Synthesis, characterization and photocatalytic activity of alkaline earth metal doped titania

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Received 17 March 2010; revised and accepted 26 August 2010

The synthesis of beryllium doped titania (Be\textsuperscript{2+}–TiO\textsubscript{2}) at different percentages (0.25, 0.5, 0.75 and 1.0 wt %) by sol-gel method and its characterization by XRD, UV-visible absorption spectroscopy, XPS, SEM and FT-IR techniques are reported. Diffraction peaks of anatase crystalline phase have been observed both in synthesized TiO\textsubscript{2} as well as in Be\textsuperscript{2+}–TiO\textsubscript{2}. Presence of Be\textsuperscript{2+} ions in the TiO\textsubscript{2} structure causes significant absorption shift towards the visible region. FT-IR and XPS data show the interstitial presence of Be\textsuperscript{2+} ion in TiO\textsubscript{2}. The photocatalytic efficiency of the synthesized Be\textsuperscript{2+}–TiO\textsubscript{2} and unsubstituted TiO\textsubscript{2} has been evaluated by the degradation of monocrotophos pesticide under visible light irradiation, wherein the degradation rate of MCP by Be\textsuperscript{2+}–TiO\textsubscript{2} is found to be higher than by unsubstituted TiO\textsubscript{2}. This may be attributed to the more efficient electron-hole creation in Be\textsuperscript{2+}–TiO\textsubscript{2} in visible light, as compared to unsubstituted TiO\textsubscript{2} which can be excited only by UV irradiation. The effect of dopant concentration, pH, catalyst dosage and pollutant concentration have been studied for obtaining optimal degradation conditions.

Keywords: Catalysts, Photocatalysts, Titania, Beryllium

Water purification by semiconductor photocatalysis is attracting a great deal of interest from research workers and water purification companies. There are several semiconducting materials readily available, amongst which TiO\textsubscript{2} has proven to be most suitable in different media for wide spread applications\textsuperscript{1,2}. Although TiO\textsubscript{2} is superior to other semiconductors\textsuperscript{3-5} for many practical uses, its high band gap (3.2 eV), which can be excited only by UV light, restricts the efficient usage of the highly available visible light. To circumvent this particular limitation, a number of strategies have been proposed to improve the light absorption features and lengthen the charge-carrier life time characteristics of TiO\textsubscript{2} such as surface chelation\textsuperscript{6}, surface derivatisation\textsuperscript{7}, platinisation\textsuperscript{8} and selective doping\textsuperscript{9}. In recent years, impurity doping has been widely used to improve photoactivity\textsuperscript{10}. Since metal elements have different valences, metal ions doped in the TiO\textsubscript{2} matrix can be superficial potential traps of photogenerated charge carriers and lengthen the life time of electron-hole pairs and increase photocatalytic activity.

Karakitsou and Verykios\textsuperscript{11} showed that doping with cations having a valence higher than that of the parent TiO\textsubscript{2} cation results in enhanced light absorption at the near UV region, while doping with lower valence cations exhibit a somewhat enhanced light absorption capacity in the visible range. On the other hand Mu et al.,\textsuperscript{12} reported that doping with trivalent or pentavalent metal ions was detrimental to the photoactivity even in the UV region. There have been many studies on transition metal, noble and rare earth metal ions as dopants\textsuperscript{13,14}. Doping with alkaline earth metal ions has been less explored compared with other metal ions. Also limited literature reports are available that the doped catalyst was tested only in the UV range of radiation\textsuperscript{15}. Hence, in the present study doping of TiO\textsubscript{2} with beryllium (Be\textsuperscript{2+}) ion has been taken up.

Since beryllium is an acceptor atom, a P-type semiconductor is created on doping with TiO\textsubscript{2}. A P-type semiconductor has Fermi energy levels, which are closer to the valence band and enhance charge transfer during absorption of visible light. Hence, beryllium has been selected as dopant and tested in visible region.

