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Editor's choice paper

Metal oxides as photo catalysts: Modified sodium tantalate as catalyst for photo reduction of carbon dioxide

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ABSTRACT

Sodium tantalate (NaTaO₃), a typical mixed metal oxide with orthorhombic structure, has been modified by incorporation of lanthana (La_xNa_{(1-x})TaO_(3+y) or LNTO), followed by doping/co-doping with N and Fe³⁺, with the objective of improving visible light absorption and photo physical properties. XRD and XPS results reveal that La³⁺ occupies Na⁺ ion sites, Fe³⁺ ions Ta⁵⁺ ion sites and N the O²⁻ ion sites, possibly as N³⁻ in the tantalate matrix. Incorporation of the dopants in the tantalate matrix has been confirmed by SEM-EDXA and STEM-EDS elemental mapping and surface composition analysis by XPS. Fe and N codoping in tantalate matrix results in the narrowing of the band gap due to the creation of additional energy levels within the band gap and consequently, visible light absorption. Presence of Fe³⁺ and La³⁺ dopants in the tantalate lattice ensures electro-neutrality. Efficient charge trapping and de-trapping by Fe³⁺ and Fe⁴⁺ ions reduce the probability of charge carrier recombination as revealed by photo luminescence spectroscopy and further promote charge migration and interfacial charge transfer. The catalysts display significant activity for photo catalytic reduction of carbon dioxide (PCRC) in aqueous alkaline medium, with methanol as major product. Synergetic effect due to co-doping of LNTO with Fe and N improves visible light absorption, retards recombination of charge carriers and thus helps to enhance PCRC activity by nearly three times vis-à-vis pristine NaTaO₃.

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1. Introduction

Metal oxides and mixed metal oxides as versatile catalysts for various conversion processes have been explored extensively [1–3]. Of recent, application of metal oxides like TiO₂ as photo catalysts in energy conversion and environment control processes has gained global attention, especially, for removal of pollutants in gaseous and liquid streams, hydrogen production by splitting of water and reduction of CO₂ to hydrocarbons [4]. CO₂ emissions from the burning of fossil fuels pose serious environmental issues like greenhouse gas effect and unusual weather patterns [5]. Conversion of CO₂ into fuels/hydrocarbons by utilizing photo catalytic routes is an effective strategy that can provide solution to the two key challenges, meeting energy demand and mitigating green house gas effect, besides exploring the scope for utilization of CO₂ as alterna-

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http://dx.doi.org/10.1016/j.mcat.2017.11.021 2468-8231/© 2017 Elsevier B.V. All rights reserved. tive and renewable energy source. Photo catalytic reduction of CO_2 (PCRC) into fuels/hydrocarbons or *artificial photosynthesis*, using water as the reductant, is a complex, multi-step and challenging process. Several investigations focusing on metal oxides like TiO₂ and a wide range of mixed metal oxides as catalysts have been reported for the artificial photo synthesis [6–11].

Essential criteria for selection of catalysts for PCRC have been brought out explicitly by Inoue et al. [12]. In addition, longer life time of the photo generated charge carriers and shorter diffusion path length of excitons to the catalyst surface, where redox reactions occur, are the other desirable parameters that maximize the efficiency of the photo catalysts.

Tantalum based perovskite materials of the type ATaO₃ (A=Li, Na, K) possess requisite photo physical properties for photo catalytic water splitting and CO₂ reduction [13–21]. Even though La modified NaTaO₃ is highly efficient (quantum yield-56% with UV light) for water splitting [13,14], its application is limited to UV region due to its wide band gap, which absorbs only <5% of solar energy. To this end, engineering the band gap of NaTaO₃ to improve visible light absorption by doping with cations and anions have

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been studied in detail [17–38], mainly for the application in photo catalytic splitting of water. Influence of doping/band gap engineering of NaTaO₃ towards activity for PCRC has not been explored so far.

Earlier studies on $La_xNa_{(1-x)}TaO_{(3+y)}$ or LNTO by the authors have highlighted the role of co-catalysts like Pt, Ag, Au, CuO, NiO & RuO₂ [20] and application of visible light harvesting sensitizers like porphyrins [21] in improving the overall activity for PCRC. As a part of our studies to improve the PCRC activity of LNTO, we now have undertaken investigations on the influence of doping/co-doping on the structural, morphological, electronic states and photo physical properties of the tantalate and understand their relevance to the activity for PCRC.

Choice of dopants in the present work is based on the crystallographic and electronic structures of NaTaO₃. Conduction band of tantalates is mainly made up of Ta 5d orbitals. A downward shift in the conduction band can be achieved by doping metal ion with lower energy orbital (3d, 4d) like Fe³⁺ at Ta⁵⁺ site. Simultaneously, presence of La³⁺ and Na⁺, could help to maintain the cationic charge balance in the tantalate lattice (Na⁺ + Ta⁵⁺ = La³⁺ + Fe³⁺). Studies have demonstrated that the modification of NaTaO₃ by doping with Bi [19,20], Fe [21], Sr [22], Cu [27]. N [28–31] and co-doping with La-Cr [32,33], La-Co [34], La-Fe [35], La-Ir [36], La-N [37] promote its photo catalytic activity in the visible region.

