Preparation and characterization of nitrogen doped K\textsubscript{2}M\textsubscript{2}Ti\textsubscript{6}O\textsubscript{16} (M = Cr and Fe) with enhanced photocatalytic activity

S Ramakrishna\textsuperscript{a}, N Mahender\textsuperscript{a}, J R Reddy\textsuperscript{a}, Sreenu Kurra\textsuperscript{a}, E Nagabhushan\textsuperscript{b} & M Vithal\textsuperscript{a, *}

\textsuperscript{a}Department of Chemistry, University College of Science, Osmania University, Hyderabad 500 007, India
Email: mugavithal@gmail.com

\textsuperscript{b}Department of Chemical Engineering, University College of Technology, Osmania University, Hyderabad 500 007, India

Received 18 April 2015; revised and accepted 24 July 2015

Hollandite type K\textsubscript{2}M\textsubscript{2}Ti\textsubscript{6}O\textsubscript{16} (M = Cr, Fe) oxides have been prepared and doped with nitrogen to increase its photocatalytic activity. The N-doped analogues have been synthesized by heating the mixture of K\textsubscript{2}M\textsubscript{2}Ti\textsubscript{6}O\textsubscript{16} and urea at 400 °C and characterized by powder X-ray diffraction, FT-IR, SEM-EDS and UV-visible diffuse reflectance spectra. The band gap energy of all the compounds has been obtained by their DRS spectra. The photocatalytic properties of the catalyst samples have been studied by the degradation of methylene blue under visible light irradiation.

Keywords: Photocatalysts, Band gap, Dye degradation, Nitrogen doping, Doping, Sol-gel method, Hollandite, Titanates, Oxides

The removal of organic dye pollutants from wastewater has been the subject of several investigations to protect the aquatic habitats and reduce the environmental pollution. Many industries based on textiles, printing, dyeing, food and cosmetics use dyes to color their products, which leads to expulsion of large quantities of organic pollutants into the aquatic habitats. Most of the dye pollutants are dangerous and create severe environmental pollution by releasing toxic substances into the aqueous phase and do not decompose quickly. For example, organic dyes such as methylene blue (MB), rhodamine B, methyl orange, remazol black B, acid red G, etc., are common contaminants of industrial wastewater. Among these, MB is widely used as a paper dye, microscopy stain, chemical intermediate, medicinal agent and cosmetic dye, which may result in its release to the environment through various waste streams. The presence of MB in water is harmful to the skin, eyes, respiratory tract and causes vomiting and anemia. Therefore, the removal of organic contaminants/dyes (MB) from aqueous systems is an important task for the protection of the environment and public health. Several investigations have been directed towards the development of novel, efficient and eco-friendly materials for the removal of harmful organic dye pollutants. Various physical and chemical methods such as chemical precipitation, ultra-filtration, flocculation, ion exchange and adsorption, etc., have been developed for the removal of dye pollutants from aqueous solutions. Photocatalytic technique using semiconductor as photocatalysts has been found to be an efficient method for the degradation of organic pollutants. Titanium dioxide (TiO\textsubscript{2}) has been intensively investigated as a photocatalyst for environmental clean-up and solar energy conversion. Titanium containing ternary and quaternary oxides are also investigated extensively due to their structural diversity and potential applications. For instance, alkali titanates form different types of tunnel framework structures suitable for photocatalytic, ion exchange, ferroelectric and fast ion conducting applications. One such tunnel structure is adopted by hollandites, a group of oxides in the M\textsubscript{2}O − M\textsubscript{3}III\textsubscript{2}O\textsubscript{16} − M\textsubscript{IV}O\textsubscript{16} system. Titanates belonging to the hollandite family, having the general formula M\textsubscript{2}M\textsubscript{′}\textsubscript{2}Ti\textsubscript{6}O\textsubscript{16}, exhibit many interesting physical and chemical properties. A few studies have been carried out on the synthesis and structure determination of these compounds. However, the photocatalytic studies of these titanate hollandites are less explored.

