



g-C₃N₄/NaTaO₃ organic–inorganic hybrid nanocomposite: High-performance and recyclable visible light driven photocatalyst



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ABSTRACT

Novel g-C₃N₄/NaTaO₃ hybrid nanocomposites have been prepared by a facile ultrasonic dispersion method. Our results clearly show the formation of interface between NaTaO₃ and g-C₃N₄ and further loading of g-C₃N₄ did not affect the crystal structure and morphology of NaTaO₃. The g-C₃N₄/NaTaO₃ nanocomposites exhibited enhanced photocatalytic performance for the degradation of Rhodamine B under UV-visible and visible light irradiation compared to pure NaTaO₃ and Degussa P25. Interestingly, the visible light photocatalytic activity is generated due to the loading of g-C₃N₄. A mechanism is proposed to discuss the enhanced photocatalytic activity based on trapping experiments of photoinduced radicals and holes. Under visible light irradiation, electron excited from the valence band (VB) to conduction band (CB) of g-C₃N₄ could directly inject into the CB of NaTaO₃, making g-C₃N₄/NaTaO₃ visible light driven photocatalyst. Since the as-prepared hybrid nanocomposites possess high reusability therefore it can be promising photocatalyst for environmental applications.

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1. Introduction

Transition metal oxides with perovskite structure (such as titanium, tantalum-based semiconductor materials) have been attracted considerable attention in recent decades due to their interesting properties and potential applications [1]. Recently, NaTaO₃ has been found to be a highly active photocatalyst for water splitting and environmental remediation under UV light irradiation due to its physical, chemical and structural properties [2–4]. Moreover, NaTaO₃ has favourable band edge potentials and delocalized nature of photoexcited electrons which are primary reasons for higher efficiency [5–7]. The photocatalytic activity of NaTaO₃ is further enhanced by doping of alkaline earth metal ions and certain lanthanides [8,9]. In a significant development, Kato et al. showed that a maximum quantum efficiency of 56% at 270 nm irradiation can be obtained by La-doped NaTaO₃ loaded with NiO particles [10]. However, their activities are limited to ultraviolet (UV) region, and the component of UV in the solar spectrum is only about 4%. In order to utilize the solar energy with high conversion efficiency, absorption of wavelengths greater than 420 nm is essential. To date, studies on visible light active NaTaO₃ is limited. Nitrogen-doped NaTaO₃ catalyst has been studied for visible light driven photocatalytic degradation of methylene blue

as well as gaseous formaldehyde [11,12]. A solid solution photocatalyst (Na_{1-x}La_xTa_{1-x}Co_xO₃ for x = 0.0 to x = 0.25) has been developed to tune the band gap towards visible region that showed hydrogen evolution from aqueous methanol solution [13]. These studies suggest that absorption can be achieved by modification of the band structure via substitutional doping of appropriate cations at 'Ta' site in NaTaO₃ lattice. Recently, bismuth-doped NaTaO₃ nanoparticles prepared by hydrothermal method have been studied for photocatalytic hydrogen evolution under visible light irradiation without adding any co-catalyst [14].

Making composite with another semiconductor material is one of the most successful ways to alter the band structure of host material and induce absorption [15–19]. In semiconductor composite materials, the recombination of photoinduced electrons and holes can be suppressed, because they can act as electron trap and promote interfacial charge transfer processes in the composite systems, thus improving photocatalytic activity by changing the dynamics of electron–hole recombination and interfacial transfer. More recently, H.W. Kang et al. reported NaTaO₃-C composite powder as efficient photocatalyst for the evolution of hydrogen from water splitting without adding any co-catalyst [20]. Therefore, detailed studies on coupled NaTaO₃ and their photocatalytic activities are important in order to develop NaTaO₃ based photocatalysts for solar energy application.

It is well known that catalytic behaviour is not only material dependent, but also size dependent. The one generalized behaviour of the materials is "Smaller the particle size, larger the specific

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surface area". Therefore, the great demand of fine particles of this perovskite oxide has stimulated a lot of activity towards their synthesis by soft chemical methods. A number of methods have been reported for the preparation of NaTaO_3 [21–25]. The conventional technique for preparing NaTaO_3 powder is mainly based on the solid state reaction, which requires long time and higher temperature (typically 1000–1300 °C). Recently, many efforts have been made to synthesize NaTaO_3 , for example, He and Zhu have successfully synthesized the perovskite-type NaTaO_3 powder with a cubic morphology, via the solvothermal method [26]. Nelson and Wagner have obtained NaTaO_3 nanorods from TaCl_5 by the alkalide reduction method [27]. More recently, our group reported the modified reverse micellar route to synthesize nanocrystalline NaTaO_3 with an average particle size of about 40 nm (much smaller than other methods such as solid state, hydrothermal and sol–gel techniques) [28]. Reverse micellar route is one of the most successful techniques for preparing the nanosized metallic oxide materials with controlled geometric properties, such as surface morphology, surface area, and particle size. Reverse micellar route also avoids steps such as refluxing of alkoxides (sol–gel) result the uniform and homogeneous nanoparticles [29]. Moreover, the properties of composite catalyst are closely related to the fabrication processes such as sol–gel, hydrothermal and ultrasonic dispersion method. Especially, the ultrasonic dispersion technique is known to be a suitable route for synthesizing composite of two different semiconductor powders as it can easily control the solid solution with stoichiometric and homogeneous mixture. Since this method is a solution process, it allows flexibility to control the parameters with its relatively slow reaction process [30–33].

In this present work, first the nanocrystalline NaTaO_3 was prepared by modified reverse micellar method with average particle size of 43 nm and then $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposites were prepared by a facile ultrasonic dispersion method at room temperature. The prepared samples were well characterized by PXRD, FTIR, TGA, FESEM, TEM and surface analyser. The photocatalytic activity of the prepared samples was evaluated for the degradation of Rhodamine B under both UV–visible and visible light irradiation. The recyclability of the as-prepared $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite was also investigated. However, to the best of our knowledge there is no report on the synthesis of $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite photocatalyst.

