https://doi.org/10.30799/jnst.252.19050401 J. Nanosci. Tech. - Volume 5 Issue 4 (2019) 748–750

ISSN: 2455-0191

Share Your Innovations through JACS Directory

Journal of Nanoscience and Technology

Visit Journal at http://www.jacsdirectory.com/jnst

Enhanced Visible Light Photocatalytic Activity of TiO_2 Nanospheres/SnO_2 Quantum Dots Composite for Degradation of 4-Nitrophenol

Jayesh Bhatt[1], Surbhi Benjamin[2], Rakshit Ameta[2], Suresh C. Ameta[1,*]

[1]Department of Chemistry, PAHER University, Udaipur – 313 003, Rajasthan, India.
[2]Department of Chemistry, Faculty of Science, J.R.N. Rajasthan Vidyapeeth (Deemed-to-be University), Udaipur – 313 002, Rajasthan, India.

ARTICLEDETAILS

Article history:
Received 10 May 2019
Accepted 28 May 2019
Available online 11 June 2019

Keywords:
Quantum Dots
Endocrine Disrupting Chemicals (EDCs)
Waste Water Treatment

ABSTRACT

A composite of SnO_2 quantum dots (QDs) decorated on TiO_2 nanospheres was prepared and then used as photocatalyst in photodegradation of 4-nitrophenol. The structure of TiO_2/SnO_2 QD composites revealed that the SnO_2 quantum dots are uniformly dispersed on the surface of TiO_2 nanospheres. The effect of various parameters such as pH, concentration of dye, amount of semiconductor and light intensity was observed. The photocatalytic behavior of as-prepared samples shows better activity than pure TiO_2 nanospheres. This study presents a choice for potential applications of quantum dots in water pollution treatment.

1. Introduction

The chemical-based industries played an important role in human civilization but industrial activities introduced large quantities of chemicals in the environment causing potential harm to environment. It has only increased ever increasing scarcity of potable water because of increase in its immediate demand. Among all the pollutions, water pollution is one of the world's worst problems in these days, we are facing. Water pollution is increasing day by day due to rapid industrialization, transportation, construction, etc. Only 1% of water on Earth can be used for human utilization. Organic compounds i.e. phenols, heavy metals, drugs, detergents, insecticides, pesticides, fertilizers, surfactants, dyes and other chemical products are thrown into the water resources without any effective treatment strategy. Most of these are highly toxic to living beings. Endocrine disruptors are chemicals that can interfere with endocrine (or hormone) systems. Most of them are carcinogenic, xenogenic and toxic in nature. Environmental contamination by these toxic chemicals is causing major global problem. These substances are very toxic for animals and harmful for human life and health.

Various methods and techniques such as AOPs, biological methods, physical methods, etc. are developed to remove these pollutants [1-11]. Cost-effectiveness, ecofriendly nature and applicability on large scale for different kind of pollutants are the key factors behind this. Present study makes an attempt towards solving the problem of water pollution. Composite of TiO_2 and SnO_2 QDs may prove to be beneficial for efficient decomposition of Endocrine Disrupting Chemicals (EDCs). Exposure to EDCs in nature is a basic worry with unclear long-term negative impacts [12-21]. EDCs are discharged into nature by people, animals and industry; and therefore, enters in bodies through soil, surface water and ground water. So, degradation and decomposition of EDCs become highly important.

The use of efficient photocatalysts, nanomaterials and novel photocatalysts in various shapes and sizes with a wide range of variations with respect to their composites are employed just to increase their efficiency in decomposition of EDCs [22-25].

*Corresponding Author:ameta_sc@yahoo.com(Suresh C. Ameta)

https://doi.org/10.30799/jnst.252.19050401

2. Experimental Methods

2.1 Preparation of Nanocomposite

The composite of SnO_2 and TiO_2 was fabricated by a bottom-up approach. An amount of 0.05 g of TiO_2 was added into 10 mL of ethanol (95 vol%) under stirring for 15 min, followed by addition of 300 μL of ethanolic suspension of SnO_2 QD. The product SnO_2 QD@TiO_2 was then collected with centrifuge and rinsed with ethanol several times before being dried in vacuum oven set at 80 °C overnight to get the final product. This synthesized composite was characterized by several techniques like HRTEM and EDX before use in experiment.

