Enhanced Photocatalytic Activity of N-doped Li_2VPO_6 Under Visible Light Irradiation

Suresh Palla · Ravinder Guje · G. Ravi · Radha Velchuri · M. Vithal

Received: 14 April 2014 / Revised: 29 May 2014 / Published online: 13 December 2014
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2014

Abstract Substitutional doping of framework heteroatoms in photocatalysts is one of the approaches for harvesting visible light. The present work aims to utilize the visible light for photocatalytic degradation of organic pollutant by tailoring the bandgap energy of Li_2VPO_6 through nitrogen doping. Li_2VPO_6 and N-doped Li_2VPO_6 are prepared by solid-state method. These materials were characterized by powder X-ray diffraction, energy-dispersive spectra, Raman spectra, UV–Vis diffuse reflectance spectra (UV–Vis DRS), and ^{31}P MAS NMR. The absorption edge of N-doped Li_2VPO_6 is shifted to longer wavelength region considerably. The photocatalytic activity was tested against the degradation of methylene blue. The higher visible light photocatalytic activity of N-doped Li_2VPO_6 compared to pristine Li_2VPO_6 was discussed. The catalysts are stable even after fourth cycle of photodegradation.

KEY WORDS: Photocatalysis; Characterization; Degradation

1 Introduction

The uncontrolled release of colored organic dye stuff from textile, paper, rubber, and plastic industries have led to serious environmental contamination [1]. It is adversely affecting the quality of water, inhibits sunlight penetration, and reduces photosynthetic reactions. In addition, some dyes are either toxic or carcinogenic [2]. The water treatment technologies (sedimentation, filtration, chemical, and membrane technologies) either concentrate the pollutants by transferring them to other phases (adsorption or coagulation) or involve of high operating costs with possible generation of toxic secondary pollutants into the ecosystem [3]. Further, in most of the cases, these methods are slow,

ineffective, and environmentally incompatible. Advanced oxidation processes (AOPs), which depend on the production of reactive radical species and their subsequent redox reactions with pollutants, have been proposed in recent years and found to be promising in catalysis. Among the different AOPs, heterogeneous catalysis using semiconducting oxides and sunlight/visible light has been applied extensively for the degradation of pollutants due to its compliance with green chemistry concept. Titanium dioxide, a semiconductor with a bandgap of 3.2 eV [1–3], has been extensively used for several photocatalytic reactions due to its remarkable physical and chemical properties. It is used as photocatalyst [4–6] in pristine, or doped with anion/cation [7, 8], or with other semiconducting oxides forming heterostructures in these reactions [9]. The large bandgap energy of TiO_2 , however, prevents its applications in visible light, the large component of solar energy.

Vanadium oxophosphates in the system $A\text{--V}^{5+}\text{--P--O}$ (A represents monovalent alkali ions) have been investigated due to their structural versatility and interesting materials characteristics such as electrochemical [10–12],

Available online at <http://www.link.springer.com/journal/40195>

S. Palla · R. Guje · G. Ravi · R. Velchuri · M. Vithal (✉)
Department of Chemistry, Osmania University,
Hyderabad 500 007, India
e-mail: muga_vithal@rediffmail.com

