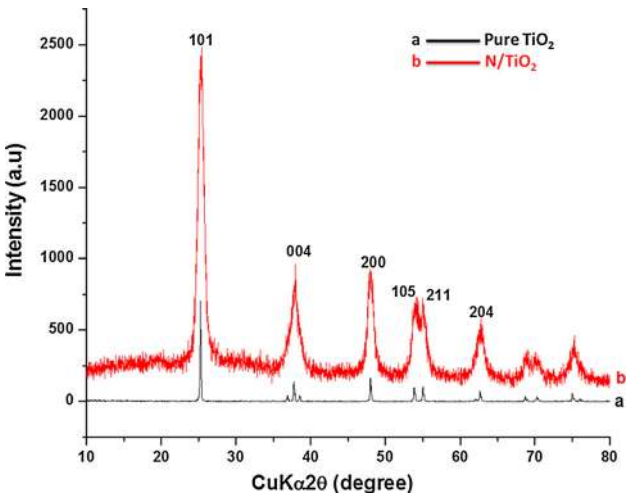

Fig. 3 Powder X-ray diffraction patterns of **a** TiO_2, **b** coated N-doped TiO_2 polyscales

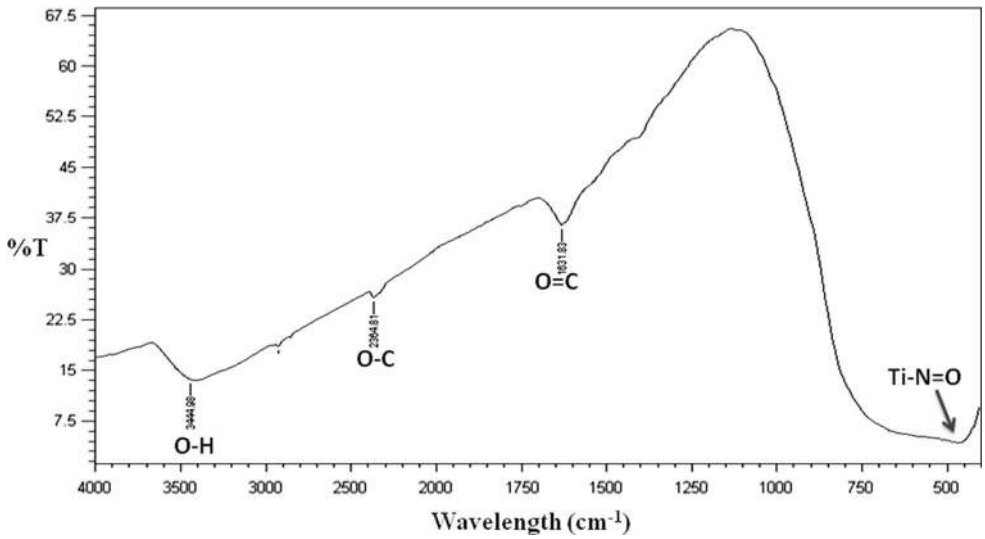

Fig. 4 FTIR spectrum of coated N-doped TiO_2 polyscales

complex, even for a simple molecule such as water. The rotational fine structure of the H–O–H bending mode of water is commonly observed at the range in 1200 to 2000 cm^{-1} (1500 cm^{-1}). Since water is a most polar solvent, bands of solutes in aqueous solution are usually broader than in any other solvent. When functional groups such as O–H are hydrogen-bonded, the width of the stretching bands may be >100 cm^{-1}. The bands in near-infrared spectra are overtones or combinations of fundamentals (C–H, O–H and N–H); the widths of these bands are typically greater than the widths of bands from which they are derived (Gomathi Devi and Kavitha 2014; Shivaraju et al. 2010a, b). A characteristic band with strong and wide absorption at lower energy region (<420 cm^{-1}) is attributed to the formation of anatase O–Ti–O lattice. The stretching band corresponding to the nitrogen in the lattice structure (Ti–N=O) may be identified at lower energy absorption region in the spectrum.