Valence band maximum (VBM) of NaTaO₃ is formed mainly by O 2p orbitals. Upward shift of VBM can be achieved by doping with anions having energy higher than that for oxygen [28–31]. Wang et al. [38] have demonstrated the effect of doping with different anions like N, S, C, P and co-doping with N-N, C-S, P-P and N-P pairs on NaTaO₃ on the basis of theoretical calculations and have shown that N doped NaTaO₃ shifts VBM towards more positive energy level as compared to pristine and other anion doped NaTaO₃ and towards more positive energy level with respect to the reduction potential for O_2 as well, to produce H_2 and O_2 . Since both N [38] and Fe [25,39,40] are considered to be the most effective anionic and cationic dopants respectively, co-doping of LNTO with Fe and N would be a more effective strategy to achieve reduction in the band gap energy, increase in the efficiency of the photo catalyst by improving visible light absorption and decreasing recombination rate of charge carriers. Thus, the synergetic influence of co-doping LNTO with N and Fe on the properties has been studied in detail and correlated with the activity for PCRC.

2. Experimental methods

2.1. Preparation of catalysts

NaTaO₃ and 2.0% (w/w) cation/anion doped catalysts were prepared by hydrothermal route [41,42]. La modified NaTaO₃, (Na_(1-x)La_xTaO_(3+x) with x = 0.00014 for 2.0% w/w of La) was prepared by the same procedure, by adding 0.0117 g of La₂O₃ along with NaOH and Ta₂O₅ in the autoclave. 2 wt% La, 2 wt% Fe, 2 mole of N modified NaTaO₃ (Na_(1-x) La_xTa_(1-y)Fe_yO_(3-z)N_z) was prepared by the same procedure, by adding La₂O₃ as La source, Fe₂O₃ as Fe source, urea as N source along with NaOH and Ta₂O₅. La doped NaTaO₃ (Na_(1-x)La_xTaO_(3+x)) denoted as LNTO, N doped Na_(1-x)La_xTaO_(3+x) as Fe/LNTO and Fe and N co-doped Na_(1-x)La_xTaO_(3+x) as Fe-N/LNTO in further discussions.

2.2. Characterization of catalysts

The crystal phase of the catalysts was analysed by X-ray diffractometer (Rigaku-MiniFlex-II) using Cu K α radiation (λ = 1.54056 Å) with the scan range of 2 θ = 5–90° at a speed of 3°/min. The crystallite sizes were calculated by the Scherrer's formula, $t = K\lambda/\beta \cos\theta$, where t is the crystallite size, K is the constant dependent on crystallite shape (0.9 for this case) and $\lambda = 1.54056$ Å, β is the FWHM (full width at half maximum) and θ is the Bragg's angle.

Diffuse reflectance spectra of the catalysts in the UV–vis region were recorded using a Thermo Scientific Evolution 600 spectrophotometer equipped with a Praying Mantis diffuse reflectance accessory.

Photoluminescence spectra were recorded under the excitation with a 450W Xenon lamp at 290 nm and the spectra were collected using Jobin Yvon Fluorolog-3-11 spectro fluorimeter.

Surface area and pore volume of the catalysts were measured using Micromeritics ASAP 2020. Samples were degassed at 373 K for 2 hours and at 423 K for 3 hours. Pure nitrogen at liquid nitrogen temperature (77 K) was used.

Transmission electron micrographs were recorded using JEOL 3010 model. Few milligrams of the samples (1-2 mg) were dispersed in few mL (1-2 mL) of ethanol by ultra-sonication for 15 minutes and a drop of the dispersion was placed on a carbon coated copper grid and allowed to dry in air at room temperature.

Scanning electron micrographs were recorded using FEI, Quanta 200, equipped with EDXA attachment for elemental analysis. The samples in the powder form were taken on the carbon tape and mounted on the SEM sample holder.

The X-ray photoelectron spectra of the catalysts were recorded using Omicron Nanotechnology instrument with Mg K α radiation. The base pressure of the analysis chamber during the scan was 2×10^{-10} millibar. The pass energies for individual scan and survey scan are 20 and 100 eV, respectively. The spectra were recorded with step width of 0.05 eV. The data were processed with the Casa XPS program (Casa Software Ltd, UK), and calibrated with reference to the adventitious carbon peak (284.9 eV) in the sample. Peak areas were determined by integration employing a Shirley-type background. Peaks were considered to be a 70:30 mix of Gaussian and Lorentzian functions. The relative sensitivity factors (RSF) were obtained from literature.

2.3. Photo catalytic reduction of CO₂

Activity of the catalysts in UV visible region (300–700 nm) was evaluated in batch mode using jacketed all glass reactor (620 ml) described in the earlier work [43]. Apparent quantum yield (AQY) was calculated (Supporting information- Experimental) based on the quantities of different products formed per hour per gram of the catalyst and using the formula

$$AQY(\%) = \frac{Number of reacted electrons}{Number of incident protons} \times 100$$

Details on the procedures and methods followed for evaluation of PCRC activity of the catalysts the blank experiments and removal of residual carbon the catalyst surface have been described elsewhere [20,21]. Details on the gas chromatographic analysis of the CO_2 reduction products are given in Supplementary information-Experimental

3. Results and Discussion

Doping of LNTO with N and Fe³⁺ brings about significant changes in the structural, morphological, electronic states and photo physical properties. These aspects are discussed in detail below.

3.1. Structural features

XRD patterns for the synthesized materials are shown in Fig. 1. Peaks at 2θ values of 22.9(020), 32.5(200), 40.1(022), 46.6(202), 52.4(301), 58.2(123) correspond to orthorhombic crystal structure

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