3. Results and Discussion

3.1 Characterization

HRTEM images were taken to determine the shape and size of nanoparticles. These results were clearly show the formation of TiO_2 nanospheres along with SnO_2 quantum dots. HRTEM recorded on The Tecnai G^2 20 (FEI) S-Twin 200 kV transmission electron microscope. Moreover, the morphological analysis confirmed that the stannic oxide nanoparticles were quantum dots with an average diameter about 5 nm and titanium dioxide was in form of nanospheres with an average diameter of about 29 nm. EDX mapping showed the presence and uniform distribution of respective elements (SnO_2 and TiO_2) along with the absence of any impurities in the as-synthesized composite.

3.2 Degradation Process

The photocatalytic activity of the catalyst was evaluated by measuring the rate of degradation of 4-dinitrophenol (4-NP). A stock solution of (1.0 x 10^{-3} M) was prepared by dissolving 0.0139 g of 4-NP in 100 mL doubly distilled water. Further working solutions were prepared from this stock solution as and when required. The absorbance of experimental solution was determined by spectrophotometer at λ_{max} = 400 nm. The desired pH of 4-nitrophenol solution was adjusted by the addition of standard 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. Experimental solutions were irradiated with a 200 W tungsten lamp and about 3 mL aliquot was taken out every 30 min. The intensity of light was varied by changing the distance between the light source and reaction mixture. The absorbance of the solution at various time intervals was measured with the help of a spectrophotometer (Model UV-1700 Pharmaspec). A

Cite this Article as: Jayesh Bhatt, Surbhi Benjamin, Rakshit Ameta, Suresh C. Ameta, Enhanced visible light photocatalytic activity of TiO_2 nanospheres/SnO_2 quantum dots composite for degradation of 4-nitrophenol, J. Nanosci. Tech. 5(4) (2019) 748–750.

decrease was observed in the absorbance of 4-nitrophenol solution with increasing time of exposure. A plot of 1 + log A versus time was found to be linear, which indicates that the photocatalytic degradation of 4-nitrophenol followed pseudo-first order kinetic. The rate constant was calculated using the expression k = 2.303 × slope. A typical run has been given in Table 1 and graphically represented in Fig. 3. The rate constant calculated in presence of TiO_2 was found to be 1.16 × 10^{-5} sec^{-1} whereas rate constant in presence of TiO_2/SnO_2 was 3.34 × 10^{-5} sec^{-1}, which is almost 187.93 % higher. It may be concluded that SnO_2 decoration of nano-TiO_2 increases its photocatalytic efficiency in visible range for degradation of 4-nitrophenol.

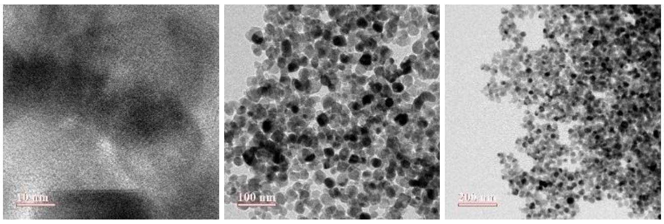

Fig. 1 HRTEM images of TiO_2/SnO_2 QDs Composite

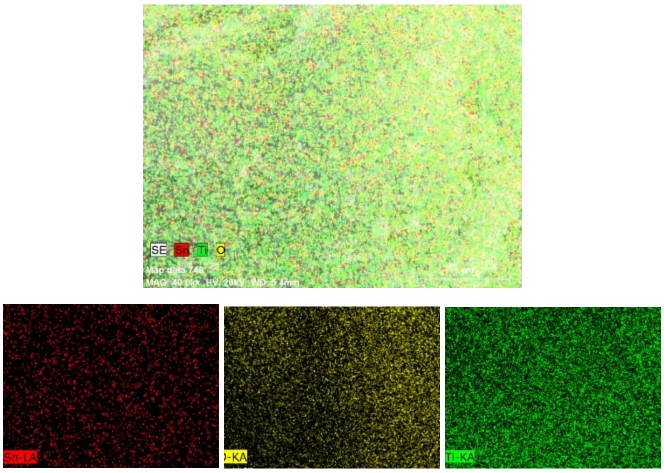

Fig. 2 EDX mapping image of TiO_2/SnO_2 QDs composite

Table 1 Typical run (pH = 8.0, [4-NP] = 4.70 × 10^{-5} M Semiconductor = 0.10 g, Light intensity = 50.0 $mWcm^{-2}$)

