Contents lists available at ScienceDirect



Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Corrigendum

Corrigendum to "Synthesis and characterization of samarium and nitrogen doped TiO₂ photocatalysts for photo-degradation of 4-acetamidophenol in combination with hydrodynamic and acoustic cavitation" [Sep. Purif. Technol. 209 (2019) 254–269]



Senaratio

Sunil Rajoriya^a, Swapnil Bargole^a, Suja George^a, Virendra Kumar Saharan^{a,*}, Parag R. Gogate^b, Aniruddha B. Pandit^{b,*}

^a Department of Chemical Engineering, MNIT, Jaipur 302017, India

^b Chemical Engineering Department, Institute of Chemical Technology, Matunga, Mumbai 400019, India

The corrigendum applies to the paper "Synthesis and characterization of samarium and nitrogen doped TiO₂ photocatalysts for photodegradation of 4-acetamidophenol in combination with hydrodynamic and acoustic cavitation", published in Separations and Purification Technology, 209 (2019) pp. 254-269. The authors identified some errors in the XRD and UV-Vis DRS spectra and the authors felt that more explanation was required to describe the XRD peaks for the samarium and nitrogen doped photocatalysts including their corresponding chemical formulae and phases. Accordingly, the correct analysis of XRD has been included and explanation of XPS analysis has been elaborated with respect to both major and minor peaks for correct species identification and bond formation in the doped photocatalyst. The corresponding figures of XRD patterns (Fig. 3(a) & (b)), UV-vis DRS spectra (Fig. 7(a) & (b)) and Table 1 of the published article has been corrected and is as included below. The authors apologize for the inconvenience created.

The list of corrections are as follows

• *Lines* 1–34 of *Section* 3.1.1. (*page* 258–259) described as "XRD patterns of ultrasonically and conventionally preparedand the values are presented in Table 1." should be read as given below.

XRD patterns generated using X'Pert HighScore of ultrasonically and conventionally prepared un-doped and Sm/N-doped photocatalysts (Sm/TiO₂: 1.5; N/TiO₂: 1) are shown in Fig. 3. In the case of pure TiO₂ photocatalyst obtained using USP, as shown in Fig. 3(a), the XRD patterns showed major diffraction peaks at $2\theta = 25.49^{\circ}$, 37.89°, 48.51°, 53.97°, 55.19°, 62.88° and 75.19° confirming the presence of anatase phase (JCPDS card no. 21-1272) as the most predominant species. It was reported that anatase phase of synthesized TiO₂ has higher photocatalytic activity as compared to other crystalline phases (rutile and

brookite) [1]. Further in case of N doped TiO₂, the intensity of anatase peaks were higher than pure TiO₂ which indicate that doping of nitrogen promotes the phase transformation from amorphous phase to anatase [2,3]. Additional peaks of Ti-N species in the form of Ti₂N and Ti₃N_{1.29} were observed at $2\theta = 37.06^{\circ}$ and at $2\theta = 38.11^{\circ}$, 48.29° , 55.30° respectively. In case of Sm doped TiO₂ samples, reduction in peak intensity was observed as well as the anatase phase was absent indicating that samarium ion doping inhibited the phase transformation from amorphous to anatase [4,5]. New species of samarium titanium oxide were observed in the form of Sm₄Ti₃O₁₂, at $2\theta = 13.56^{\circ}$, SmTiO₃ at $2\theta = 23.41^{\circ}$ and Sm₂TiO₅ at $2\theta = 30.40^{\circ}$, 31.68° .