In the present investigation, we aimed to prepare hollandites, K\textsubscript{2}M\textsubscript{2}Ti\textsubscript{6}O\textsubscript{16} (M = Cr, Fe), using sol-gel method and increase its photocatalytic property by doping a foreign ion. Photo-absorption ability of the...
semiconducting material can be increased by doping with non-metal ions. For example, nitrogen is the most popular dopants because of its appropriate ionic radius with oxygen and the partial replacement of O\(^{2-}\) by N\(^{3-}\) narrows the band gap of the parent oxides by shifting their valence band upward.\(^{17,18}\) In addition, nitrogen doping has been proven to be a promising method, because the implantation of nitrogen creates oxygen vacancies which act as traps for excited electrons leading to a reduction in recombination rate of photo-induced electron-hole pairs.\(^{19}\) Therefore, in this work we present sol-gel synthesis, characterization and photocatalytic studies of parent and nitrogen doped K\(_2\)M\(_2\)Ti\(_6\)O\(_{16}\) (M = Cr, Fe).

**Materials and Methods**

Reagent grade and commercially available KNO\(_3\), Cr(NO\(_3\))\(_3\), Fe(NO\(_3\))\(_3\), and Ti powder were used as received starting materials for preparation of the studied compounds. The room temperature X-ray diffractograms of all samples were recorded using Rigaku MiniFlex 600 X-ray diffractometer (Cu-K\(_\alpha\), \(\lambda = 1.5406 \, \text{Å}, 20 = 10–80^\circ\), step size (20) = 0.02° and scan step time = 0.15 s) for phase confirmation. The SEM-EDS images were recorded on the Hitachi SU-1500 variable pressure scanning electron microscope (VP-SEM). FT-IR spectra were recorded using Shimadzu spectrometer in the form of KBr pellets. Jasco V-650 UV-vis spectrophotometer was used for recording the UV-vis diffuse reflectance spectra measurements in the range of 200–800 nm, with BaSO\(_4\) as the reference standard.

**Synthesis of K\(_2\)M\(_2\)Ti\(_6\)O\(_{16}\) (M = Cr, Fe)**

The compositions, K\(_2\)M\(_2\)Ti\(_6\)O\(_{16}\) (M = Cr, Fe), were prepared by sol-gel method. In a typical process, stoichiometric amount of titanium metal powder was dissolved in a solution containing H\(_2\)O\(_2\) and ammonia (e.g. 1 g of Ti powder requires 100 mL of H\(_2\)O\(_2\) and 40 mL of ammonia) in an ice bath. It took about 10 hours for complete dissolution of titanium powder. A yellow gel, titanium peroxy complex (Ti(OH)\(_2\) xH\(_2\)O), was formed by an exothermic reaction. Stoichiometric amounts of KNO\(_3\) and Cr(NO\(_3\))\(_3\), (Fe(NO\(_3\))\(_3\)) were separately dissolved in doubly distilled water. These nitrate solutions were mixed with yellow gel under constant stirring. The chelating agent, citric acid (CA), was added to this solution such that the mole ratio of citric acid to the metal ion was 2:1. The pH of the resultant metal citrate solution was adjusted to 6–7 by adding dilute ammonia solution. The solution was slowly evaporated on a hot plate until a viscous liquid was obtained. At this stage ethylene glycol (EG), the gelating reagent, was added. The mole ratio of EG and CA was 1:1.2. This mixture solution was heated on the hot plate at 100 °C with constant stirring. The temperature was increased to 180 °C at the onset of solidification. The obtained porous solid mass was ground in an agate mortar and heated at 400 °C in small amounts in an electric burner to remove the organic matter. The resultant solid was heated in a muffle furnace at 900 °C/12 h and 950 °C/6 h with an intermittent grinding.