The SEM image was used to determine the morphology of coated N-doped TiO_2 polyscales. The growth of mixed and agglomerated spherical shaped particles of coated N-doped TiO_2 polyscales can be clearly seen in Fig. 5. This SEM indicates that coated N-doped TiO_2 polyscales have spherical morphology creating high surface area and porosity, which is quite suitable for enhancing photocatalytic degradation of pollutants. The experiments conducted for the determination of stability of coated N-doped TiO_2 polyscales in aqueous medium was found to be neglected, and it confirmed the strong adherence of N-doped TiO_2 on the surface of the supporting substrates. As Fig. 5 presents, the N-doped TiO_2 particles are heterogeneous morphology, i.e., a mixture of nano- and microscale; hence, the term polyscale was used to define the size nature of the N-doped TiO_2 particles.

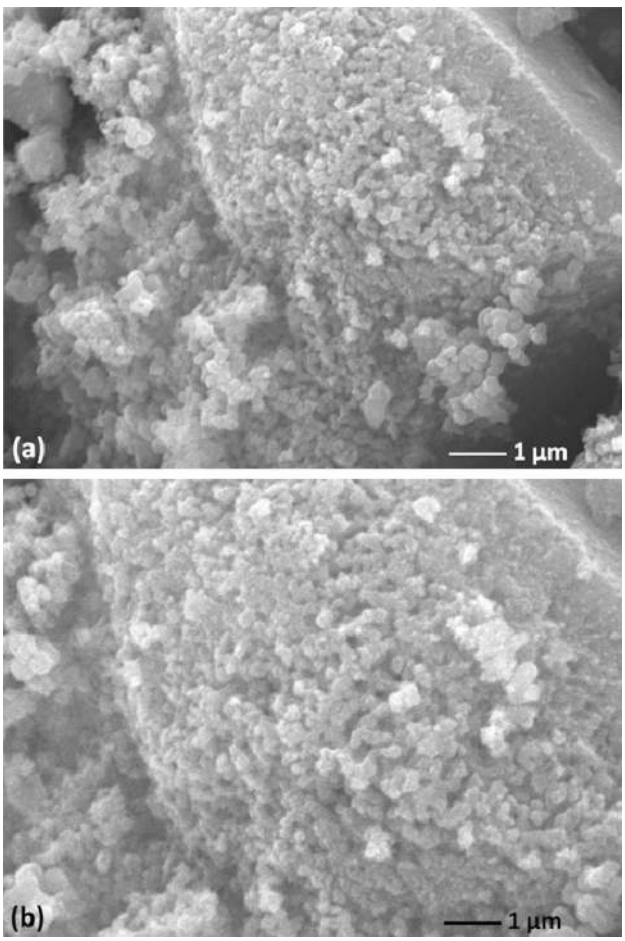

Fig. 5 SEM image of coated N-doped TiO_2 polyscales onto **a** ceramic beads supporting substrate; **b** thermocol beads supporting substrates

The photocatalytic activity of coated N-doped TiO_2 polyscales was determined using a model dye, brilliant green (Himedia, laboratory grade), under visible light

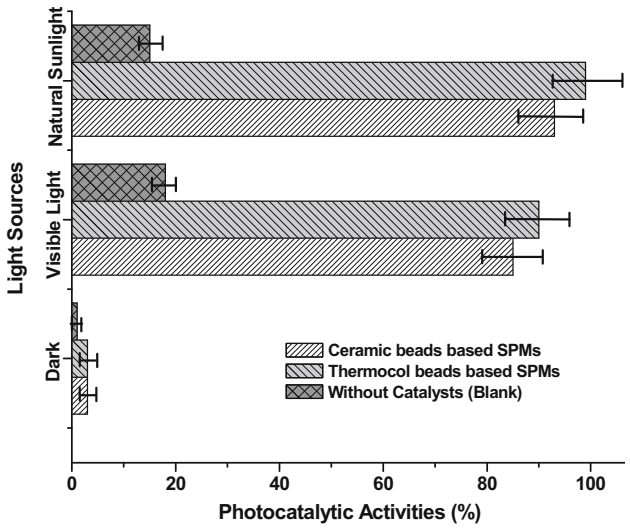

Fig. 6 Photocatalytic activities of coated N-doped TiO_2 polyscales under the different light sources