magnetic [13–15], catalytic (conversion of *n*-butane [16, 17] and *n*-pentane [18] to maleic acid anhydride), and NLO properties [19, 20]. A few noncentrosymmetric (NCS) compounds in the A–V⁵⁺–P–O system exhibit second-harmonic generation (SHG) [21], piezoelectricity, ferroelectricity, and pyroelectricity properties [20, 22]. The combination of VO_{*n*} polyhedra (VO₄ tetrahedra, VO₅ square pyramids, and VO₆ octahedra) with PO₄ tetrahedra has generated variety of structural topologies (chains, layers, and three-dimensional frameworks including tunnel structures) with interesting properties like incorporation of organic templates [23, 24], connected together by bridging HPO₄ groups [25, 26], etc. Despite these remarkable properties, the vanadium oxophosphates have been less explored in the field of catalysis [27]. Lithium vanadium (V) monophosphate (Li₂VPO₆) is a layered material composed of distorted VO₆ octahedra and PO₄ tetrahedra sharing their corners and edges forming anionic layers of type [VO_{2/1}O_{4/2}]^{3–} [PO_{4/2}]^{2–} [28]. These anionic layers are separated by Li⁺ ions. The substitutional doping of heteroatom is one of the methods to reduce the bandgap, and hence beneficial for photoactivity studies. In the present investigation, an attempt is made to substitute oxygen (partially) by nitrogen in the phosphate lattice. The catalytic properties of Li₂VPO₆, to our knowledge, are not reported. In this work, the photodegradation of methylene blue in the presence of Li₂VPO₆ and N-doped Li₂VPO₆ was investigated.

2 Experimental

2.1 Synthesis of Li₂VPO₆ and N-doped Li₂VPO₆

Li₂VPO₆ was prepared by solid-state method [28, 29] using lithium carbonate, vanadium pentoxide, and ammonium dihydrogen orthophosphate (All SD-Fine Chemicals, purity of 99%). Stoichiometric amounts of all the reactants were thoroughly ground in an agate mortar using spectral grade acetone and pressed into pellets. These pellets were gradually heated to 580 °C for 18 h in an alumina crucible and furnace cooled to room temperature at 10 °C/h. These pellets were ground into a fine powder and again pressed into pellets and slowly heated to 580 °C for 18 h and cooled to room temperature at 10 °C/h. A light brown-colored compound was obtained.

The N-doped Li₂VPO₆ was obtained by heating of a thoroughly ground mixture of Li₂VPO₆ and urea (CO(NH₂)₂) at 400 °C for 2 h in a muffle furnace. The weight ratio of Li₂VPO₆ to urea was 1:2. The color of the N-doped Li₂VPO₆ was found to be dark ash (Li₂VPO₆ and Li₂VPO_{6–*x*}N_{*x*} hereafter referred as LVP and N-LVP).

2.2 Characterization

The room temperature powder X-ray diffractograms were recorded on Rigaku miniflex 600 X-ray diffractometer using Nickel filtered CuKα radiation of wavelength 1.5406 Å for phase confirmation in the 2θ range of 10°–80°, with step size (2θ) of 0.02° and scan step time of 0.15 s. The unit cell parameters were calculated by least square refinement technique using POWD program. The EDS were recorded on the HITACHI SU-1500 variable pressure scanning electron microscope (VP-SEM). The room temperature ³¹P solid-state MAS NMR spectra were recorded with a Bruker MSL-300 MHz solid-state high-resolution spectrometer operating at 121.49 MHz with a 10 kHz spinning speed. The samples were packed in a 4-mm Zirconia rotor. Pulses of 90° with 5 μs durations were used with a recycle delay of 5 s between pulses. The chemical shift values are given with respect to an 85% H₃PO₄ Solution. UV–Vis DRS and UV–Vis absorption spectra were recorded with JASCO V-650 UV–Vis spectrometer in the range of 200–800 nm.

The photocatalytic activity of the samples was evaluated by photodegradation of methylene blue (MB) using HEBER Visible Annular Type Photoreactor, model HVAR 1234 (Haber Scientific, India), under visible light irradiation using 300 W tungsten lamp as a light source. In a typical process, 60 mL of aqueous methylene blue solution with an initial concentration, C₀ = 3.33 × 10^{–5} mol/L, and 60 mg of catalyst are taken in a cylindrical-shaped glass reactor at room temperature in air and natural pH conditions. The suspension was stirred in the dark for 60 min to establish adsorption–desorption equilibrium. Then the solution was exposed to light with continuous (air bubbling) stirring. At regular intervals of 20 min, about 2–3 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 (λ_{max} of MB) using a JASCO V-650 UV–Vis spectrometer.