Time (min)	Absorbance in presence of TiO_2 (A)	1 + log A	Absorbance in presence of TiO_2/SnO_2 (A)	1 + log A
0	0.860	0.9345	0.86	0.9345
30	0.838	0.9232	0.77	0.8865
60	0.813	0.9101	0.68	0.8325
90	0.783	0.8938	0.615	0.7889
120	0.77	0.8865	0.555	0.7443
150	0.749	0.8745	0.508	0.7059
180	0.711	0.8519	0.473	0.6749

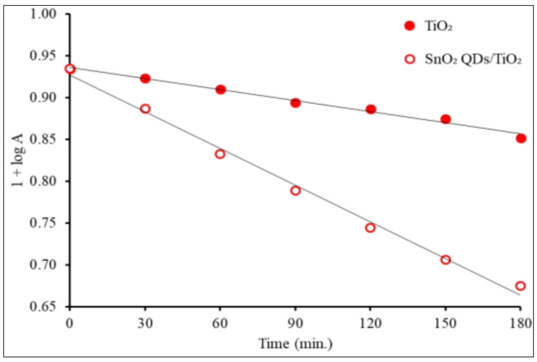

Fig. 3 Comparative typical runs with TiO_2 and TiO_2/SnO_2

3.3 Effect of Parameters

3.3.1 pH Variation

The effect of variation of pH was studied in the range 5.0 – 9.5 and reported in Fig. 4. It was observed that the rate increases with an increase in pH up to 8.0, but the rate of degradation decreases with a further increase in pH. An electron from conduction band is abstracted by dissolved oxygen to generate $O_2^{\bullet-}$. An increase in the rate of photocatalytic degradation of 4-NP with the increase in pH may be due to the availability of more $O_2^{\bullet-}$ anion radicals. A decrease in the rate of photocatalytic degradation of the 4-nitrophenol may be due to the fact that 4-NP is present in its anionic form, which will experience a force of repulsion with the negatively charged surface of the semiconductor due to absorption of more OH^- ions on the surface of the photocatalyst.

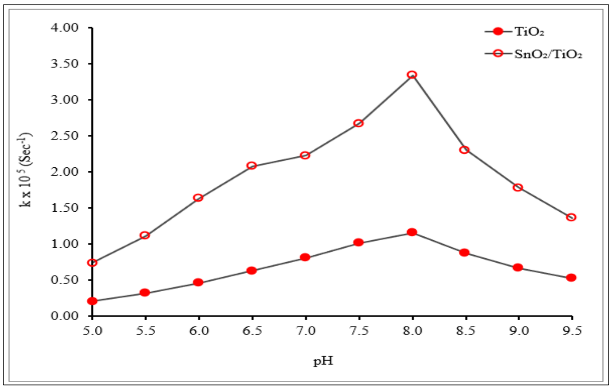

Fig. 4 Variation of rate constant with pH ([4-NP] = 4.7 ×10^{-5} M, Semiconductor = 0.10 g, Light intensity = 50.0 $mWcm^{-2}$)

3.3.2 4-Nitrophenol Concentration Variation

The effect of 4-nitrophenol concentration on its photocatalytic degradation was observed in the range of 3.2 × 10^{-5} to 6.0 × 10^{-5} M. The results are reported in Fig. 5. As the concentration of the 4-dinitrophenol was increased, it was observed that the degradation increases due to more availability of 4-DNP molecules for excitation but after 4.70 × 10^{-5} M (optimum condition), the efficiency of the photocatalytic degradation showed a declining behaviour. Here, 4-dinitrophenol will start acting as an internal filter and it will not allow the desired light intensity to reach the surface of the semiconductor present at the bottom of the reaction vessel.

