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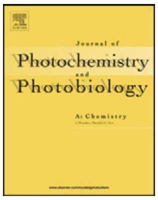

# Synthesis and structural features of mesoporous $NiO/TiO_2$ nanocomposites prepared by sol–gel method for photodegradation of methylene blue dye

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ABSTRACT

A novel series of mesoporous $NiO/TiO_2$ nanoparticles was successfully synthesized by sol–gel method using cetyltrimethylammonium bromide as controlling template in attempts to study the photodegradation of methylene blue dye. Structural and textural features of the composite samples were investigated by X-ray diffraction (XRD), nitrogen adsorption–desorption isotherm, Fourier transformer infra-red (FTIR) and transmission electron microscope (TEM). The band energy gap of the samples was estimated using UV–vis spectrometer. A remarkable reduction in particle size to 4 nm and increasing the surface area up to 220 $m^2/g$ is detected upon increasing nickel oxide contents revealing the successful role of dopants in controlling the crystal growth and pore structure of the catalyst. Nearly complete mineralization of methylene blue dye occur significantly at higher rate over doped samples compared with pure titanium oxide. The degradation of the dye follows a pseudo first-order kinetics and the apparent rate constant increases with increasing the nickel oxide content up to 5 mol%. The exceptional photocatalytic activity of the samples was attributed to reduction in particle size, increasing in surface area, photoelectron/hole separation efficiency and the extension of the wavelength range of photoexcitation.

## 1. Introduction

The existences of hazardous organic dyes and phenolic compounds in water wastes, soil and air is a primary cause of serious problems that concerned with human health and environmental problems that require a complete removal of these toxic and carcinogenic organic material [1,2]. Nano titanium oxide is the most suitable candidate photocatalyst that extensively involved in degradation and complete mineralization of various toxic organic pollutants [3,4] owing to its high efficiency, strong oxidizing power, non-toxicity, high photochemical and biological stability, corrosive resistance and low cost [5,6]. As $TiO_2$ is illuminated by light with energy higher than its band gap, the electrons will jump from the valence band to the conduction band that accompanied with formation of negative electron ($e^-$) and the positive hole ($h^+$) pairs on the photo catalyst surface [7–10]. The main purpose of the mineralization process is to enhance a reaction between the activated electrons with an oxidant to produce a reduced product, and also a reaction between the generated holes with a reductant to produce an oxidized product. In addition, the photocatalytic process involves formation of many active species as superoxide radical anion $O_2^{-\bullet}$ and $OH^\bullet$ radicals which are responsible for the heterogeneous $TiO_2$ photodecomposition of several organic dyes [11–14]. The photocatalytic efficiency of titania is hampered by two main drawbacks which are the rapid recombination of photogenerated electron and hole pairs and its wide band gap energy that limit its application to UV region only. Several authors report that modifications of titanium oxide by transition elements improve its optical activity by narrowing the energy band gap, extending the absorption to visible region and prevent the electron–hole recombination [15,16]. Tada et al. prepare iron oxide modified anatase and anatase-rutile titania by ligand exchange method and they indicate that the existence of ferric oxide chemisorbed on titania surface improves the photocatalytic response of the samples under both the ultraviolet and visible light. Moreover, they indicate that the surface iron oxide species rapidly capture the excited electrons in the conduction band of $TiO_2$ to suppress recombination via surface oxygen vacancy levels [17,18]. Nickel oxide is an interesting p-type transition element semiconductor that possesses unique catalytic, electric and magnetic properties that extend its application in many industrial fields [19,20]. Recently, several authors pointed that mixing of p-and n-type semiconductors create composites with exceptional electrical and optical features [21,22]. Nakhate et al. prepare $Ni_xTiO_2$ by hydrothermal method and they indicate that the prepared catalyst exhibit high photocatalytic activity in degradation of methylene blue compared with pure titanium oxide [23]. Woo et al. indicate that doping nickel oxide with titania improve the photocatalytic activity in 4-chlorophenol degradation [24]. The photocatalytic activity of pure and doped titania is more

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influenced by its surface area and pore structure. More emphasize has been paid on mesoporous nano titanium oxide owing to its particular pore structure. This structure exhibit high ability to interact with atoms, ions and molecules exist in the nano large surface as well as throughout the bulk structure which maximize the performance of these materials in many photocatalytic processes [25]. Several methods are proposed for synthesis of photocatalytic active mesoporous nanocomposites as hydrothermal [26], sol–gel [27], solvothermal [28] and surface coating [29]. Sol–gel was considered the most successful method in creating nanoparticles system with controlled pore structure. This method involves two stages which are hydrolysis of metal precursors and condensation of gel particles. The resulting material is usually amorphous hydroxide which converted into crystalline oxide by calcinations. However, a progressive agglomeration of particles is usually occurs during the calcinations stage which may lead to disorder large particle system. The existence of template agent provides a desirable solution in preventing the particle agglomeration and fabricate define nanocomposites shape [30,31].