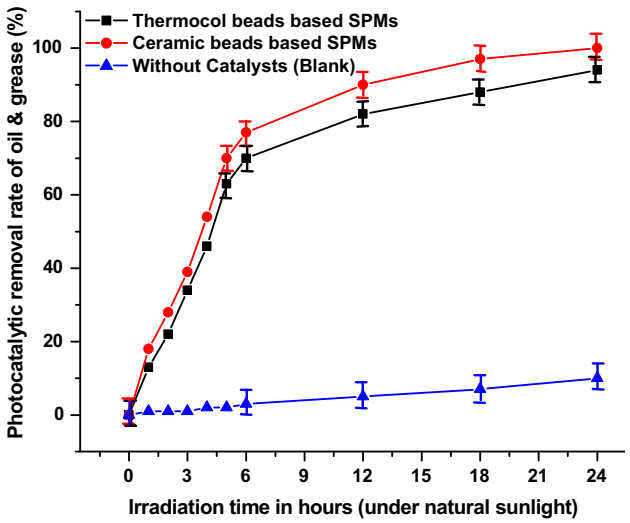

Fig. 7 Photocatalytic removal rate of oil and grease contamination in the aqueous media

source (100 W Tungsten bulb) and natural sunlight illumination. Natural sunlight illumination was showed an average exposure value of 9.72×10^3 lx which is comparatively greater than artificial visible light source (3.62×10^3 lx) which attributed higher removal efficiency under sunlight (99 % ± 2) than visible light sources (93 % ± 2) which can be seen in Fig. 6. Simultaneously, blank experiments were also maintained without coated N-doped TiO_2 polyscales. Both ceramic and thermocol beads based on coated N-doped TiO_2 polyscales exhibited efficient photocatalytic activities under both light sources. Ceramic bead-based coated N-doped TiO_2 polyscales showed comparatively higher photocatalytic activities (8–10 %) than the thermocol-based coated N-doped TiO_2 polyscales under different light sources. This could be attributed to the high porosity and surface areas of ceramic beads, which induce the interaction and contact rate between the organic molecules and photocatalyst in the ceramic bead-based, coated N-doped TiO_2 polyscales (Fig. 6).

Photocatalytic degradation of oil and grease

The photocatalytic degradation of oil and grease contamination alone in the aqueous media (model sample) was carried out using coated N-doped TiO_2 polyscales under natural sunlight illumination as an alternative driving energy source. The experiments were carried out for 6-h duration and continued up to 24 h by irradiating the samples to natural sunlight for 6 h on each day ($\approx 9.72 \times 10^3$ lx). Both the ceramic and thermocol beads-based coated N-doped TiO_2 polyscales showed the potential degradation efficiencies up to 100 % ± 2 and 94 % ± 2, respectively, for 24-h irradiation time. The ceramic bead-based coated N-doped TiO_2 polyscales showed comparatively higher degradation efficiency (>10 %) than the thermocol-based coated N-doped TiO_2

Table 1 Photocatalytic removal rate of chemical oxygen demand using supported photocatalytic materials under natural sunlight

Irradiation time (h)	Removal of COD level (mg/l) under natural sunlight using supported photocatalyst		
	Blank (without catalyst)	N-doped TiO_2 polyscales coated thermocol beads	N-doped TiO_2 polyscales coated ceramic beads
0	10,400	10,400	10,400
1	10,296	9256	8528
2	10,192	8320	7280
3	10,088	7072	5928
4	9984	6136	4784
5	9880	5616	3744
6	9880	3952	3120
12	9776	2496	1664
18	9464	1768	832
24	9152	1396	490