2. Experimental details

2.1. Materials

Melamine (Aldrich, 99.0%), tantalum isoprooxide (Aldrich, 10%, w/v; 99.9% metal based), tergitol NP9 (Aldrich, 99.0%), ethylene glycol (Qualigens, 99.5%), citric acid (Qualigens, 99.5%), cyclohexane (Qualigens, 99.5%), 1-octanol (Qualigens, 99.5%), sodium hydroxide (Merck, 98%) and Rhodamine B (Aldrich, 85.0%) were used as received. All other reagents used in this work were of analytically pure and used without further purification.

2.2. Method

The $\text{g-C}_3\text{N}_4$ was prepared by direct heating melamine to 550 °C for 2 h in N_2 atmosphere [34]. Nanocrystalline powder of NaTaO_3 has been synthesized by a modified reverse micellar method [28]. Preparation of $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposites was as follows: In brief, an appropriate amount of $\text{g-C}_3\text{N}_4$ was ultrasonicated in 50 mL of methanol for 30 min. To this, 0.1 g of NaTaO_3 was added and stirred in a fume cupboard for 24 h. After evaporation of methanol, a solid product was obtained and dried at 100 °C for 1 h. The $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalysts with different

weight ratios of $\text{g-C}_3\text{N}_4$, particularly 5% and 10% were synthesized and named as CNNT05, and CNNT010, respectively. The pure $\text{g-C}_3\text{N}_4$ named as CN and NaTaO_3 named as NTO.

2.3. Characterization

X-ray diffraction studies (XRD) were carried out on a Bruker D8 Advance Diffractometer using Cu K_α radiation with Ni filter for striping Cu K_β radiation. TGA/DTA experiments were carried out on PerkinElmer Pyris Diamond TGA/DTA system on well ground samples in flowing nitrogen atmosphere with a heating rate 10 °C/min. The FTIR spectra were recorded in transmission mode from 4000 to 400 cm^{-1} on a Nicolet Protégé 460 FTIR spectrometer using KBr discs. FESEM studies of samples were carried out on a FEI quanta 3D FEG-FESEM operated at 10 kV by coating the powder sample with gold. TEM was done on a JEOL, JSM-6700F instrument. UV–vis diffuse reflectance spectra were recorded on a Lambda/20 Instruments (UV–vis NIR spectrophotometer), equipped with an integrating sphere to record the diffuse reflectance spectra of the samples, and BaSO_4 was used as a reference. The nitrogen adsorption–desorption isotherms were recorded using Quanta Chrome NOVA 1200e.

2.4. Photocatalytic activity

Rhodamine B (RhB), a widely used dye, was chosen as a model pollutant. The photocatalytic activity of the prepared samples (0.125 g) was examined by monitoring the degradation of RhB aqueous solution (250 mL, 5 mg L^{-1}) in a beaker under stirring condition at 250 rpm throughout the test at room temperature under both UV–visible and visible light irradiation. The visible light source for the photo-irradiation is solar simulator 300 W Xe lamp (Asahi Spectra Co., Ltd.) with a super cold filter, which provides the visible light region ranging from 400 nm to 700 nm and the light intensity is around 115 mW cm^{-2} and UV–visible light source for photo-irradiation is Hg lamp (125 W, Philips Co, Ltd). Prior to irradiation, solutions suspended with photocatalysts were stirred in dark condition for 30 min to ensure that surface of catalyst was saturated with RhB. During photocatalytic processes, the sample was periodically withdrawn, centrifuged to separate the photocatalyst powder from the solution, and used for the absorbance measurement. The absorption spectra were recorded on a UV–vis spectrophotometer. The photocatalytic activity of the hybrid nanocomposites compared with the pure $\text{g-C}_3\text{N}_4$ and NaTaO_3 under the same experimental conditions.

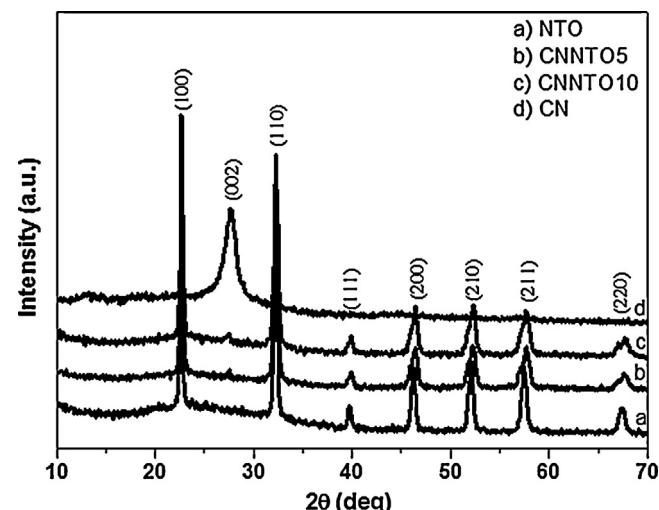


Fig. 1. XRD patterns of the prepared $\text{g-C}_3\text{N}_4$, NaTaO_3 and $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalysts.

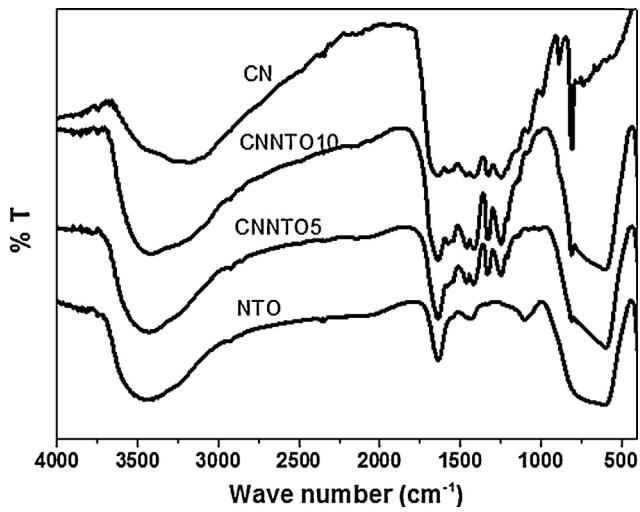


Fig. 2. FTIR of the prepared $\text{g-C}_3\text{N}_4$, NaTaO_3 and $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalysts.