In the case of pure TiO₂ photocatalyst obtained using CSP, as shown in Fig. 3(b), a major peak was observed at $2\theta = 25.81^{\circ}$, whereas the minor peaks were observed at $2\theta = 38.44^{\circ}, 48.72^{\circ}, 54.55^{\circ}, 55.6, 63.07^{\circ},$ 69.38° (JCPDS card no. 21-1272) corresponding to the anatase phase. In case of N doped TiO₂ prepared using CSP, anatase phase was dominant with major peak observed at $2\theta = 25.81^\circ$, and additional peaks of titanium nitride (Ti₂N) were observed at $2\theta = 38.33^{\circ}$ and 69.49° [6]. The XRD spectrum of the Sm doped TiO_2 prepared using CSP method, indicated the presence of amorphous phase of TiO₂ at $2\theta = 42.12^{\circ}$, whereas anatase phase was absent as also observed in case of doped TiO2 using USP method. Moreover, additional peaks were observed that correspond to samarium oxide (Sm₂O₃) at $2\theta = 30.62^{\circ}$ and samarium titanium oxides (Sm₂Ti₂O₇) at $2\theta = 14.16^{\circ}$ and 23.73° and SmTiO₃ at $2\theta = 32.14^{\circ}$. As depicted in Fig. 3, the crystallinity and peak intensities are higher and sharper for the photocatalysts prepared using USP as compared to that prepared by CSP. Higher peak intensity exhibited that the anatase phase of TiO₂ was more crystalline in nature. The crystallite sizes of the synthesized photocatalysts were also calculated using Scherrer's formula according to Eq.3 [7] and the values are presented in Table 1.

* Corresponding authors.

https://doi.org/10.1016/j.seppur.2018.10.061

Received 13 September 2018; Received in revised form 29 October 2018; Accepted 29 October 2018 Available online 30 October 2018

1383-5866/ © 2018 Elsevier B.V. All rights reserved.

DOI of original article: https://doi.org/10.1016/j.seppur.2018.07.036



Fig. 3. XRD patterns of pure TiO₂, N-doped TiO₂ and Sm-doped TiO₂ synthesized using (a) ultrasound assisted sol-gel (b) conventional sol gel process.

- Corrected Fig. 3 is as given below in place of Fig. 3 of the published article.
- Corrected Table 1 is as given below in place of Table 1 of the published article.
- Line 17 of Section 3.1.5. (page 259) should be read as "The band gap energies of pure TiO₂, Sm-TiO₂ and N-TiO₂ photocatalysts were found to be 2.89 eV, 2.64 eV and 2.0 eV respectively." The band gap value of pure TiO_2 (2.89 eV) was found to be slightly lower than the earlier reported value of 3.2 eV in the literature [1-3]. The reduction in the band gap energy can be attributed to the effect of cavitation as asymmetric collapse of cavities cause a huge energy release at the molecular level known as hot spots with very high temperature (upto 5000 K) and pressure (upto 1000 atm) which can alter the surface characteristics of the TiO₂ anatase crystals. Dette et al. [8] reported a highly reactive titanium-terminated anatase surface with a reduced bandgap of less than 2 eV. They reported that the reduced band gap originated from the presence of surface gap states associated with the exposed Ti_{4C} and Ti_{5C} sites in the TiO_2 crystals due to the removal of outermost layer of bridging oxygen atoms (O_{2C}) from the stoichiometric oxygen terminated surface. This new surface called as titanium-terminated nonstoichiometric anatase phase is created on the stoichiometric oxygen-terminated surface due to increase in temperature of the oxygen annealing from 670 to 920 K in the synthesis of dopant-free TiO₂.
- Corrected Fig. 7 is as given below in place of Fig. 7 of the published article.
- Lines 17–31 of Section 3.1.6. (page 261) "Previous studies suggested that the N 1s peak........... 399 eV respectively." should be read as follows.

Previous studies suggested that the N 1s peak of the N-doped TiO_2 was commonly observed between 395 and 402 eV [2,3,9]. In this study as observed in Fig. 9(c), the presence of peaks at the binding energy of 399 eV and 397.3 eV confirmed the successful doping of nitrogen into

the TiO₂ lattice structure. The N 1s peak of the N doped TiO₂ at 399 eV may be attributed to the interstitial N species with the possibility of N-O-Ti or Ti-N-O bond formation [2]. The minor N 1s peak at 397.3 eV can be attributed to the Ti-N-Ti linkages in the Ti-N species formed by the replacement of oxygen atoms in the TiO₂ crystal lattice, indicating that the nitrogen atom is substitutionally doped into the TiO₂ lattice [6]. This has also been confirmed from the XRD spectrum. When nitrogen is doped into the TiO₂ lattice it causes a reduction in the electron density around nitrogen due to the lower electronegativity of nitrogen than the oxygen atom. Therefore, the peak at 399 eV corresponding to N-Ti-O species is higher than that of Ti-N species appearing at 397.3 eV. It is concluded that nitrogen doped into TiO_2 exists in both substitutional and interstitial N. Fig. 9(d) depicts the XPS spectrum of Sm 3d, in which the peak at 1083.43 eV corresponds to the bond of Sm-O-Ti. The XRD results also indicated the formation of samarium titanium oxide in the doped TiO2. Therefore, the XPS study indicated the successful incorporation of samarium at binding energy of 1083.43 eV and nitrogen at binding energies of 399 eV and 397.3 eV as dopants into TiO₂.