**Synthesis of N-doped K\(_2\)M\(_2\)Ti\(_6\)O\(_{16}\) (M = Cr, Fe)**

Nitrogen doped K\(_2\)M\(_2\)Ti\(_6\)O\(_{16}\) was obtained by heating a thoroughly ground mixture of K\(_2\)M\(_2\)Ti\(_6\)O\(_{16}\) and urea at 400 °C for 2 h in a muffle furnace. The weight ratio of K\(_2\)M\(_2\)Ti\(_6\)O\(_{16}\) to urea was 1:2. The obtained powder was washed with doubly distilled water several times to remove unreacted urea and byproducts. Henceforth, the parent K\(_2\)Cr\(_2\)Ti\(_6\)O\(_{16}\) (K\(_2\)Fe\(_2\)Ti\(_6\)O\(_{16}\)) and N-doped K\(_2\)Cr\(_2\)Ti\(_6\)O\(_{16}\) (K\(_2\)Fe\(_2\)Ti\(_6\)O\(_{16}\)) are designated as KCTO (KFTO) and KCTON (KFTON) respectively.

**Photocatalytic studies**

The photocatalytic activity of all the samples was evaluated by photodegradation of MB using Heber visible annular type photo-reactor (model HVAR1234, Haber Scientific, India), under visible light irradiation using 300 W tungsten lamp as a light source. In a typical process, 60 mL of aqueous MB solution (initial conc. \(C_0 = 2.5 \times 10^{-5} \, \text{mol/L}\)) was stirred with 0.06 g of catalyst individually in a cylindrical-shaped glass reactor at room temperature in air. The suspension was stirred in the dark for an hour to establish adsorption-desorption equilibrium. Then the solution was exposed to light with continuous stirring. At regular 30 min intervals, about 3 mL of solution was collected and centrifuged to remove the catalyst particles. The change in the concentration of MB was obtained by recording the absorbance at 664 nm using a UV-vis spectrophotometer.

**Results and Discussion**

**Characterization of the catalysts**

The phase purity of all the prepared compositions was analyzed by recording the powder X-ray diffraction (XRD) profiles. Figure 1 shows the XRD patterns of KCTO, KCTON, KFTO and KFTON.
XRD patterns of all compounds are consistent with the previously reported powder diffraction data of K$_2$Fe$_2$Ti$_6$O$_{16}$, which crystallizes in the hollandite type structure. The similarity of the powder patterns of nitrogen doped oxide to that of the corresponding parent oxide suggests that the parent structure was undisturbed upon nitrogen doping. Though the powder patterns of parent and N-doped material are identical, small shifts in the d-lines towards lower 2θ values were noticed in nitrogen doped compounds, which is shown in the inset of Fig. 1 in an expanded scale. This shift in peak position confirms the doping of N into the hollandite lattice. The shift is due to the difference in ionic radius of O$^-$ (1.40 Å) and N$^{3-}$ (1.71 Å).

The incorporation of nitrogen into KCTO and KFTO lattices was further supported by SEM-EDS measurements. The energy dispersive spectra (EDS) of parent and nitrogen doped hollandites are shown in Fig. 2. The appearance of N peak in KCTON and KFTON reveals the partial substitution of oxygen by nitrogen in the lattices. The morphology of all compounds was studied by scanning electron microscope (SEM). The SEM image of parent and nitrogen doped samples show a regular molecular sieves/rod like shaped microcrystallites with considerable agglomeration (Fig. 3).

The FT-IR spectra of the samples are similar to each other and to that of an earlier report. The strong and broad bands observed in the 400–1000 cm$^{-1}$ region are attributed to vibrational modes of M/TiO$_6$ (M = Cr, Fe) framework. The bands observed around 850–750 cm$^{-1}$ and 650–550 cm$^{-1}$ are due to stretching and bending vibrations of M/TiO$_6$ (M = Cr, Fe) octahedra, respectively.