The properties and photocatalytic activity of a photocatalyst are greatly influenced by their preparation methods. Previous workers have developed numerous techniques for fine TiO\textsubscript{2}
powders preparation which includes vapor decomposition, hydrolysis, hydrothermal treatment, hydrolysis, oxidation, hydrothermal oxidation, mechanical alloying, co-precipitation and impregnation and sol-gel method. Sol-gel process permits fabrication of oxide materials under mild conditions and with a wide range of adjustable experimental parameters. The sol-gel approach permits infinite variations of the composition, structure and properties of the oxide matrices themselves. Sol-gel methods can be used to introduce a seemingly unlimited array of guest species (dopants), including a wide array of metal complexes, into oxide materials. Basing on the literature survey and limitations in the established processes, we have selected sol-gel method for doping of metal into TiO₂ and evaluated its photocatalytic efficiency in the degradation of monocrotophos pesticide, an endocrine disruptor.

**Materials and Methods**

**Preparation of photocatalysts**

Titanium tetra-n-butoxide [Ti(O-Bu)₄] and beryllium nitrate obtained from E. Merck (Germany) were used as titanium and beryllium sources for preparing anatase TiO₂ and Be²⁺–TiO₂ photocatalysts. Monocrotophos solution was used as a model compound for degradation. All chemicals used in this work were of analytical grade and doubly distilled water was used for the solution preparation.

Initially 21.0 ml of titanium tetra-n-butoxide was dissolved in 80.0 ml absolute ethanol (100%) and the resulting solution was stirred vigorously. Then 2.0 ml of water and 0.5 ml of acetic acid (50%) were added to another 80.0 ml of ethanol to make an ethanol-water-acetic acid solution. This solution was slowly added to the Ti(O-Bu)₄-ethanol solution under vigorous stirring. When the resulting mixture turned to sol, the beryllium nitrate solution (0.25, 0.5, 0.75 and 1.0 wt.%) was added dropwise.

The resulting transparent colloidal suspension was stirred for more than 2 h and was aged at 25 °C until the formation of gel. The gel was dried at 70 °C in vacuo at a pressure of 600 psi and then ground. The resulting powder was calcined at 400 °C for 2 h in 50 °C increments for every 30 min until temperature of 400 °C was attained. After calcination period, the furnace was allowed to cool for 2 h. The calcined powders were crushed using an agate mortar and pestle under similar conditions in an attempt to produce powders with similar ‘fineness’ and particle size distributions.

An unsubstituted TiO₂ sample was also prepared by adopting the above procedure without adding the metal nitrate. The doping concentrations are expressed as weight percentage. The powders were stored in black coated air-tight glass containers and were used for XRD analysis, UV-visible absorption studies, XPS, SEM, FT-IR studies and for evaluating the photocatalytic activity.

**Characterization of photocatalysts**

The crystal phase composition of the prepared photo catalysts (TiO₂, Be²⁺–TiO₂) was determined by X-ray diffraction measurement carried out at room temperature using a PANalytical, D/Max- III A diffractometer with CuKα radiation (λ = 0.15148 nm) with a liquid nitrogen gas-cooled germanium solid state detector. An accelerating voltage of 35 kV and emission current of 30 mA were used, and studied in the range of 2θ = 2 - 65° with a step time of 0.1°/s. To study the valence state of the photocatalysts, X-ray photoelectron spectroscopy (XPS) was recorded with a PHI quantum ESCA microprobe system, using the AlKα line of a 250 W X-ray tube as a radiation source with the energy of 1253.6 eV, 16 mA × 12.5 kV and a working pressure lower than 1 × 10⁻⁸ Nm⁻². As an internal reference for the absolute binding energies, the C 1s peak of hydrocarbon contamination was used as reference to 284.8 eV. The fitting of XPS curves was analyzed with Multipak 6.0 A software. UV-visible absorption spectra of the samples were obtained using a Schimadzu, UV-2101 spectrophotometer, to study the optical absorption properties of the photo catalysts. The spectra were recorded at room temperature in the wavelength range 250-850 nm. The infrared spectra of the synthesized samples were recorded on Thermo Nicolet Nexus 670 spectrometer, with a resolution of 4 cm⁻¹ in KBr pellets.