- *Lines 17–18* of *Section 3.2.4 (page 263)* "which is attributed to the reduced band gap energy from 3.19 to 2.98 eV" should be read as "which is attributed to the reduced band gap energy from 2.89 to 2.0 eV".

Higher photocatalytic efficiency obtained in N-doped TiO_2 as compared to Sm-doped TiO_2 even with the low molar ratio (N/TiO₂:1) can be attributed to the reduced band gap energy (2.0 eV) of N-doped TiO_2 as compared to the Sm-doped TiO_2 (2.64 eV) and pure TiO_2 (2.89 eV).



Fig. 7. (a) UV–Vis diffuse reflectance spectra. (b) Kubelka-Munk plots and band gap energy estimation of pure TiO_2 , $Sm-TiO_2$, and $N-TiO_2$.

Table 1

The crystallite sizes of photocatalysts synthesized using USP and CSP.

Type of	USP		CSP	
photocalarysts	Crystal size, nm	Crystal phase	Crystal size, nm	Crystal phase
Pure TiO ₂ Sm-doped TiO ₂ N-doped TiO ₂	13.14 8.53 9.86	Anatase Amorphous Anatase	16.89 12.80 10.75	Anatase Amorphous Anatase

References

[1] M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S. Dunlop,

J.W. Hamilton, J.A. Byrne, K. O'shea, M.H. Entezari, D.D. Dionysiou, A review on the visible light active titanium dioxide photocatalysts for environmental applications, Appl. Catal., B Environ. 125 (2012) 331–349.

- [2] M. Xing, J. Zhang, F. Chen, New approaches to prepare nitrogen-doped TiO₂ photocatalysts and study on their photocatalytic activities in visible light, Appl. Catal. B. Environ. 89 (2009) 563–569.
- [3] J. Ananpattarachai, P. Kajitvichyanukul, S. Seraphin, Visible light absorption ability and photocatalytic oxidation activity of various interstitial N-doped TiO₂ prepared from different nitrogen dopants, J. Hazard. Mater. 168 (2009) 253–261.
- [4] V. Dinkar, S. Shridhar, E. Madhukar, E. Anil, H. Nitin, Sm-doped TiO₂ nanoparticles with high photocatalytic activity for ARS dye under visible light synthesized by ultrasonic assisted sol-gel method, Oriental J. Chem. 32 (2016) 933–940.
- [5] Y. Ma, J. Zhang, B. Tian, F. Chen, L. Wang, Synthesis and characterization of thermally stable Sm, N co-doped TiO₂ with highly visible light activity, J. Hazard. Mater. 182 (2010) 386–393.
- [6] D.H. Wang, L. Jia, X.L. Wu, L.Q. Lu, A.W. Xu, One-step hydrothermal synthesis of Ndoped TiO₂/C nanocomposites with high visible light photocatalytic activity, Nanoscale 4 (2012) 576–584.
- [7] H. Eskandarloo, A. Badiei, M.A. Behnajady, G.M. Ziarani, Ultrasonic-assisted sol-gel synthesis of samarium, cerium co-doped TiO₂ nanoparticles with enhanced sonocatalytic efficiency, Ultrason. Sonochem. 26 (2015) 281–292.
- [8] C. Dette, M.A. Pérez-Osorio, C.S. Kley, P. Punke, C.E. Patrick, P. Jacobson, F. Giustino, S.J. Jung, K. Kern, TiO₂ anatase with a band gap in the visible region, Nano Lett. 14 (2014) 6533–6538.
- [9] Y.C. Zhang, M. Yang, G. Zhang, D.D. Dionysiou, HNO3-involved one-step low temperature solvothermal synthesis of N-doped TiO₂ nanocrystals for efficient photocatalytic reduction of Cr (VI) in water, Appl. Catal. B Environ. 142–143 (2013) 249–258.