3 Results and Discussion

Powder XRD patterns of both the materials were recorded for phase identification. Figure 1 shows the powder XRD patterns of LVP and N-LVP. The powder XRD pattern of LVP is free from impurities and identical to that reported by Korthuis et al. [28, 29] (JCPDS-ICDD 81-2405). The parent LVP crystallized in orthorhombic lattice with space group *Pna*21. The structure of Li₂VPO₆, as discussed in the introduction, composed of VO₆ octahedra and PO₄ tetrahedra linked to form a covalently bonded layer with an

Fig. 1 Powder X-ray diffraction patterns of Li₂VPO₆ and N-doped Li₂VPO₆: **a** Patterns at 2θ range of 0°–80°; **b** broadened patterns at 2θ around 20°

overall negative charge which is balanced by lithium cations present between the layers. The lithium ions have distorted octahedral coordination. In this lattice, when nitrogen is substituted for oxygen partially, the skeletal structure remains the same and, therefore, the powder pattern of N-doped LVP is expected to be the same compared to LVP. The powder pattern of N-LVP is found to be similar to that of parent compound (LVP) (Fig. 1a). However, a close examination of d-lines of N-LVP compared to LVP shows a systematic shift toward lower 2θ value (Fig. 1b) indicating the substitution of nitrogen into the lattice [30]. As the ionic radius of N^{3−} (0.171 nm) is larger than that of O^{2−} (0.140 nm), the unit cell parameters should increase resulting in a decrease, in the 2θ values [31]. The powder patterns of N-LVP were least square fitted using POWD software [32]. The observed *d*-spacings of N-LVP and unit cell parameters of LVP are given as input parameters to obtain unit cell parameters of N-LVP. The unit cell parameters of N-LVP are found to be $a = 10.31 \text{ \AA}$, $b = 4.63 \text{ \AA}$ and $c = 8.56 \text{ \AA}$ which are close to those observed for parent LVP [28, 29]. Thus, N-LVP also crystallizes in orthorhombic lattice with space group *Pna*21. The slight increase in the unit cell parameter of N-LVP is due to partial substitution of N into oxygen lattice. The color of the sample also provided supportive information regarding the substitution of nitrogen into the oxygen lattice.

The Raman spectra of LVP and N-LVP are recorded in the range of 50–1,500 cm^{−1} to identify the building blocks (VO₆ and PO₄ units) of the structure. Figure 2 shows the Raman spectra of LVP and N-LVP. Both the samples show groups of bands in the regions 1,150–850 and 650–150 cm^{−1}. The Raman spectra of both samples are characterized by bands belonging to V–O (VO₆) and P–O (PO₄) vibrations [33]. Majority of the observed bands correspond to isolated tetrahedral PO₄ units. The absence of the band at 730–740 cm^{−1} indicates the absence of pyrophosphate (P₂O₇)^{4−} impurity. The Raman band

Fig. 2 Raman spectra of Li₂VPO₆ and N-doped Li₂VPO₆

positions and their assignment are shown in Table 1 along with band positions (IR) obtained for Li₂VPO₆ [28].

The incorporation of nitrogen into vanadium oxophosphate lattice was further substantiated by the energy-dispersive spectra (EDS). Figure 3 shows the EDS profiles of LVP and N-LVP compositions. The appearance of N peak at 0.4 eV in EDS profile of N-LVP indicates the presence of N in the Li₂VPO₆ lattice.