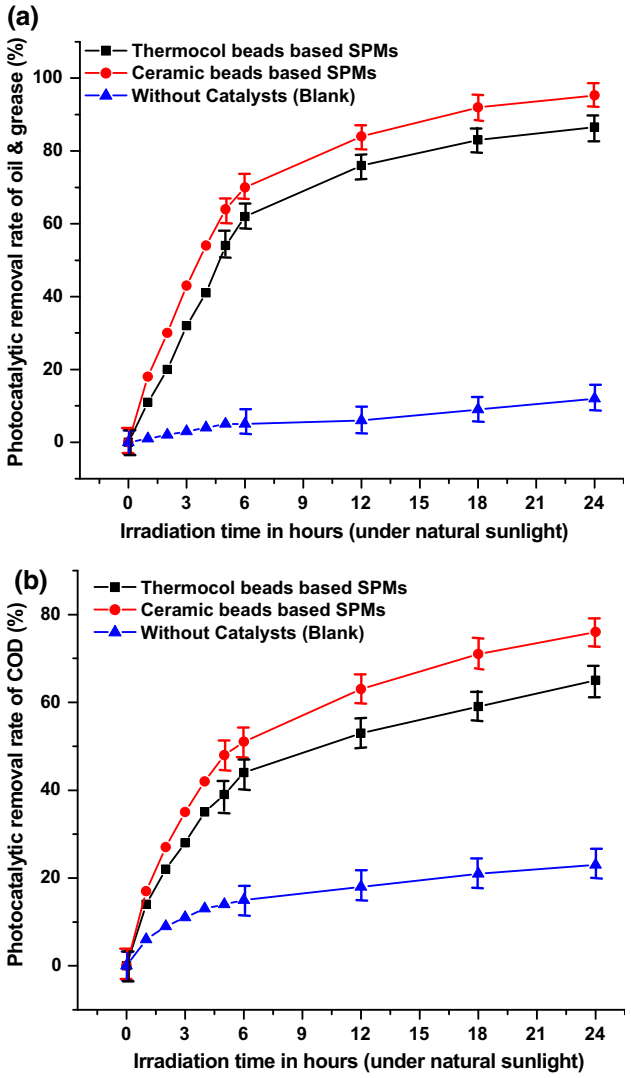

Fig. 8 Photocatalytic degradation efficiency of coated N-doped TiO_2 polyscales in the removal of **a** oil and grease in real-time wastewater; **b** COD in real-time wastewater

polyscales, and the degradation efficiency of oil and grease in aqueous media is shown in Fig. 7.

The photocatalytic treatment of oil and grease in the real-time industrial wastewater was carried out using ceramic and thermocol beads-based coated N-doped TiO_2 polyscales under natural sunlight illumination, and the degradation efficiency was 86.57 % ± 2 and 95.28 % ± 2, respectively, for 24-h irradiation time. In addition to the removal of oil and grease contamination in the wastewater, both coated N-doped TiO_2 polyscales showed potentiality reduction of COD level in the wastewater after photocatalytic treatment under natural sunlight illumination. The photocatalytic treatment efficiency of coated N-doped TiO_2 polyscales in removal of oil and grease and in reduction of COD level (Table 1) in the real-time wastewater is shown in Fig. 8a, b, respectively. Moreover, the research revealed that both coated N-doped TiO_2 polyscales showed comparatively higher degradation efficiency (5–6 %) in the model aqueous medium than the real-time wastewater. Perhaps this happened due the other contaminants that reduce the photocatalytic activities by reduction in the irradiation rate by obstructing the light waves to reach the surface of photocatalyst. The reduction in COD level in the wastewater confirmed the photocatalytic degradation of oil and grease contamination along with the other organic pollutants in the wastewater. Apparently, coated N-doped TiO_2 polyscales can be utilized as potential catalysts by harvesting the natural sunlight as a renewable and potential alternative driving energy for the treatment of water and wastewater.