3. Results and discussion

3.1. Characterization of photocatalysts

Fig. 1 shows the X-ray diffraction patterns of pure NaTaO_3 , $\text{g-C}_3\text{N}_4$, and as-prepared $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ nanocomposite samples. Monophasic NaTaO_3 has been obtained by modified reverse micellar method followed by heat treatment at 600°C for 12 h. All the reflections can be readily indexed as the cubic phase (JPCDS#742488). In the spectrum of hybrid nanocomposites, no

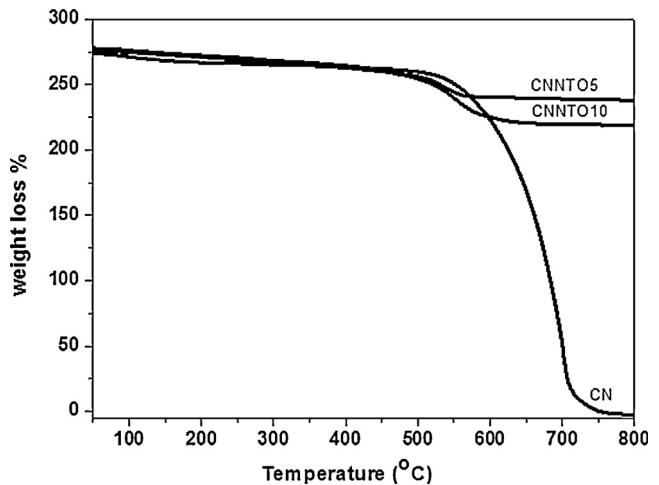


Fig. 3. TG curves of the prepared $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalysts.

change was observed in the crystal structure of NaTaO_3 but a new peak at 27.54 appears which is corresponding to the (0 0 2) plane of $\text{g-C}_3\text{N}_4$. A significant X-ray diffraction peak broadening in composite system indicates a decreasing crystallinity due to the loading with $\text{g-C}_3\text{N}_4$. However no impurity peak was found, indicating the presence $\text{g-C}_3\text{N}_4$ with NaTaO_3 to yield a novel two phase hybrid nanocomposite. The peak intensity of (0 0 2) plane was increased with increasing amount of $\text{g-C}_3\text{N}_4$ loading. The estimated average crystallite size of NaTaO_3 is 47.25 nm in pure NaTaO_3 and 46.13 nm in composite. The grain size was further supported by TEM results.

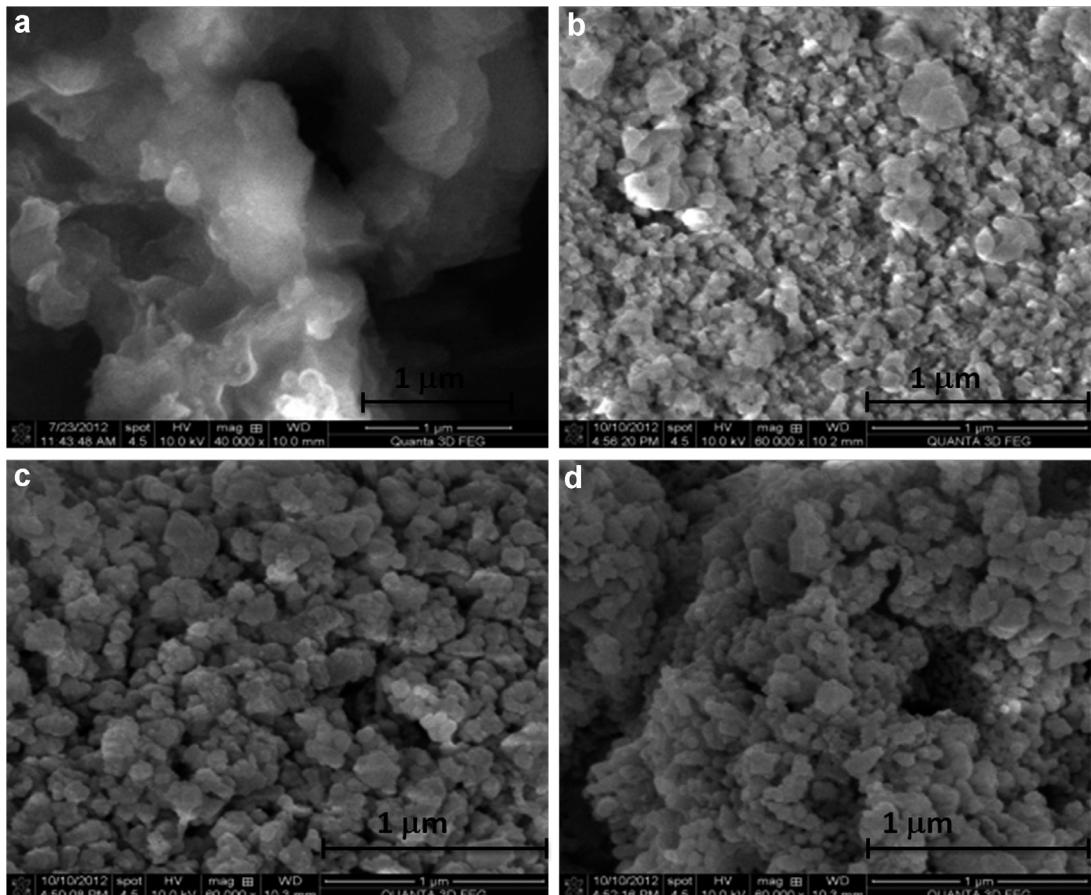


Fig. 4. FESEM of the prepared $\text{g-C}_3\text{N}_4$, NaTaO_3 and $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalysts: (a) pure NaTaO_3 , (b) pure $\text{g-C}_3\text{N}_4$, (c) 5 wt% $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ and (d) 10 wt% $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$.

Fig. 2 shows the FTIR spectrum of pure NaTaO_3 , $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposites. The broad Ta–O band in the powder sample heated above 500°C is clearly visible in all compositions in the region $225\text{--}850\text{ cm}^{-1}$ [35]. However, a broad band was observed pertaining to adsorbed water around $3300\text{--}3600\text{ cm}^{-1}$ and 1658 cm^{-1} are corresponding to OH stretching vibrations, and another peak at 1384 cm^{-1} is corresponding to the H–O–H bending band of adsorbed H_2O molecules on the surface of sample. The IR-band due to adsorbed water arises as a result of water being released as a decomposition product and later gets adsorbed during the measurement. In the FTIR spectrum of $\text{g-C}_3\text{N}_4$, the broad band around 3100 cm^{-1} is indicating N–H stretching vibrations, the peaks at 1243 cm^{-1} and 1637 cm^{-1} were corresponding to the C–N and C=N stretching vibrations, respectively.