The information pertaining to the local structure of phosphorous was obtained from the ³¹P MAS NMR spectra. Figure 4 shows the ³¹P MAS NMR spectra of LVP and N-LVP. It is well known that ³¹P MAS NMR gives different signals for different oxidation states or crystallographically inequivalent sites of the phosphorous ion [34, 35]. The ³¹P MAS NMR spectrum of LVP is characterized by symmetric single peak at 13.15×10^{-6} indicating that all the phosphorous ions have same oxidation state and occupy only one site which is consistent with its crystal structure [28, 29]. The ³¹P MAS NMR spectrum of N-LVP also gives a single (main) peak centered at 7.85×10^{-6} with very low intensity shoulders on either

Table 1 The observed Raman band positions (cm^{-1}) of both the samples compared with the reported Li_2VPO_6 FT-IR bands (cm^{-1})

Assignments	Li_2VPO_6 (IR cm^{-1}) ^a	Li_2VPO_6 (Raman cm^{-1})	N- Li_2VPO_6 (Raman cm^{-1}) ^b
ν_{as} P–O	1,112	1,100	1,100
	1,075	1,080	1,080
	1,019	1,032	1,032
V=O stretch	1,002	–	–
	977	949	949
ν_{s} P–O stretch	967	–	–
	941	–	–
	926	927	927
	902	–	–
δ_{as} O–P–O	882	880	880
	623	622	622
	616	–	–
$\delta_{\text{PO}} + \delta_{\text{VO}}$	572	575	575
	507	509	509
δ_{s} O–P–O	470	467	467
	427	–	–

^a Korthuis et al. 1993 [29] and Lee et al. 2013 [28]^b Present work **Fig. 3** EDS spectra of Li_2VPO_6 (a) and N-doped Li_2VPO_6 (b)

side of the main peak. The linewidth of the main peak is slightly higher than the linewidth observed for LVP. To our knowledge, the ^{31}P -MAS NMR spectra of Li_2VPO_6 and

Fig. 4 ^{31}P MAS NMR of Li_2VPO_6 (a) and N-doped Li_2VPO_6 (b)

related materials ($M_2\text{VPO}_6$, $M=\text{Ag}$, Na , K) [36, 37] are not reported so far and, therefore, the chemical shift values of the present compounds (LVP and N-LVP) are not compared. The observed difference in the chemical shift values of N-LVP with LVP can be explained by the variation in the electron density at phosphorous site in the lattice due to the electronegativity difference of oxygen and nitrogen. Since oxygen has a higher electronegativity (3.44 on Pauling's scale) than nitrogen (3.04), in N-LVP the electron density at P increases marginally compared to P in parent LVP. An increase in the electron density increases the induced magnetic field and, therefore, resonates at higher magnetic field (lower chemical shift). Thus, P of N-LVP has lower chemical shift value compared to LVP. When oxygen is replaced by nitrogen (partially) in the N-LVP lattice, the possible coordinations for P are PO_4 , PO_3N , PO_2N_2 , PON_3 , and PN_4 (the probability of last three types will be very less) which give rise to NMR signals close to that observed for PO_3N leading to a higher line width [38].

The optical properties of LVP and N-LVP are obtained from their UV–Vis diffuse reflectance spectra (UV–Vis DRS). The spectra of both samples are characterized by a flat profile in the 800–550 nm region followed by a steeply rising portion in the 550–200 nm region with the

Fig. 5 UV–Vis diffuse reflectance spectra (*Inset* shows color of the respective samples) (a) and KM plots (b) of Li_2VPO_6 and N-doped Li_2VPO_6

absorption maxima (Fig. 5a) [39, 40]. The absorption maximum in the DRS profile of N-LVP has been shifted to higher wavelength considerably. The absorption edges, obtained from the extrapolation of steeply increasing region onto the wavelength axis, are found to be 434 nm (2.85 eV) and 505 nm (2.45 eV) for LVP and N-LVP, respectively. Accurate bandgap energy, however, can be obtained from Kubelka–Munk equation. The DRS profiles are converted into KM function and plotted (Fig. 5b). The bandgap energy of LVP and N-LVP are found to be 3.05 and 2.55 eV, respectively. The obtained results are consistent with the reports on N-doping in metal oxides and other materials [4–9, 41]. The reduction in the bandgap energy of N-LVP is due to the overlap of N 2p states with O 2p states in the valence band of the material [42].