**Photoreactor and catalytic activity of the catalysts**

The apparatus employed in the photo catalytic experiments has been described in detail elsewhere. It consists of light source with 400 W high pressure mercury vapour lamp emitting predominantly visible radiation at a wavelengths between 436 and 546 nm with 35000 lumen. Cutoff filters were placed (in the path of the light) before the sample container for complete removal of UV radiation. A UV filter Oriel 51472 was used and a running water was
circulated around the sample container to filter IR radiation\textsuperscript{29} and also to keep the reaction mixture at room temperature.

The photoreactor system was used to study the photocatalytic degradation of monocrotophos pesticide in the presence of visible light, using the doped and un-doped TiO\textsubscript{2} photocatalysts. The required amount of catalyst was suspended in 100 ml of solution in a 150 ml Pyrex glass vessel with constant stirring, for uniform illumination of all the catalyst particles. The catalysts were agitated with a solution of monocrotophos for 45 min in the absence of light to attain the adsorption/desorption equilibrium on the catalysts surface.

The suspensions were then irradiated under visible light (wavelength range 436 – 546 nm). The distance between the light and the reaction vessel was 20 cm. At regular intervals of time, 5 ml of the aliquots were transferred into quartz curettes with 0.45 µm Millipore syringe for absorbance measurements.

The major degradation products of organophosphorus pesticides are PO\textsubscript{4}\textsuperscript{3-}, CO\textsubscript{2} and NO\textsubscript{3} ions\textsuperscript{30,31}, and their formation during the progress of the degradation of MCP was confirmed by simple qualitative analysis tests\textsuperscript{32}. The rate of formation of PO\textsubscript{4}\textsuperscript{3-} in the solutions can thus express the rate of degradation of organophosphorus pesticides\textsuperscript{33-37}. PO\textsubscript{4}\textsuperscript{3-} was determined calorimetrically by the molybdenum blue method\textsuperscript{35,36}.

Results and Discussion
Characterization of the catalysts

XRD patterns of unsubstituted TiO\textsubscript{2} and Be\textsuperscript{2+}–TiO\textsubscript{2} (0.25, 0.5, 0.75 and 1.0 wt.%) samples calcined at 400 °C are given in Fig. 1. The XRD patterns (JCPDS 89-4921) of unsubstituted TiO\textsubscript{2} and doped samples of 0.25 and 0.5 wt.% Be\textsuperscript{2+}–TiO\textsubscript{2} show peaks corresponding to the anatase form\textsuperscript{38}. In the case of 0.75 wt.% Be\textsuperscript{2+}–TiO\textsubscript{2} (Fig. 1b), peaks corresponding to anatase form and beryllium oxide are observed (JCPDS 03-1035)\textsuperscript{39}. This indicates the presence of excess of beryllium oxide which is formed during calcinations at 400 °C from beryllium nitrate on the undoped-TiO\textsubscript{2}. For 1.0 wt.% Be\textsuperscript{2+}–TiO\textsubscript{2}, (Fig. 1 a) no particular phase is formed. At higher doping the gel powder subjected to heat treatment at 400 °C for 2 h, showed only amorphous nature with no characteristic peaks related to TiO\textsubscript{2} anatase form; probably high temperature is required to force crystallinity. Higher temperature is also reported to favor rutile phase formation\textsuperscript{38,39}.

Preliminary photocatalytic activity studies with different wt.% of Be\textsuperscript{2+}–TiO\textsubscript{2} samples (0.25, 0.5, 0.75 and 1.0 wt.%) show less catalytic activity except the 0.5 wt% sample. For the 0.25 and 0.5 wt% samples, catalytic activity increased with increasing in Be content. However, further increase in Be content, i.e., 0.75 and 1.0 wt% led to a decrease in catalytic activity. Hence, 0.5 wt% Be doped catalyst was chosen for the further studies as this was the optimum dopant concentration showing catalytic activity investigated.