The peak at 808 cm^{-1} was related to the s-triazine ring vibrations [36–38]. All characteristic peaks of $\text{g-C}_3\text{N}_4$ and NaTaO_3 were observed in $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite samples.

Thermogravimetric analysis of the dried sample of pure $\text{g-C}_3\text{N}_4$ and as-prepared hybrid nanocomposite samples performed as shown in **Fig. 3**. As can be seen that the decomposition of $\text{g-C}_3\text{N}_4$ starts at 550°C and is completed at $\sim 720^\circ\text{C}$ could be attributed to the burning of $\text{g-C}_3\text{N}_4$. This weight loss region could be seen in the $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite samples. The amount of $\text{g-C}_3\text{N}_4$ in the hybrid nanocomposite was calculated from the corresponding weight loss. The $\text{g-C}_3\text{N}_4$ in loaded 5, 10 weight percentages of $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ were found 4.94 wt% and 9.87 wt%, respectively. Therefore, the amount of $\text{g-C}_3\text{N}_4$ was nearly consistent to the loaded composition of $\text{g-C}_3\text{N}_4$.

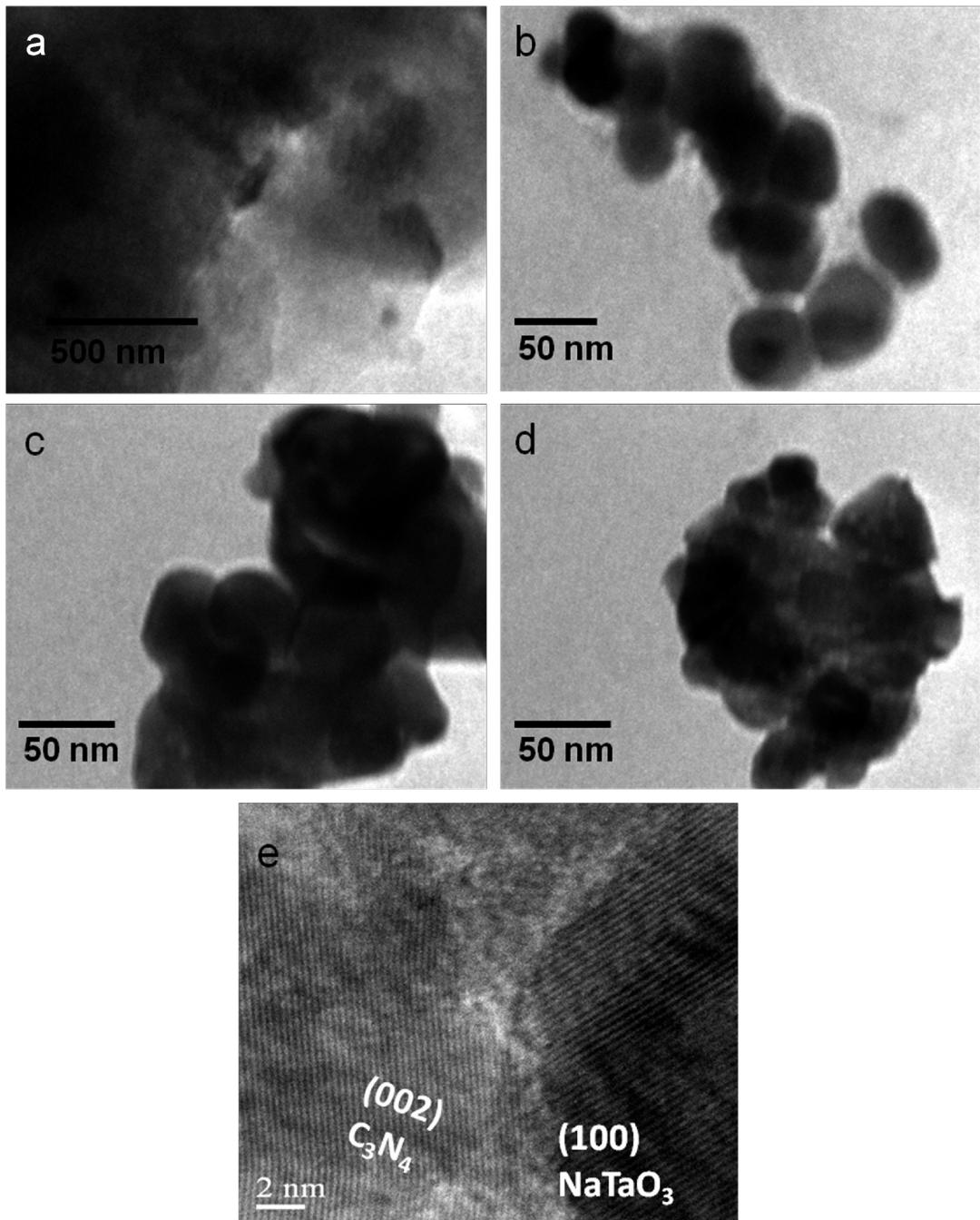


Fig. 5. TEM and HRTEM of the prepared pure $\text{g-C}_3\text{N}_4$, NaTaO_3 and $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalysts: (a) pure $\text{g-C}_3\text{N}_4$, (b) pure NaTaO_3 , (c) 5 wt% $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$, (d) 10 wt% $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ and (e) HRTEM of 5 wt% $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$.

The morphology and nanostructures of the prepared samples were then investigated by FESEM and TEM. Fig. 4 shows the FESEM images of NaTaO_3 nanoparticles and $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposites. It can be seen that the NaTaO_3 possesses cube morphology with high agglomeration. However, FESEM images have no enough resolution for the analysis of heterostructure and particle size distributions. TEM images (Fig. 5a) indicated that the average particle size of the prepared NaTaO_3 is 43 nm. Fig. 5b shows sheet structure of pure $\text{g-C}_3\text{N}_4$. The $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ nanocomposite showed almost similar morphology (Fig. 5c and d) as compared with NaTaO_3 nanoparticles. HRTEM studies confirm the formation of the interface between $\text{g-C}_3\text{N}_4$ and NaTaO_3 in the composite system (Fig. 5e). However, $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposites also exhibit a certain degree of particle agglomeration.