The photocatalytic activity of LVP and N-LVP was evaluated by photodegradation of MB aqueous solution. Blank experiments viz., its degradation in the visible light without any catalyst and its adsorption in the dark were carried out. The visible light degradation of MB in the absence of the catalyst and its adsorption in dark are found to be negligible (<5%). The photocatalytic activity of LVP and N-LVP was investigated, as described in the experimental section, by monitoring the optical density (OD) at 664 nm by recording the UV–Vis spectrum at different time intervals of visible light irradiation. The amount of degradation of MB solution was calculated by

$$D = \left(\frac{C_0 - C}{C_0} \right) \times 100\%,$$

where D is the percentage of degradation, C_0 is the initial concentration of MB, and C is the concentration at time t . It is observed that the degradation of MB in the presence of both the catalysts increased with increase in the irradiation time as shown in Fig. 6. However, N-LVP has shown more photoactivity compared to LVP. The percentages of MB

Fig. 6 Photocatalytic degradation of MB using Li_2VPO_6 , N-doped Li_2VPO_6 , and P25

degradation after 120 min of visible light irradiation were found to be 50 and 95% for LVP and N-LVP, respectively. The efficiency of photoactivity of catalysts was also compared with Degussa P25 (Fig. 6). Compared to Degussa P25, N-LVP shows higher activity in the MB degradation. However, Degussa P25 shows higher activity compared to that of LVP in the degradation of MB. Thus the photoactivity order of these materials is N-LVP > P25 > LVP. The first step in the photocatalysis involves the absorption of photons by the semiconductor (SC) leading to the excitation of an electron from the valence to conduction bands. The photogenerated electrons (in CB) and the holes (in VB) are highly reactive and participate in a series of redox reactions. The holes and electrons react with water and dissolved oxygen to form highly active hydroxyl radicals ($\cdot\text{OH}$) and superoxide anions ($\text{O}_2^{\cdot-}$), respectively. These reactive species participate in a cascade of reactions leading to the degradation of MB [43, 44]. A few of the reactions are shown below:

Fig. 7 **a** Cyclic runs in the photocatalytic degradation of MB in the presence of N-doped Li₂VPO₆ under the visible light irradiation; **b** XRD patterns of N-doped Li₂VPO₆ before and after photocatalysts

The photoactivity of a material depends on several factors such as surface structure, extent of crystallinity, surface area, crystal structure, the nature of the pollutant, adsorption ability of the pollutant, and bandgap energy of the material. It is observed that nitrogen (N^{3-}) doping in place of oxygen (O^{2-}) in the crystal lattice often produces oxygen vacancies that help in reducing the rate of electron–hole recombination [1–3]. The higher photoactivity of N-LVP in the present work may be attributed to its lower bandgap energy and a considerable reduction in the electron–hole recombination due to oxygen vacancies [1–3].

The chemical stability and reusability of the photocatalysts are important for practical applications. In the present investigation, the photocatalysts were reused four times for MB degradation. Representative photodegradation profiles of N-LVP are shown in Fig. 7a. It is observed that N-LVP catalyst exhibits almost the same activity for photodegradation of MB in all the cycles. The powder XRD patterns of the catalyst (N-LVP) recorded after 4 cyc photocatalysts was found to be the same (Fig. 7b). Therefore, structure/composition of the N-LVP remains the same even after the fourth cycle of photodegradation. Similar results were obtained for LVP photocatalyst. Thus, both these materials can be considered as striking photocatalysts for industrial waste/pollutant purification.