Although several studies were performed on degradation of methylene blue over titania doped transition elements. However, there is a lack in literature on deep studies on investigation the role of existence of various molar composition of nickel oxide on the physicochemical and photocatalytic features of mesoporous titania nanoparticles. In the present work, we make an attempt to synthesize novel mesoporous NiO/$TiO_2$ nanoparticles with definite pore structure by sol–gel route using cetyltrimethylammonium bromide template. The composite samples were investigated using powerful techniques as FTIR, X-ray, BET and TEM to assist the role of the existence of different compositions of nickel oxide on the structure, particle size, pore texture, morphology and optical features of the composite samples. Moreover, the photocatalytic degradation of methylene blue dye over the novel mesoporous nanocomposites is estimated using UV–vis spectrophotometry.

## 2. Experimental

An appropriate amount of titanium chloride (Aldrich, 99.9%) and nickel acetylacetonate (Aldrich, 99%) were dissolved in ethanol by certain proportion in order to obtain 0, 1, 2, 5 and 10 mol% NiO. An appropriate amount of cetyltrimethylammonium bromide surfactant dissolved in ethanol is added to the above solution at level just below its critical micelle concentration above which micellization process occur, then the mixture solution is subjected to vigorous stirring for 3-h. A diluted solution of ammonia was subsequent added drop by drop to the above solution until the turbid sol start to appear. The sol mixture was left for 48 h for aging in air until the gel particles were detected. Filtration and successive washing with de-ionized water was repeated several times to remove both ammonia and chloride ions until all chloride ions had been removed (by examining the filtrate solution using aqueous silver nitrate solution). The gel was then dried in an oven at 100 °C for 24 h to remove the physical adsorbed species. Finally, the samples were calcined at 800 °C for 3 h to ensure the complete decomposition of the organic surfactant, stabilize the mesostructure of the porous materials and induce crystallization of particles. The pure composite sample was denoted as $TiO_2$ and the composite samples denoted as TN1, TN2, TN5 and TN10 corresponding to samples contain 1, 2, 5 and 10 mol% nickel oxide contents, respectively.

### 2.1. Material characterization

Fine and homogeneous powders of the different samples were back-loaded into the sample holder of a P Analytical X'PERT MPD diffractometer using Cu ($K\alpha_1/K\alpha_2$) radiation. The XRD patterns were recorded in a diffraction angle range from 20° to 100° with a step of 0.03° and integration time of 4 s per step. The diffraction patterns have been treated with the Rietveld refinement method using the MAUD program. The instrumental imperfections were evaluated with a sample of LaB6 calibrated against a sample of NIST SRM-640b and provided by the Gem Dugout Company.

Fourier-transform infrared (FT-IR) spectra were measured at room temperature on an ATT Mattson series FT-IR TM spectrometer using the KBr disk technique.

- Adsorption–desorption isotherms of purified $N_2$ at 77 K were determined using a conventional volumetric apparatus connected to a vacuum system that allowed prior outgassing to a residual pressure of $10^{-5}$ Torr.
- The evolution of the morphology and particle size of the nano mixed oxide powders was examined by transmission electron microscopy TEM using a JEOL 2000FX microscope.
- Photocatalytic activity of the composites was investigated by degradation of methylene blue under high pressure mercury lamp with maximum absorption at 254 nm. The initial concentration of MB was $1 \times 10^{-5}$ mol/l. The dosage of the $TiO_2$ powders was 0.1 g for 100 ml MB solution. Before switching on irradiation, MB solution was continuously stirred in the dark for 30 min to ensure adsorption–desorption equilibrium. The solution samples were collected from the reactor at regular intervals, centrifuged and analyzed to determine the amounts of remainder MB after photo-irradiation, using UV–vis spectrophotometer. The photocatalytic degradation rate (DC) was calculated by the following formula:

$$\mathrm{DC} = \frac{C_0 - C_t}{C_0} \times 100\%$$

where $C_0$ is the initial concentration of methylene blue solution which reached absorbency balance and $C_t$ is the concentration of the methylene blue dye solution at the irradiation time ($t$).

## 3. Results and discussion

### 3.1. X-ray diffraction

Fig. 1 depicts the X-ray diffraction pattern of pure and mixed oxide samples. Several peaks are observed at $2\theta = 25.3°$, 36.9°,

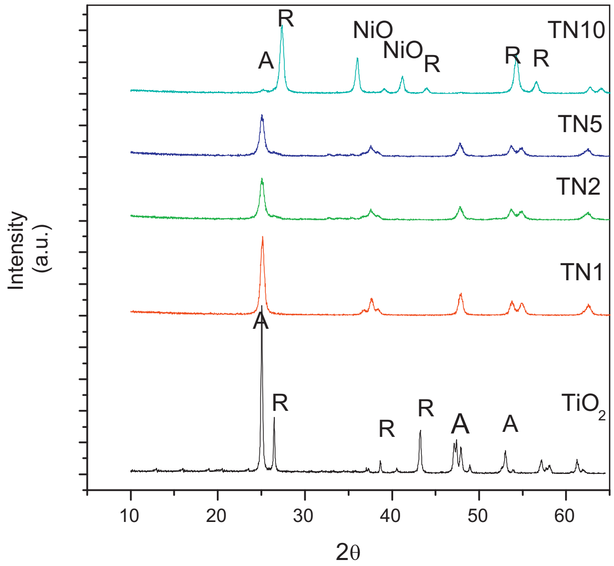

**Fig. 1.** X-ray diffraction of $TiO_2$, TN1, TN2, TN5 and TN10 [A, anatase; R, rutile].