The light absorption properties of the KCTO, KCTON, KFTO and KFTON are investigated. Figure 4a shows the diffused reflectance spectra (DRS) of KCTO and KCTON in the range of 200–900 nm. The spectra
are characterized by peaks belonging to Cr$^{3+}$ in the visible region. Trivalent chromium (3$d^3$) with a ground state of $^2A_2$ ($F$) gives three spins allowed transitions (Eqs 1, 2 and 3) and a spin forbidden transition (Eq. 4).

$$^4A_2g(F) \rightarrow ^4T_{2g}(F)$$  \hspace{1cm} \ldots(1)

$$^4A_2g(F) \rightarrow ^4T_{1g}(F)$$  \hspace{1cm} \ldots(2)

$$^4A_2g(F) \rightarrow ^4T_{1g}(P)$$  \hspace{1cm} \ldots(3)

$$^4A_2 \rightarrow ^2E$$  \hspace{1cm} \ldots(4)

In the optical absorption spectra of Cr$^{3+}$, the transitions (1), (2), (3) and (4) appear at $\approx$ 640–700, $\approx$480–550, below 300 and $\approx$ 750–800 nm respectively. A comparison of optical spectra of Cr$^{3+}$ with that of KCTO (Fig. 4a) shows that the transitions at $\approx$ 663, 413 and 745 nm correspond to transitions (1), (2), and (4) respectively. The transition (1), viz., $^4A_2g(F) \rightarrow ^4T_{2g}(F)$ corresponds to 10$Dq$. The transition (3), i.e., $^4A_2g(F) \rightarrow ^4T_{1g}(P)$ is overlapped with charge transfer transition and hence is not detectable. The energies of electronic states $E$ of Cr$^{3+}$ are influenced by the crystal field strength $Dq$ and Racah parameters ($B$ and $C$). The interrelation of these parameters, neglecting spin-orbit effects, is given by the Tanabe-Sugano strong field matrices.$^{23}$

The obtained values of $Dq$, $B$, $Dq/B$, $C$ and $C/B$ for KCTO are 1508 cm$^{-1}$, 1234 cm$^{-1}$, 1.22, 1297 cm$^{-1}$ and 1.05, respectively. The value of $B$ is 918 cm$^{-1}$.
for Cr\(^{3+}\) free ion. Thus, the observed \(B\) value is increased by about 34\%. The increase in \(B\) value may be due to bonding effects in this quarternary oxide. It is seen that, in the Tanabe-Sugano diagram, the crossing of the \(2E_g\) and \(4T_{2g}\) levels occurs near \(Dq/B = 2.3\) and any value lower than 2.3 for \(Dq/B\) corresponds to weak ligand field sites.\(^{24}\) Thus, the Cr\(^{3+}\) ion in KCTO is in the weak ligand field site.

Materials with trivalent high spin iron with a ground state of \(6A_1\) (S) are likely to give three types of electronic transitions: (i) ligand field transitions, (ii) charge transfer transitions and (iii) transitions which result from the simultaneous excitation of magnetically-coupled Fe\(^{3+}\) species.\(^{25,26}\) The expected ligand field transitions for high-spin Fe\(^{3+}\) are: \(6A_1(S) \rightarrow 4T_1(G),\) \(6A_1(S) \rightarrow 4T_2(G),\) and \(6A_1(S) \rightarrow 4E,\) \(4A_1(G).\)

A notable feature about the absorption spectra of KFTO (KFTON) is merging of ligand field transition in the region, 300–800 nm, with the envelope at lower wavelengths. Hence, Racah parameters for these samples were not evaluated.