4 Conclusions

N-doped Li₂VPO₆ was obtained by heating Li₂VPO₆ and urea at 400 °C for 2 h. Both LVP and N-LVP crystallized in orthorhombic crystal lattice with space group *Pna*21. The incorporation of nitrogen into Li₂VPO₆ lattice was confirmed from (i) a shift in the *d*-lines toward lower 2θ value, (ii) appearance of N peak at 0.4 eV in the EDS spectra, and (iii) color change of Li₂VPO₆ from light yellow to ash. The Raman spectra of both samples were characterized by bands belonging to V–O and P–O vibrations. The ³¹P MAS NMR of N-LVP gave a slightly broad single peak confirming that the coordination and oxidation state of P were unchanged. The lower chemical shift value was attributed to a change in the electron density at the P site. The significant shift of the absorption edge of N-LVP was due to the overlap of N 2p states with O 2p states. The lower bandgap energy (2.55 eV) of N-LVP compared to LVP (3.05 eV) may be responsible for higher photocatalytic activity of N-LVP. Both the catalysts are stable and can be used in a cyclic manner for photodegradation of MB.

Acknowledgments The authors thank to Dr. B. Jagadeesh, NMR Research centre, ICT, Hyderabad for ³¹P MAS NMR facility. Financial assistance from UGC-UPE New Delhi is gratefully acknowledged. One of the authors (Suresh Palla) thanks to CSIR, New Delhi for the award of Senior Research Fellowship.

References

- [1] V. Gombac, L. De Rogatis, A. Gasparotto, G. Vicario, T. Montini, D. Barreca, G. Balducci, P. Fornasiero, E. Tondello, M. Graziani, *Chem. Phys.* **339**, 111 (2007)
- [2] X. Zhang, Q. Liu, *Appl. Surf. Sci.* **254**, 4780 (2008)
- [3] X. Cheng, X. Yu, Z. Xing, J. Wan, *Energy Proc.* **16**, 598 (2012)
- [4] P.P. Zamora, A. Kunz, S.G. de Moraes, R. Pelegrini, P.D. Moleiro, J. Reyes, N. Duran, *Chemosphere* **38**, 835 (1999)