Fig. 6 shows the UV-vis diffuse reflection spectra of pure NaTaO_3 , $\text{g-C}_3\text{N}_4$ and as-prepared $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite samples. The pure NaTaO_3 and $\text{g-C}_3\text{N}_4$ samples show high photo-absorption in UV region around 314 nm and in visible region around 452 nm, consistent with white and light yellow colours, respectively. The $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite samples present photo-absorption in UV region around 320 nm as well as visible region around 460 nm, consistent with the pale yellow colour, suggesting that the composite catalysts have potential for the degradation of organic pollutants under visible light irradiation. The wavelength threshold is determined by elongating the baseline and steepest tangent of the UV-vis spectrum [39]. According to Kubelka Munk function, the band gap energies of pure NaTaO_3 and $\text{g-C}_3\text{N}_4$ estimated to be 3.95 eV and 2.74 eV, respectively [40]. However, these above band gap energies were observed in composite system. These are 3.92 eV and 2.71 eV in

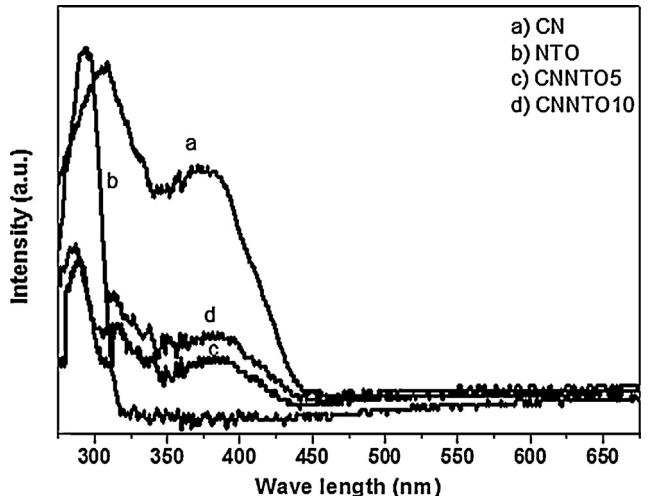


Fig. 6. UV-vis DRS of the prepared $\text{g-C}_3\text{N}_4$, NaTaO_3 , and $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalysts.

CNNTO5, and 3.87 eV and 2.69 eV in CNNTO10, respectively. A slight red shift in the band edge positions of NaTaO_3 and $\text{g-C}_3\text{N}_4$ may be due to hybridization with $\text{g-C}_3\text{N}_4$ which can act as a sensitizer, suggesting that the recombination rate of photoinduced electron-hole pair successfully suppressed in the $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposites.

Fig. 7 shows nitrogen adsorption-desorption isotherms of pure $\text{g-C}_3\text{N}_4$, NaTaO_3 and as-prepared $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ samples. The specific surface area of the NTO, CN, CNNTO5, and CNNTO10 was

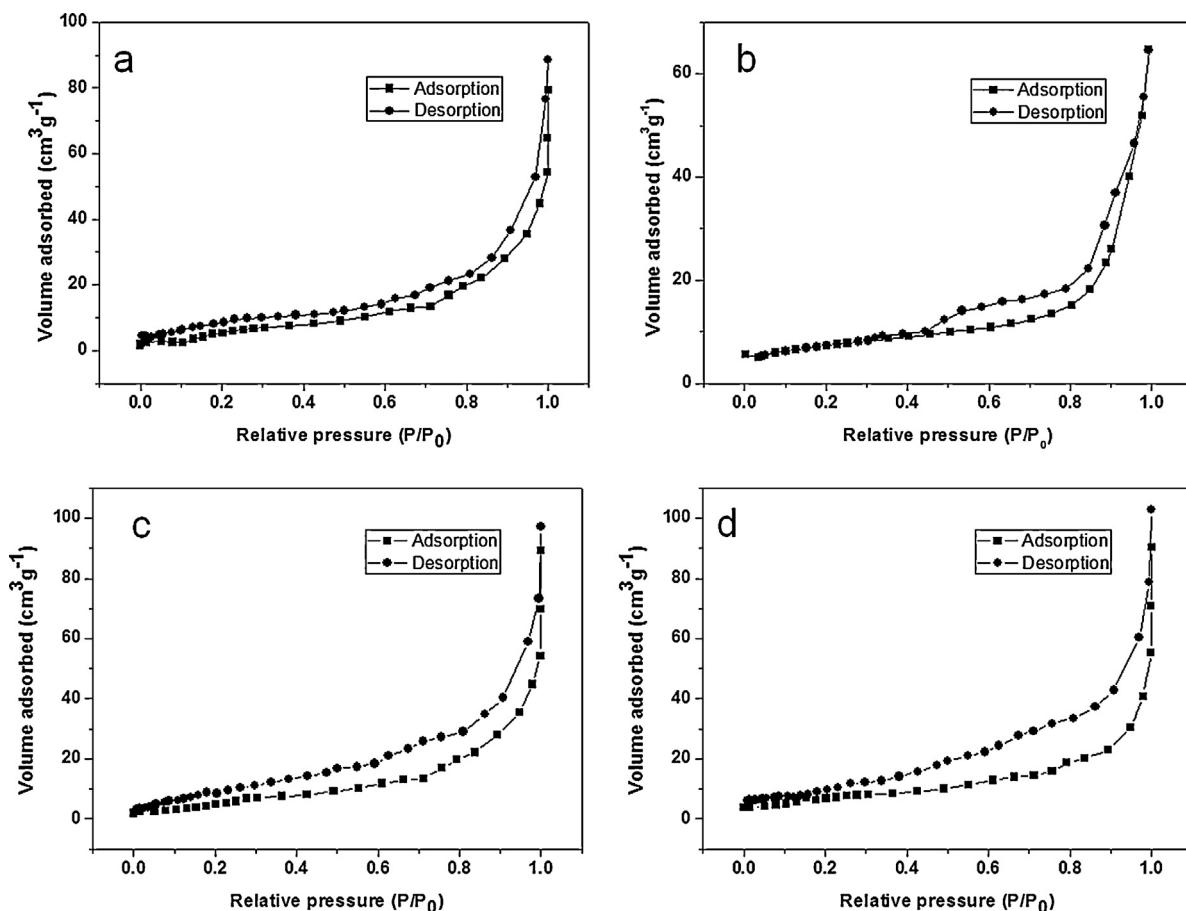


Fig. 7. Nitrogen adsorption-desorption isotherm of the prepared photocatalysts: (a) pure NaTaO_3 , (b) pure $\text{g-C}_3\text{N}_4$, (c) 5 wt% $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ and (d) 10 wt% $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$.