The absorption edges of nitrogen doped KCTO and KFTO were red shifted compared to their parent samples. The red shift of absorption edges of nitrogen doped compounds may be due to the hybridization of N 2p orbitals with O 2p orbitals.\(^{27}\) The band gap energies of the materials were calculated according to their onset absorption edges and using the equation \(E_g (eV) = 1240/\lambda (nm),\) where \(\lambda\) is the wavelength of the absorption band edge. It is well known that the band gap energy of materials can be determined from the Kubelka-Munk (KM) plot of \((Kh\nu)^{1/2}\) versus \(h\nu\) where \(K\) is reflectance transformed according to Kubelka-Munk \((K = (1-R)^{2}/2R),\) where \(R\) is reflectance (\%) and \(h\nu\) is photon energy. Extrapolation of the linear portion of the plot to \((Kh\nu)^{1/2} = 0\) (i.e. onto the x-axis) gives an estimation of the band gap energy. Figure 5 shows the KM plots for all the samples. The estimated band gap energies of KCTO, KFTO, KCTON and KFTON are found to be 1.96, 1.79, 1.82 and 1.74 eV respectively. Thus, incorporation of nitrogen into hollandite lattice reduced the band gap energy marginally.

**Photocatalytic activity**

Methylene blue (MB) is a widely used organic dye pollutant to examine the photoactivity of the catalyst. Therefore, MB has been selected as the model contaminant to evaluate the photocatalytic property of KCTO, KFTO, KCTON and KFTON under visible light irradiation. The catalyst and dye suspension was stirred in the dark for an hour to establish the adsorption-desorption equilibrium. After reaching equilibrium, the reaction mixture was exposed to light irradiation. It is observed that with increasing time intervals the concentration of aqueous MB dye was decreased over all the catalysts. The temporal changes in the concentration of MB with irradiation time in the presence of all the four catalysts are shown in Fig. 6. Figure 6 clearly shows that the nitrogen doped samples exhibited higher activity than their parent analogues. The extent of MB degradation by KCTO, KFTO, KCTON and KFTON after 180 min of visible light irradiation is found to be 78\%, 71\%, 88\% and 83\% respectively. It is known that aqueous

---

**Fig. 5—KM plots of KCTO (1), KCTON (2), KFTO (3) and KFTON (4).**

**Fig. 6—Variation of MB concentration in the absence and the presence of the catalysts. [1, MB photolysis; 2, KFTO; 3, KCTO, 4, KFTON; 5, KCTON].**
solution of MB in presence of visible light undergo self-photolysis. To differentiate between the photocatalysis and photolysis of MB, experiments were carried out in the presence and absence of catalysts under identical experimental conditions. The degradation curve obtained without the addition of the photocatalyst (Fig. 6, MB Photolysis) shows about 25% degradation only. Therefore, the results indicate that the degradation of MB increases considerably in the presence of catalysts due to photodegradation only and not due to the photosensitization of MB.

Conclusions

Hollandites of composition, $K_2M_2Ti_6O_{16}$ ($M = Cr, Fe$), have been synthesized by ethylene glycol assisted sol-gel process. N-doped $K_2Cr_2Ti_6O_{16}$ ($K_2Fe_2Ti_6O_{16}$) was prepared by heating the mixture of $K_2Cr_2Ti_6O_{16}$ ($K_2Fe_2Ti_6O_{16}$) and urea at 400 °C for 2 h. Powder XRD patterns of all the prepared samples confirm their phase formation. The doping of nitrogen into the hollandite lattice was confirmed by the shift in the $d$-lines of XRD patterns and appearance of N peak in their EDS. Compared to parent oxides, the band gap energy of N-doped materials was reduced marginally. The decrease in the band gap energy may be due to the overlap of N $2p$ orbitals with O $2p$ orbitals in the valence band of the hollandite phase. All the compounds exhibited photocatalytic property under visible light irradiation. However, the nitrogen doped compounds showed higher activity against the degradation of MB compared to the corresponding parent oxides.

Acknowledgement

Authors would like to thank Department of Science & Technology (DST), New Delhi, India, under PURSE and FIST schemes and University Grants Commission (UGC), New Delhi, India, under UPE programme.

References