The coated N-doped TiO_2 polyscales used in the present study have special features like a less denser and spherical shape that helps to float on the surface of water and apparently enhance the degradation rate of oil and grease which floats on the surface (Shivaraju et al. 2010a, b; Muhammad et al. 2013; Nangrejo et al. 2008; Zhongxin et al. 2014; Han-Yu et al. 2015; Yeon et al. 2001; Hawley et al. 1984; Jinzhou et al. 2015). Due to lesser dense and spherical in shape, irradiation rate of the coated N-doped TiO_2 polyscales to the light will be enhanced gradually and also achieve high contact rate between pollutants and catalytic active sites by easy rotation through the terrestrial winds in the ambient environment (Shivaraju et al. 2010a, b; Muhammad et al. 2013; Nangrejo et al. 2008; Zhongxin et al. 2014; Han-Yu et al. 2015; Yeon et al. 2001; Faisal et al. 2007). Therefore, the composition of supporting substrates and multifunctional design of coated N-doped TiO_2 polyscales provide higher contacting rate and addition kinetic energy that enhances the overall degradation rate of oil and grease molecules along with the other organic pollutants in water and wastewater (Shivaraju et al. 2010a, b; Muhammad et al. 2013; Nangrejo et al. 2008; Boudjemaa et al. 2016; Shivaraju 2011). The schematic of multifunctional coated N-doped TiO_2 polyscales and photocatalytic degradation mechanism is illustrated in Fig. 9. The present study revealed that both coated N-doped TiO_2 polyscales presented considerable degradation efficiency by utilizing natural sunlight, which is cost-effective, pollution free, and also reduces the dependency on the convention energy sources for the water and wastewater treatment purposes. In addition, coated N-doped TiO_2 polyscales were found to be easily recovered after the completion of treatment and were easy to handle without any sophisticated infrastructure.

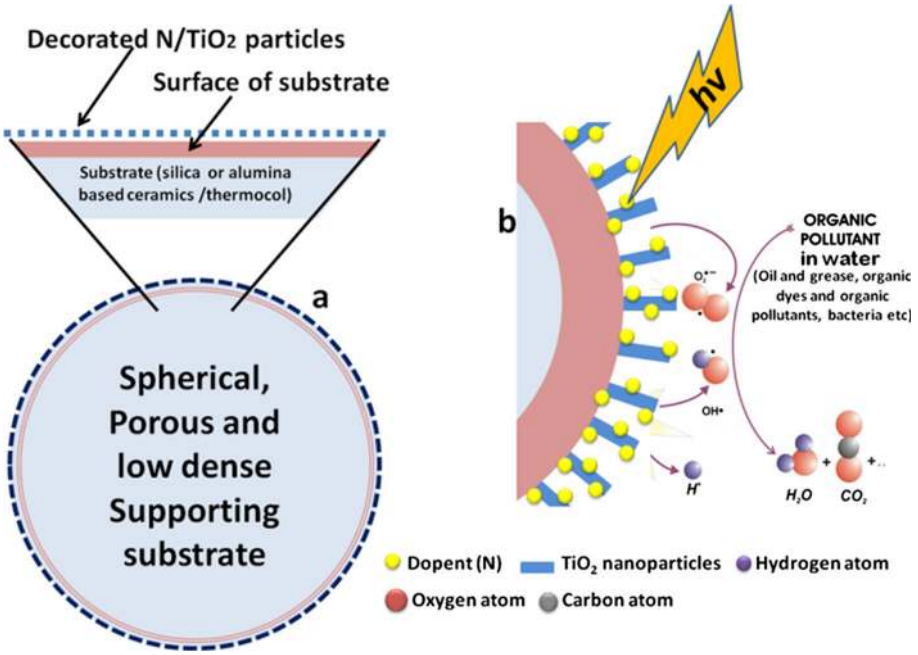

Fig. 9 Schematic of multifunctional coated N-doped TiO_2 polyscales design and its photocatalytic degradation mechanism

Conclusion

The present study addressed the preparation of the potential visible light responsive coated N-doped TiO_2 polyscales through sol–gel technique. The characterization results revealed well-crystalline phase, desired structural elucidation and morphology, considerable shifting and narrowing of bandgap energy from 322 to 3.12 eV, and higher photocatalytic activities (92–99 % ± 2) in coated N-doped TiO_2 polyscales. Multifunctional coated N-doped TiO_2 polyscales were successfully designed using thermocol and ceramic beads as the potential supporting substrates that enhanced the overall photocatalytic degradation efficiency under natural sunlight illumination along with the easy recovery and handling. Moreover, coated N-doped TiO_2 polyscales confirmed the up to 96 % ± 2 and 100 % ± 2 removal efficiency of oil and grease in both model and real-time wastewater, respectively, under the renewable and alternative energy sources like natural sunlight. N-doped TiO_2 polyscale-assisted treatment techniques with desired fabrication will be substituting the conventional and inefficient treatment methods in the removal of oil and grease and other organic contaminants in the polluted water bodies under the natural sunlight.

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