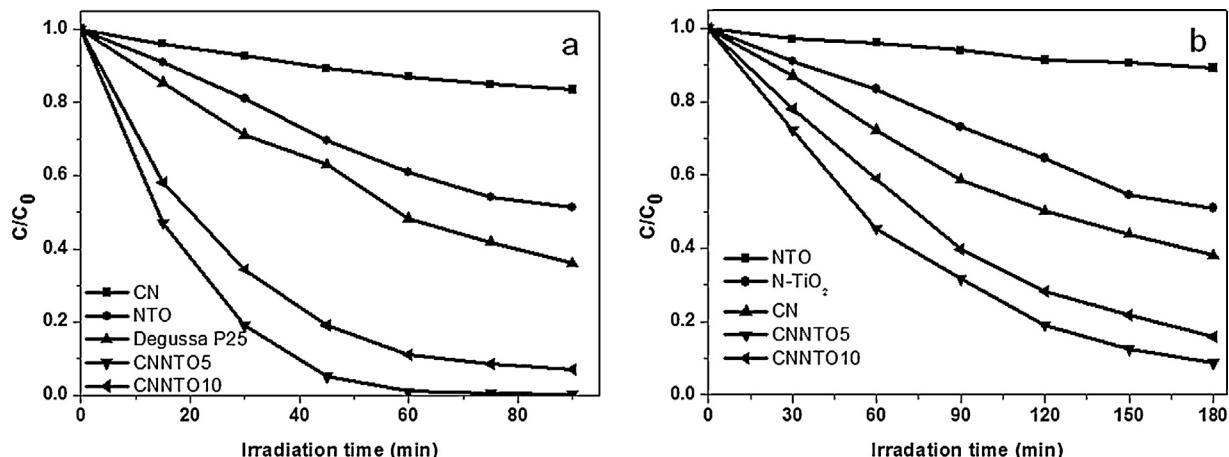


Fig. 8. (a) Comparison of photocatalytic activities of pure NaTaO_3 , $\text{g-C}_3\text{N}_4$, Degussa P25 or N-doped TiO_2 and $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ for the degradation of RhB: (a) UV-visible light and (b) visible light irradiation.

found to be $22.18 \text{ m}^2 \text{ g}^{-1}$, $8.13 \text{ m}^2 \text{ g}^{-1}$, $23.26 \text{ m}^2 \text{ g}^{-1}$ and $24.38 \text{ m}^2 \text{ g}^{-1}$, respectively. Relatively, large specific surface area of the hybrid nanocomposite is useful for the better adsorption of organic compounds and also provides more number of reactive sites for photocatalytic process, thereby enhances the photocatalytic activity.

3.2. Photocatalytic activity

Fig. 8 shows the photocatalytic degradation of RhB with different photocatalyst under both UV-visible and visible light irradiation. The as-prepared $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposites exhibits significantly enhanced photocatalytic activity compared to pure NaTaO_3 , $\text{g-C}_3\text{N}_4$ and Degussa P25 (commercial TiO_2) under UV-visible light irradiation as shown in Fig. 8a. The dramatic photocatalytic activity is generated under visible light irradiation is due to the loading of $\text{g-C}_3\text{N}_4$ in which electron excited from VB to CB could directly inject into the CB of NaTaO_3 , making $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ visible light driven photocatalyst. The visible light photocatalytic activity of CNNTO5 is much higher than that of pure $\text{g-C}_3\text{N}_4$ as well as commercial N-TiO₂. However, pure NaTaO_3 did not show the activity under visible light irradiation. The highest photocatalytic activity was obtained for CNNTO5 under both UV-visible and visible light irradiation. The blank test demonstrates that the irradiation without photocatalyst has little effect on the degradation process, suggesting the excellent photocatalytic

activity of the hybrid nanocomposites under both UV-visible and visible light irradiation. The enhanced photocatalytic activity may be due to enhanced charge separation efficiency in the $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ system.

3.3. Reusability

The reusability of a photocatalyst can be considered as one of the important factors for practical applications. Interestingly, the $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalysts can be easily reused by simple filtration or low-speed centrifugation and thus avoids the second pollution. To study the reusability of the 5 wt% $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalyst, five successive photocatalytic experimental runs were carried out by adding used photocatalyst to fresh RhB solutions with no change in overall concentration of the catalyst under both UV-visible and visible light irradiation. The photocatalytic activity of 5 wt% $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite photocatalyst is retaining over 90% of its original activity after five successive experimental runs in both UV-visible and visible light irradiation as shown in Fig. 9. The XRD studies were performed for reused $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalyst (after five successive experimental runs) and no change was observed in the resulting spectrum which indicates the high structural stability of $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ (Fig. 10). Therefore, $\text{g-C}_3\text{N}_4/\text{NaTaO}_3$ nanocomposites can be used as high-performance visible light photocatalysts for environmental applications.

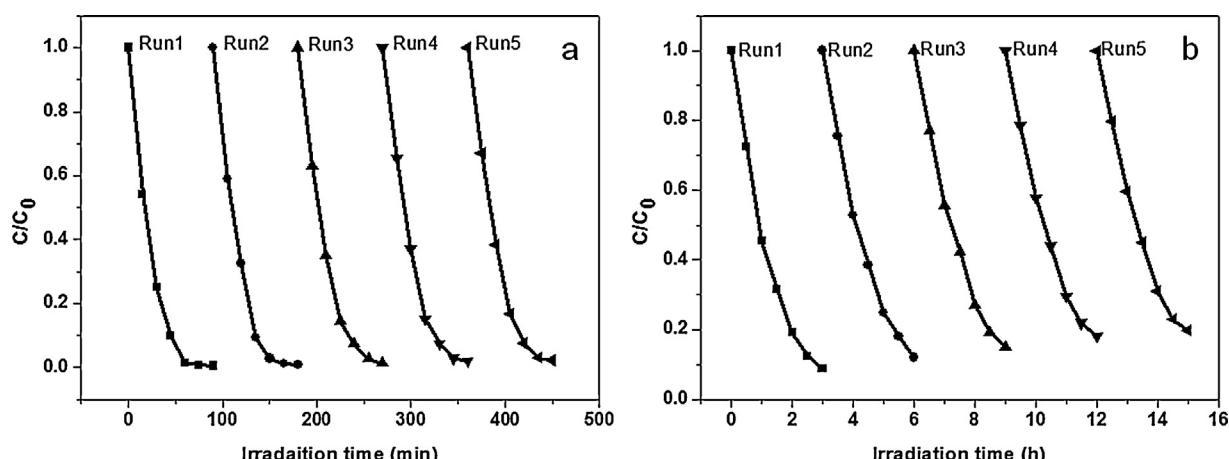


Fig. 9. Recyclability of CNNTO5 photocatalyst (five successive experiments) for the degradation of RhB: (a) UV-visible light and (b) visible light irradiation.