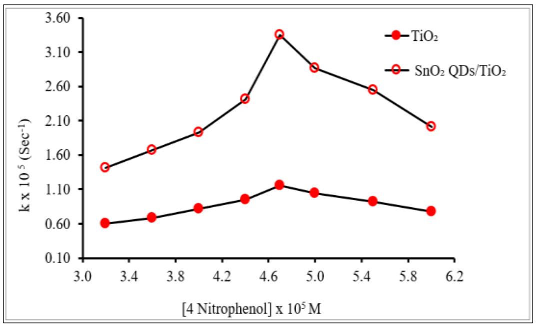

Fig. 5 Variation of rate constant with concentration of 4-nitrophenol (pH = 8.0, Semiconductor = 0.10 g, Light intensity = 50.0 $mWcm^{-2}$)

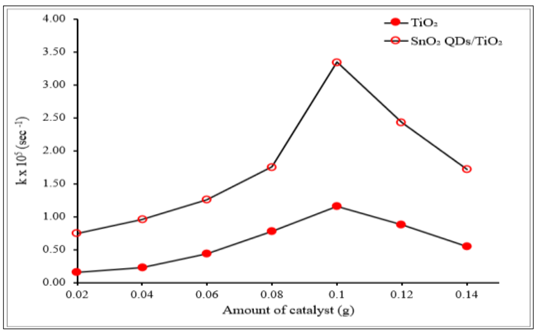

Fig. 6 Variation of rate constant with amount on photocatalyst (pH = 8.0, [4-NP] = 4.70 × 10^{-5} M, Light intensity = 50.0 $mWcm^{-2}$)

3.3.3 Amount of Composite Variation

The amount of composite may also affect the degradation of dye and hence, different amounts of TiO_2/SnO_2 composite were used. Their results are graphically represented in Fig. 6. It was observed that the rate of photocatalytic degradation increases with increase in amount of composite up to a certain value (0.10 g), but on further increasing the amount of composite, the rate of the reaction gradually declined.

https://doi.org/10.30799/jnst.252.19050401

Cite this Article as: Jayesh Bhatt, Surbhi Benjamin, Rakshit Ameta, Suresh C. Ameta, Enhanced visible light photocatalytic activity of TiO_2 nanospheres/SnO_2 quantum dots composite for degradation of 4-nitrophenol, J. Nanosci. Tech. 5(4) (2019) 748–750.

As the amount of composite was increased, the exposed surface area of the composite increases but above 0.10 g, an increase in the amount of composite will only increase the thickness of layer of the composite and not its exposed surface area. As a result, the rate of degradation decreases slightly.

3.3.4 Light Intensity Variation

The effect of light intensity on the photocatalytic degradation of 4-nitrophenol was also investigated by changing the distance between the light source and the exposed surface area of composite. The distance between the light source and exposed surface area of photocatalyst was varied from 20.0 to 70.0 mWcm^{-2} to determine the effect of light intensity on the photocatalytic degradation. The variation of results is graphically presented in Fig. 7. It was observed that as the light intensity was increased, the rate of photodegradation increases upto a certain value. Further increase in light intensity results in a decrease in the rate of photodegradation. The maximum rate was observed at 50.0 mW cm^{-2} for degradation of 4-nitrophenol.

Rate constants with different light intensities are represented in Fig. 7. It was observed that photocatalytic degradation of 4-dinitrophenol was more on increasing the intensity of light as this increases the number of photons striking per unit area of photocatalyst surface per unit time. On further increasing the intensity above 50.0 mWcm^{-2}, there was a slight decrease in the rate of photodegradation. This may be due to some thermal effects or side reactions.

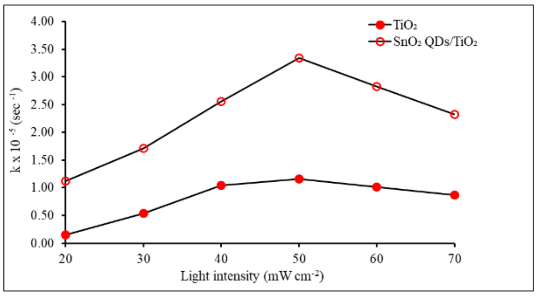

Fig. 7 Variation of rate constant with light intensity (pH = 8.0, [4-NP] = 4.70 × 10^{-5} M, Semiconductor = 0.10 g)