The UV-visible absorption spectra of 0.5 wt.% Be\textsuperscript{2+}–TiO\textsubscript{2} and unsubstituted TiO\textsubscript{2} are shown in Fig. 2. The absorption spectrum of unsubstituted TiO\textsubscript{2} consists of a single and broad intense absorption band at 380 nm due to charge-transfer from the valence band (mainly formed by 2p orbital of the oxide anions) to the conduction band (mainly formed by 3d\textsubscript{t\textsubscript{2g}} orbital of the Ti\textsuperscript{4+} cations)\textsuperscript{40}. The UV-visible absorption tailing spectrum of 0.5 wt.% Be\textsuperscript{2+}–TiO\textsubscript{2} reveal that beryllium doped TiO\textsubscript{2} absorb the photon energy in the range of 400-600 nm (visible region). Hence, it is considered as ‘red shift’.

The XPS analysis was carried out for unsubstituted TiO\textsubscript{2} and 0.5 wt.% of Be\textsuperscript{2+}–TiO\textsubscript{2} to determine the chemical composition of the catalysts. The XPS
spectrum of unsubstituted TiO$_2$ (Fig. 3a) shows the presence of Ti and O on the surface of TiO$_2$, while Fig. 3b shows the presence of Be$^{2+}$ along with Ti and O on the surface of 0.5 wt.% Be$^{2+}$–TiO$_2$. In both the spectra, the Ti 2p peaks are narrow with a slight asymmetry and have binding energies of 458.63 eV and 464.013 eV, attributable to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$. These values are consistent with those reported for titanium$^{41,42}$ in TiO$_2$. For the 0.5 wt.% Be$^{2+}$–TiO$_2$ sample, a binding energy of 113.602 eV (FWHM = 0.563) was observed for Be 1s, which is typical$^{43,44}$ of Be$^{2+}$. The O 1s peak can be resolved into two peaks, one at 528.9 eV and the other at 530.6 eV. The former can be attributed to absorbed hydroxyl groups and the latter to TiO$_2$ (refs. 45, 46).

The XPS data of 0.5 wt.% Be$^{2+}$–TiO$_2$ establishes the presence of Be$^{2+}$ in TiO$_2$ and absence of BeO peak, which explains that Be$^{2+}$ is doped interstitially rather than substituted into the TiO$_2$ lattice. The ionic radius$^{46}$ of Be$^{2+}$ (0.27 Å) which is smaller than both Ti$^{4+}$ (0.605 Å) and O$^{2-}$ (1.35 Å) also supports this.

The SEM images of unsubstituted TiO$_2$ and metal doped TiO$_2$ catalysts are shown in Fig. 4. The unsubstituted TiO$_2$ and 0.5 wt.% of Be$^{2+}$ impurity containing TiO$_2$ show the morphological changes with irregular shaped particles with an average particle size of 3.8 µm and 0.8 µm respectively. This clearly illustrates that the decrease in particle size increases in the surface area of the catalyst powders and enhances the photocatalytic activity.

FT-IR spectra of unsubstituted TiO$_2$ and 0.5 wt.% Be$^{2+}$–TiO$_2$ show the peaks corresponding to stretching vibrations of O–H and bending vibrations of adsorbed...
water molecules around 2910-3380 cm\(^{-1}\) and 1620-1625 cm\(^{-1}\) respectively. A broad peak appears at nearly 1200 cm\(^{-1}\), which can be attributed to the vibration modes of Ti-O-Ti. However, in Be\(^{2+}\)–TiO\(_2\) a peak is observed around 1320 cm\(^{-1}\), which may be due to shifting of Ti-O-Ti peak with addition of Be\(^{2+}\) impurity interstitially.

**Photocatalytic degradation of monocrotophos (MCP)**

To determine the photocatalytic efficiency of the Be\(^{2+}\)–TiO\(_2\) catalyst, the degradation of monocrotophos (MCP) pesticide was taken up as a model compound. Blank experiments conducted in the absence and presence of irradiation of the catalysts demonstrate that no significant change in the MCP concentration was observed (0.2 %) even after 10 h of irradiation. The efficiency of the photocatalytic degradation process depends on various experimental parameters such as catalyst dosage, initial concentration of pollutant and pH. Hence, it is important to establish optimum conditions to achieve higher degradation efficiency of the catalyst.