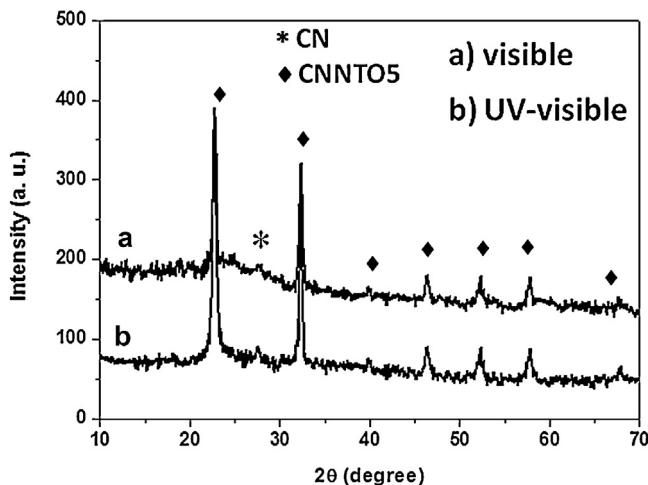


Fig. 10. The XRD pattern of the reused CNNT05 sample after five successive experimental runs.

3.4. Mechanism for the enhanced photocatalytic activity of $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite

It is well known that phase structure, adsorption, and efficient charge separation of photoinduced charge carrier can play an important role for the enhancement of photocatalytic performance under light irradiation [41–44]. Our results clearly show that the crystal phase structure of NaTaO_3 was not changed after the hybridization with $g\text{-C}_3\text{N}_4$. The adsorption ability of the NaTaO_3 and $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalysts was also investigated in the dark condition for 30 min duration. The adsorption ability of $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalyst significantly higher than that of pure NaTaO_3 photocatalyst, indicating the adsorption of RhB in composite system is not simple physical adsorption but it is also contributed from $\pi\text{-}\pi$ stacking between RhB and $g\text{-C}_3\text{N}_4$ which similar to the conjugation between aromatic molecules and graphene [45]. The enhanced adsorption ability was attributed for higher photocatalytic activity of the $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite system.

It is important to find out the role of reactive species, to propose a pathway for photocatalytic reaction. The role of reactive species in the photocatalytic reaction can be studied by the radicals and holes trapping experiments. However, methanol and ammonium oxalate (AO) can be used as radicals' scavenger and holes scavenger, respectively. As shown in Fig. 11a, a small change in

the photocatalytic activity of the as-prepared CNNT05 was observed under UV-visible light irradiation by addition of methanol as $^{\bullet}\text{OH}$ scavenger, whereas the photocatalytic activity was greatly suppressed by addition of AO as holes scavenger, indicating the photoinduced holes were primary reactive species in the $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite system under UV-visible light irradiation. On the contrary, the photocatalytic activity was highly suppressed by the addition of methanol as shown in Fig. 11b. However a small change in the activity was also observed by the addition of AO. These results clearly indicate that photoinduced radicals were primary reactive species in $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite system under visible light irradiation.

On the basis of our experimental results, a proposed mechanism is discussed to explain the enhanced photocatalytic activity of the as-prepared $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ nanocomposites for the degradation of RhB under both UV-visible and visible light irradiation. This is due to synergistic effects at interface of the $\text{NaTaO}_3/g\text{-C}_3\text{N}_4$. First, the high charge separation efficiency may be due to the energy level match between $g\text{-C}_3\text{N}_4$ and NaTaO_3 . According to the previous reports, the redox potential of both conduction band ($E_{\text{CB}} = -1.3$ eV vs. NHE) and valence band ($E_{\text{VB}} = +1.4$ eV vs. NHE) of $g\text{-C}_3\text{N}_4$ are more negative than those of conduction band ($E_{\text{CB}} = -0.98$ eV vs. NHE) and valence band ($E_{\text{VB}} = +2.96$ eV vs. NHE) of NaTaO_3 [34,46]. A scheme for the separation and transport of photoinduced charge carrier at the interface of the $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ under UV-visible and visible light is shown in Figs. 12 and 13, respectively. As the $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalyst is irradiated with UV-visible light, the photoinduced holes migrates from NaTaO_3 to the valence band (VB) of $g\text{-C}_3\text{N}_4$, suppressing the electron–hole pair recombination. The photoinduced holes on NaTaO_3 could oxidize polluted dyes effectively. The photoinduced electrons in conduction band of NaTaO_3 can also migrate to the conduction band of $g\text{-C}_3\text{N}_4$ thereby reaches the surface of $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite photocatalyst where the electrons could reduce adsorbed surface O_2 to form various reactive oxygen species, thus could assist the degradation of organic pollutants. As a result, the enhanced photocatalytic activity is observed over $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite under UV-visible light irradiation by suppressing the charge recombination. Under visible light irradiation, a high-energy photon excites an electron from the VB to CB of $g\text{-C}_3\text{N}_4$. The photoinduced electrons in $g\text{-C}_3\text{N}_4$ could directly inject into the CB of NaTaO_3 , reaches the catalyst surface where the electrons could reduced adsorb surface O_2 to various reactive species, thus could greatly enhance activity. Meanwhile, holes can transfer to the VB of $g\text{-C}_3\text{N}_4$ conveniently and assist in the