- [5] Susan J. Masten, Simon H.R. Davies, *Environ. Sci. Technol.* **28**, 180 (1994)
- [6] S. Naskar, S.A. Pillay, M. Chanda, *J. Photochem. Photobiol. A* **113**, 257 (1998)
- [7] R. Aplin, T.D. Waite, *Water Sci. Technol.* **42**, 345 (2000)
- [8] C. Hachem, F. Bocquillon, O. Zahraa, M. Bouchy, *Dyes Pigment.* **49**, 117 (2001)
- [9] I. Arslan, I.A. Balcioglu, *Coloration Technol.* **117**, 38 (2001)
- [10] J. Chen, S. Wang, M.S. Whittingham, *J. Power Sour.* **174**, 442 (2007)
- [11] C. Dai, Z. Chen, H. Jin, X. Hu, *J. Power Source* **195**, 5775 (2010)
- [12] C.J. Allen, Q. Jia, C.N. Chinnsamy, S. Mukerjee, K.M. Abraham, *J. Electrochem. Soc. A* **158**, 1250 (2011)
- [13] E. Le Fur, J.Y. Pivan, *J. Solid State Chem.* **158**, 94 (2001)
- [14] R.V. Shpanchenko, A.S. Mitiaev, V.V. Chernaya, E.V. Antipov, H. Sakurai, E. Takayama, Muromachi. *J. Solid State Chem.* **178**, 3014 (2005)
- [15] J.L. Cisneros, S. Fernandez Armas, J.L. Mesa, J.L. Pizarro, M.I. Arriortua, T. Rojo, *Mater. Res. Bull.* **41**, 2168 (2006)
- [16] E. Benser, R. Glaum, T. Dross, H. Hibst, *Chem. Mater.* **19**, 4341 (2007)
- [17] G. Centi, F. Trino, J.R. Ebner, V.M. Franchetti, *Chem. Rev.* **88**, 55 (1988)
- [18] B.K. Hodnett, *Catal. Rev. Sci. Eng.* **27**, 373 (1985)
- [19] R.E. Sykora, K.M. Ok, P.S. Halasyamani, D.M. Wells, T.E. Albrecht, Schmitt. *Chem. Mater.* **14**, 2741 (2002)
- [20] T. Sivakumar, H.Y. Chang, J. Baek, P.S. Halasyamani, *Chem. Mater.* **19**, 4710 (2007)
- [21] H. Jiang, S. Huang, Y. Fan, J. Mao, W. Cheng, *Chem. Eur. J.* **14**, 1972 (2008)
- [22] H.Y. Chang, S.H. Kim, K.M. Ok, P.S. Halasyamani, *Chem. Mater.* **21**, 1654 (2009)
- [23] Y. Zhang, C.J. Warren, A. Clearfield, R.C. Haushalter, *Polyhedron* **17**, 2575 (1998)
- [24] A.M. Chippindale, *Chem. Mater.* **12**, 818 (2000)
- [25] J. Do, R.P. Bontchev, A.J. Jacobson, *Inorg. Chem.* **39**, 3230 (2000)
- [26] Y. Cui, H. Meng, L. Liu, G. Li, C. Chen, Z. Yi, W. Pang, *Solid State Sci.* **8**, 1108 (2006)
- [27] P.R. Makgwane, E.E. Ferg, D.G. Ferg, B. Zeelie, *Catal. Lett.* **135**, 105 (2010)
- [28] E.P. Lee, D.W. Lee, Y.H. Cho, T.T. Tran, P.S. Halasyamani, K.M. Okay, *J. Solid State Chem.* **202**, 22 (2013)
- [29] V.C. Korthuis, R.D. Hoffmann, J. Huang, A.W. Sleight, *J. Solid State Chem.* **105**, 294 (1993)
- [30] H. Tian, L. Hu, C. Zhang, W. Liu, Y. Huang, L. Mo, L. Guo, J. Sheng, S. Dai, *J. Phys. Chem. C* **114**, 1627 (2010)
- [31] J.R. Reddy, G. Ravi, N.K. Veldurthi, V. Radha, P. Someshwar, M. Vithal, B. Sreedhar, *Z. Anorg. Allg. Chem.* **639**, 794 (2013)
- [32] E. Wu, *J. Appl. Crystallogr.* **22**, 506 (1989)
- [33] N. Membren, P. Xiao, K.S. Park, J.B. Goodenough, G. Henkelman, K.J. Stevenson, *J. Phys. Chem. C* **117**, 11994 (2013)
- [34] M. Barj, *J. Solid State Chem.* **100**, 141 (1992)
- [35] P. Tarte, A. Rulmont, C.A. Merckaert, *Spectrochim. Acta.* **42A**, 1009 (1986)
- [36] H.Y. Kang, S.L. Wang, P.P. Tsai, K.H. Lii, *J. Chem. Soc. Dalton Trans.* **1993**, 1525 (1993)
- [37] F. Berrah, M.M. Borel, A. Leclaire, M. Daturi, B. Raveau, *J. Solid State Chem.* **145**, 643 (1999)
- [38] L. Enrique, *Chem. Mater.* **10**, 665 (1998)
- [39] J.R. Reddy, N.K. Veldurthi, P. Suresh, G. Ravi, G. Ravinder, M. Vithal, *J. Chem. Technol. Biotechnol.* **89**, 1833 (2014)
- [40] Y. Hosogi, Y. Shimodaira, H. Kato, H. Kobayashi, A. Kudo, *Chem. Mater.* **20**, 1299 (2008)
- [41] M. Ni, M.K.H. Leung, D.Y.C. Leung, K. Sumathy, *Renew. Sustain. Energy Rev.* **11**, 401 (2007)
- [42] H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri, J. Ye, *Adv. Mater.* **24**, 229 (2012)
- [43] N. Zhang, Y. Zhang, M.Q. Yang, Z.R. Tang, Y.J. Xu, *J. Catal.* **299**, 210 (2013)
- [44] Y.S. Xu, W.D. Zhang, *Dalton Trans.* **42**, 1094 (2013)