To determine an optimum impurity concentration for the degradation of MCP, a set of experiments was carried out, using catalyst with different impurity concentrations (1.0, 0.75, 0.5, and 0.25 wt.% of Be\(^{2+}\)–TiO\(_2\)). The optimum concentration of the impurity in the TiO\(_2\) was determined based on the photocatalytic activity of the catalyst in degradation of MCP. The percentage degradation of MCP, corresponded to the phosphate formed as one of the degradation product at different irradiation time intervals. It was quantified by the spectrophotometric absorption studies and the results (Fig. 5) indicate that when the impurity fraction of Be\(^{2+}\) in TiO\(_2\) increased, the rate of MCP degradation increased up to 0.5 wt.% of beryllium ions, further increase was detrimental to the degradation.

Degradation of monochrotophos was also carried out with unsubstituted TiO\(_2\) and Degussa P-25. No appreciable degradation was observed (Fig. 5) particularly in visible region. Also, no distinguishable photocatalytic activity reports are available in the literature for these two catalysts in visible region.

The results also illustrate that catalyst with 0.5 wt.% of Be\(^{2+}\) is the optimal impurity concentration. With 1.0 wt.% of Be\(^{2+}\)–TiO\(_2\) no photocatalytic activity is observed because there is no phase formation. However, in the case of 0.75 wt.% of Be\(^{2+}\)–TiO\(_2\), the photocatalytic activity decreases. This may be due to the recombination of the charge carriers which depends on distance R separating the e/h\(^{+}\) pair according to \(K_{\text{recombination}} \propto \exp (-2R/a_0)\), where \(a_0\) is the radius of the hydrogenic wave function of the trapped carriers. As a consequence, the recombination rate increases exponentially with the impurity concentration as the average distance between trap sites decreases with increasing number of impurity confined within a particle.

Since solution pH influences adsorption and desorption of the substrate, catalyst surface charge, oxidation potential of the valence band and other physicochemical properties, the catalyst-assisted photodegradation of MCP was monitored by in situ measurements of pH of the aqueous suspension with irradiation time, at a fixed weight of catalyst and MCP concentration at different pH values. It was observed that the degradation rate is higher in the acidic pH range (pH = 3.0 and 6.0) than in alkaline (pH = 8.0) (Fig. 6). At the end of the experiment there was a drop in pH, indicating the formation of acidic products.

On the surface of TiO\(_2\), titanol (Ti-OH) is present, which is amphoteric and occurs in an acid-base equilibrium as given below.

\[
\text{TiOH} + \text{H}^+ \quad \rightarrow \quad \text{TiOH}_2^+ \quad \text{pH} < 6.25
\]

\[
\text{TiOH} \quad \rightarrow \quad \text{TiO}^- + \text{pH} > 6.25
\]

In acidic environment, H\(^{+}\) ions are adsorbed onto the surface of TiO\(_2\), which has a large proton...
exchange capacity. The photo-generated electrons can be captured by the adsorbed H\(^+\) to form H\(_{\text{ads}}\). At higher pH, the surface of catalyst has a net negative charge due to a significant fraction of total surface sites present as TiO\(_-\) and hence the degradation rate was found to be less.

The effect of the amount of catalyst on the rate of photodegradation of MCP was investigated. At a fixed pH and initial concentration of the MCP, experiments were carried out by varying concentration of Be\(^{2+}\)–TiO\(_2\) from 0.1 – 1.1 g in 100 ml of aqueous MCP solution. The degradation pattern from such experiments reveals that the rate of degradation increases linearly with increase in the amount of catalyst up to 0.5 g, and then decreases (leveling off) (Fig. 7).

As the amount of catalyst increases, the number of photons and the number of MCP molecules adsorbed also increase due to increase in the number of catalyst particles leading to the increase in photocatalytic efficiency. However, as the catalyst loading is increased beyond an optimum concentration, the increase in the number of available sites is offset by a decrease in the penetration depth of radiation, due to higher opacity of the suspension and scattering effects by the catalyst particles. The deactivation of activated molecules by collision with ground state molecules may also hinder the photocatalytic efficiency\(^{48}\). Hence, at a certain level, additional catalyst amount may not be involved in catalysis and thus the rate levels off.