3.4 Mechanism

Photocatalytic mechanism for the degradation of 4-NP in presence of the as-prepared composite TiO_2/SnO_2 photocatalysts has been proposed. Electrons in TiO_2 are excited to its conduction band on light irradiation. When two semiconductors are closely coupled in the nanocomposite, conduction and valence bands of SnO_2 act as sink for the photogenerated electrons. This minimizes the recombination of the photogenerated electron-hole pairs in TiO_2 and gives sufficient time for these electrons and holes to migrate across the surface of the coupled nanocomposite photocatalysts, where these pairs participate in redox reactions with 4-NP that are adsorbed on the surfaces of the photocatalysts. The holes can react with surface-bound H_2O (or) OH^- to produce the hydroxyl radical and the electrons can reduce surface adsorbed O_2 to generate superoxide anion radical ($O_2^{\bullet -}$). The mechanism is as follows:

$$TiO_2/SnO_2 \rightarrow e^- + h^+$$

(1) $$h^+ + OH^- \rightarrow {}^{\bullet}OH \quad \text{(Oxidation)}$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$$

(2) $$O_2 + e^- \rightarrow O_2^{\bullet -} \quad \text{(Reduction)}$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet}$$

$$O_2^{\bullet -} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$$

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2$$

(3) $${}^{\bullet}OH + \text{4-Nitrophenol} \rightarrow \text{Products}$$

4. Conclusion

The TiO_2/SnO_2 QDs composites have been prepared successfully. The nanostructure of composite samples was characterized by EDX and HRTEM. The results display the SnO_2 quantum dots are spread uniformly on the TiO_2 nanospheres. Then the samples were employed in photodegradation of 4-NP. Properties of the as-obtained photocatalysts were investigated. TiO_2/SnO_2 composites exhibited a broad absorption and excellent photocatalytic activity. The observation of present work explores the use of TiO_2/SnO_2 composites for better photocatalytic performance in treatment of polluted water.

References

[1] K.G. Pavithra, P.S. Kumar, V. Jaikumar, P.S. Rajan, Removal of colorants from wastewater: A review on sources and treatment strategies, J. Ind. Eng. Chem. 75 (2019) 1-19.

[2] M.C. Collivignarelli, A. Abbà, M.C. Miino, S. Damiani, Treatments for colour removal from wastewater: State of the art, J. Environ. Manage. 236 (2019) 727–745.

[3] L. Rizzo, S. Malato, D. Antakyali, V.G. Beretsou, M.B. Đolić, et al., Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater, Sci. Total Environ. 655 (2019) 986–1008.

[4] H.C. Yap, Y.L. Pang, S. Lim, A.Z. Abdullah, H.C. Ong, C.H. Wu, A comprehensive review on state-of-the-art photo, sono, and sonophotocatalytic treatments to degrade emerging contaminants, Int. J. Environ. Sci. Technol. 16 (2019) 601-628.

[5] M. Sathasivam, S. Shanmugapriya, V. Yogeshwaran, A.K. Priya, Industrial waste water treatment using advanced oxidation process – A review, Int. J. Eng. Adv. Technol. 8 (2019) 485-488.

[6] A. Sharma, J. Ahmad, S.J.S. Flora, Application of advanced oxidation processes and toxicity assessment of transformation products, Environ. Res. 167 (2018) 223-233.

[7] C. Teodosiu, A.F. Gilca, G. Barjoveanu, S. Fiore, Emerging pollutants removal through advanced drinking water treatment: A review on processes and environmental performances assessment, J. Clean. Prod. 197 (2018) 1210-1221.

[8] M.G. Peleyeju, O.A. Arotiba, Recent trend in visible-light photoelectrocatalytic systems for degradation of organic contaminants in water/wastewater, Environ. Sci: Water Res. Technol. 4 (2018) 1389-1411.

[9] B. Jain, A.K. Singh, H. Kim, E. Lichtfouse, V.K. Sharma, Treatment of organic pollutants by homogeneous and heterogeneous Fenton reaction processes, Environ. Chem. Lett. 16 (2018) 947-967.

[10] D. Kanakaraju, B.D. Glass, M. Oelgemöller, Advanced oxidation process-mediated removal of pharmaceuticals from water: A review, J. Environ. Manage. 219 (2018) 189-207.