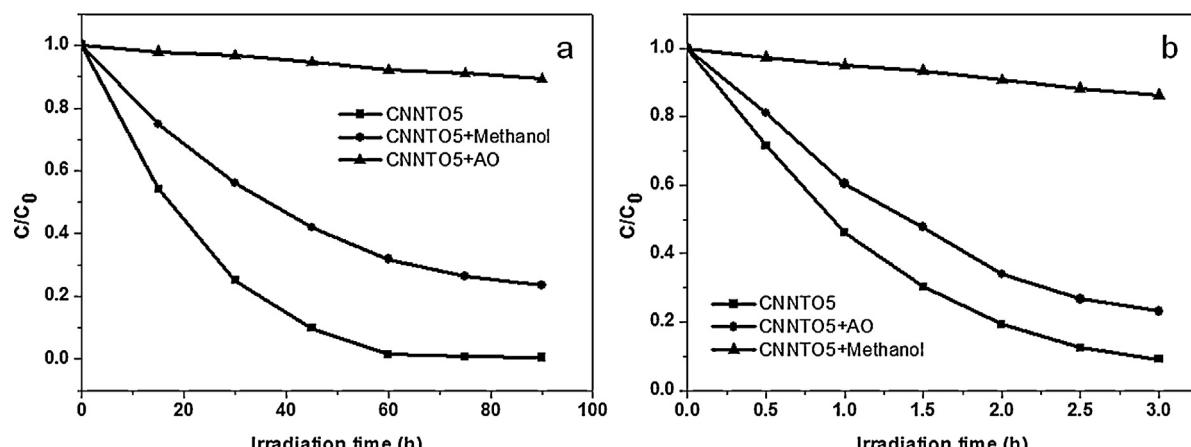


Fig. 11. The plots of photogenerated carriers trapping in the system of photodegradation of RhB by NaTaO_3 and $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$: (a) UV-visible light and (b) visible light irradiation.

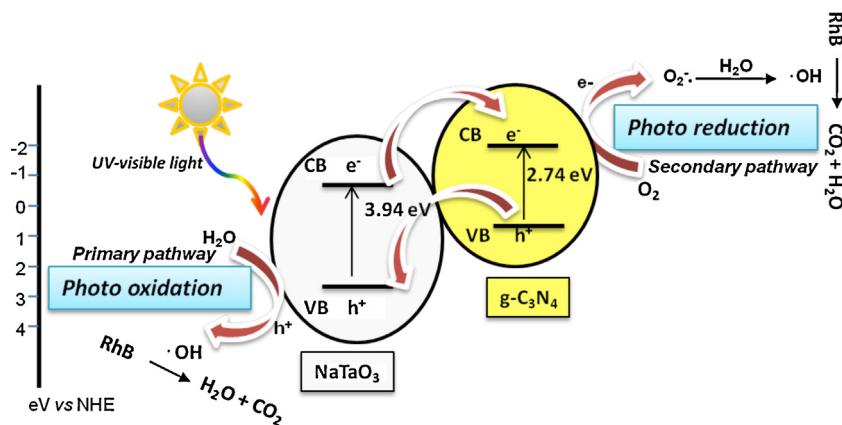


Fig. 12. Schematic drawing illustrating the mechanism of charge separation and photocatalytic activity of the $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalyst under UV-visible light irradiation.

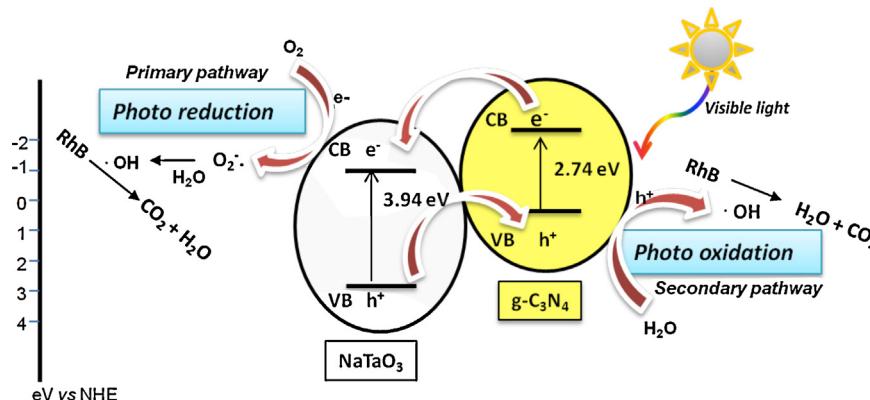


Fig. 13. Schematic drawing illustrating the mechanism of charge separation and photocatalytic activity of the $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalyst under visible light irradiation.

degradation of organic pollutant. As a result, the photogenerated electrons in $g\text{-C}_3\text{N}_4$ could directly inject into the CB of NaTaO_3 , making $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ visible light driven photocatalyst. Hence dramatic photocatalytic activity is generated over $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite under visible light irradiation. Therefore, $g\text{-C}_3\text{N}_4$ can act as both electron acceptor and donor. Interestingly, the efficient electron migration from NaTaO_3 to $g\text{-C}_3\text{N}_4$ also promotes structural stability of the $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalyst by keeping electrons away from NaTaO_3 . This effective charge separation by band potentials between two semiconductors is also reported in other systems, such as $g\text{-C}_3\text{N}_4/\text{TaON}$ [47]. The $g\text{-C}_3\text{N}_4$ can act as an electron reservoir to trap electrons emitted from NaTaO_3 particles due to irradiation by UV-visible light, thus protecting the electron–hole pair from recombination probability in the $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite. These above aspects together attributed for the enhanced photocatalytic activity and improved stability of the novel $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ photocatalyst.

4. Conclusion

In summary, we have successfully prepared novel $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ nanocomposites by a facile ultrasonic dispersion method. Our results clearly show that the crystal structure and morphology of NaTaO_3 are not changed during the hybridization. Interestingly, the hybrid nanocomposites exhibited significantly enhanced photocatalytic activity for the degradation of RhB under both UV-visible and visible light irradiation. The highest efficiency was observed for 5 wt% $g\text{-C}_3\text{N}_4/\text{NaTaO}_3$ hybrid nanocomposite. The high photocatalytic performance could be attributed to synergistic

effects which promote the migration efficiency of photoinduced electron–hole pair at the interface of the $\text{NaTaO}_3/g\text{-C}_3\text{N}_4$. More importantly, the as-prepared nanocomposite possesses high reusability. Therefore, it can be used as a promising photocatalyst for practical applications in environmental purification and clean hydrogen energy production from water splitting.

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