At a fixed concentration of the catalyst and pH, the effect of varying initial MCP concentration on photocatalytic degradation was studied and the results are presented in Fig. 8. It is observed that the degradation rate increases with increase in MCP concentration up to 50.0 mM (PO\(_4^3-\) = 515.3 mg) and a further increase in pesticide concentration leads to decrease in the rate of degradation. This may be due to decrease in the generation of •OH radicals on the catalyst surface as the active sites are covered by dye ions.
Photocatalytic mechanism

Based on the experimental results the following mechanism is proposed for the photocatalytic reactions of beryllium doped TiO₂.

i) Upon visible light illumination of photo catalyst, electrons are ejected from the valence band to the conduction band leaving positive holes in the valence band.

\[
\text{TiO}_2 + \text{hv} \rightarrow h^+_{vb} + e^-_{cb}
\]

ii) When the metal ion impurity is doped into TiO₂ lattice, these ejected electrons are trapped by impurity, eliminating the recombination process.

\[
\text{Be}^{2+} - \text{TiO}_2 + e^- \rightarrow \text{Be}^{+} - \text{TiO}_2 \quad \text{(unstable)}
\]

iii) The trapped electrons can be subsequently scavenged by molecular oxygen, which is adsorbed on the TiO₂ surface, to generate the superoxide radical, and this in turn produces hydrogen peroxide (H₂O₂), hydroperoxy (HO₂⁻) and hydroxyl (•OH) radicals.

\[
\begin{align*}
\text{Be}^{2+} - \text{TiO}_2 + \text{O}_2 & \rightarrow \text{Be}^{2+} - \text{TiO}_2 + \text{O}_2^- \\
\text{O}_2^- + \text{H}^+ & \rightarrow \text{HO}_2^- \\
\text{HO}_2^- + \text{O}_2^- + \text{H}^+ & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{H}_2\text{O}_2 + \text{e}^-_{\text{trapped}} & \rightarrow \text{•OH} + \text{OH}^- + \text{O}_2 \\
\text{OH} + h^+_{\text{vb}} & \rightarrow \text{•OH}
\end{align*}
\]

iv) The positive holes in the valence band act as good oxidizing agents available for degradation of pollutants in the solution.

\[
\text{•OH} \quad \text{(or h}^+_{\text{vb}}\text{)} + \text{Red} \rightarrow \text{Red}^+
\]

where ‘red’ is the pollutant, an electron donor (reductant).

Thus, the MCP is attacked by the hydroxyl radicals formed both by trapped electrons and hole in the VB as given in the above equations, to generate organic radicals or other intermediates.

Conclusions

The present study shows the significance of beryllium ion impurity doped into titania. It also establishes that doping of beryllium by sol-gel method is a good alternative. The study shows that doping causes better separation of electrons and holes on the doped TiO₂ and allows for more efficient channeling of the charge carriers into useful reductants and oxidants rather than recombination centers. The experimental results show that the photo catalytic activity of unsubstituted TiO₂ is lower than that of beryllium doped TiO₂. XRD patterns indicate the presence of anatase phase up to 0.5 wt.% Be²⁺–TiO₂, while 0.75 wt.% doping shows the presence of beryllium oxide along with anatase phase, the 1.0 wt.% catalyst does not show any anatase phase derived peak. The XPS data of 0.5 wt.% Be²⁺–TiO₂ establishes the presence of Be²⁺ in TiO₂ interstitially rather than by substitution, which shifts the FT-IR peak of Ti-O-Ti. SEM image of 0.5 wt.% Be²⁺–TiO₂ clearly illustrates the decrease in size and altered morphology. Due to decrease in size, there is increase in the surface area, which enhances the photocatalytic activity. The degradation of MCP with 0.5 wt.% beryllium doped titania was maximum at 0.5 g of Be²⁺–TiO₂ catalyst dosage, 50.0 mM MCP concentration and at pH = 3.

Acknowledgement

Authors are thankful for Dr. Ch. Subrahmanyam and Dr. Anandan, NIT, Trichy for providing UV-visible absorption data. One of the authors (ABK) is thankful to UGC, New Delhi, for providing necessary research funding.

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