[11] D.B. Miklos, C. Remy, M. Jekel, K.G. Linden, J.E. Drewes, U. Hübner, Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review, Water Res. 139 (2018) 118-131.

[12] T. Colborn, F.S. Vom Saal, A.M. Soto, Developmental effects of endocrine-disrupting chemicals in wildlife and humans, Environ. Health Perspect. 101 (1993) 378–384.

[13] J.M. Braun, Early-life exposure to EDCs: Role in childhood obesity and neurodevelopment, Nat. Rev. Endocrinol. 13 (2017) 161–173.

[14] I. Sidorkiewicz, K. Zareba, S. Wołczynski, J. Czerniecki, Endocrine-disrupting chemicals-Mechanisms of action on male reproductive system, Toxicol. Ind. Health. 33 (2017) 601-609.

[15] S. Sifakis, V.P. Androutsopoulos, A.M. Tsatsakis, D.A. Spandidos, Human exposure to endocrine disrupting chemicals: Effects on the male and female reproductive system, Environ. Toxicol. Pharmacol. 51 (2017) 56–70.

[16] M. Mallozzi, C. Leone, F. Manurita, F. Bellati, D. Caserta, Endocrine disrupting chemicals and endometrial cancer: An overview of recent laboratory evidence and epidemiological studies, Int. J. Environ. Res. Public Health 14 (2017) 334-1-23.

[17] S. Li, Q. Sun, Q. Wu, W. Gui, G. Zhu, D. Schlenk, Endocrine disrupting effects of tebuconazole on different life stages of zebrafish (Danio rerio), Environ. Poll. 249 (2019) 1049-1059.

[18] S. Sabir, M.S.H. Akash, F. Fiayyaz, U. Saleem, M.H. Mehmood, K. Rehman, Role of cadmium and arsenic as endocrine disruptors in the metabolism of carbohydrates: Inserting the association into perspectives, Biomed. Pharmacol. 114 (2019) 108802-1-10.

[19] G.J. Zhou, X.Y. Li, K.M.Y. Leung, Retinoids and oestrogenic endocrine disrupting chemicals in saline sewage treatment plants: Removal efficiencies and ecological risks to marine organisms, Environ. Inter. (2019) 103-113.

[20] S.Y. Wee, A.Z. Aris, F.M. Yusoff, S.M. Praveena, Occurrence and risk assessment of multiclass endocrine disrupting compounds in an urban tropical river and a proposed risk management and monitoring framework, Sci. Total Environ. 671 (2019) 431-442.

[21] B.T. Doherty, K. Hoffman, A.P. Keil, S.M. Engel, H.M. Stapleton, B.D. Goldman, et al., Prenatal exposure to organophosphate esters and behavioral development in young children in the pregnancy, infection, and nutrition study, Neuro Toxicol. 73 (2019) 150-160.

[22] J. Hou, H. Li, Y. Tang, J. Sun, H. Fu, et al., Supported N-doped carbon quantum dots as the highly effective peroxydisulfate catalysts for bisphenol F degradation, App. Catal. B: Environ. 238 (2018) 225-235.

[23] M. Tanveer, G.T. Guyer, G. Abbas, Photocatalytic degradation of ibuprofen in water using TiO_2 and ZnO under artificial UV and solar irradiation, Water Environ. Res. (2019) doi: 10.1002/wer.1104 (Accepted Article).

[24] M. Fu, J. Xing, Z. Ge, Preparation of laccase-loaded magnetic nanoflowers and their recycling for efficient degradation of bisphenol A, Sci. Total Environ. 651 (2019) 2857-2865.

[25] A. Bhatnagar, I. Anastopoulos, Adsorptive removal of bisphenol A (BPA) from aqueous solution: A review, Chemosphere 168 (2017) 885-902.

https://doi.org/10.30799/jnst.252.19050401

Cite this Article as: Jayesh Bhatt, Surbhi Benjamin, Rakshit Ameta, Suresh C. Ameta, Enhanced visible light photocatalytic activity of TiO_2 nanospheres/SnO_2 quantum dots composite for degradation of 4-nitrophenol, J. Nanosci. Tech. 5(4) (2019) 748–750.