

Enhanced Photocatalytic Activity of Core-Shell TiO₂/SnO₂ Nanostructures under UV Illumination

Priyanka Basyach, Pawan Chetri*, Amarjyoti Choudhury

Abstract: Here we report on preparation of core-shell TiO₂/SnO₂ via a simple two-step method where the core TiO₂ is first synthesized using a usual sol-gel procedure followed by addition of SnO₂ solution of three different concentrations (0.2 M, 0.4 M and 0.6 M) to avail the coating layer. Both core and the corresponding three core-shells are characterized with various spectroscopic tools such as UV-Vis-DRS spectra, PL spectra. Also the structural and morphological properties are studied via XRD, TEM and EDX spectra. Then the photocatalytic performance of the core as well as the core-shell nanostructures are investigated under UV light illumination to degrade Phenol and it is found that the core-shell TiO₂/SnO₂ nanostructures exhibit better photocatalytic activity than the core TiO₂ nanostructures.

Keywords: Component; Core-shell, XRD, TEM, EDX, Photocatalytic

Introduction

Semiconductor nanostructures are now established materials in the research field as they possess interesting optical and electrical properties which found them a place for the application in photovoltaics and photocatalysis. Generally core-shell nanostructure is achieved by coating a lower energy gap nanomaterial by a higher energy gap material where the cores and shells may be any kind of colloidal particles, i.e. metals, insulators and all classes of semiconductors[1]. Two types of core-shell nanostructures namely TYPE 1 and TYPE 2 core-shell are reported till date. An enhanced luminescence is observed with TYPE 1 core-shell nanostructures while the adverse effect is prominent in TYPE 2 core-shell nanostructures due to less charge recombination[2]. Inverted core-shell nanostructures are also reported where the core material is typically a higher band gap material and the shell material is a lower band gap material[3]. Photocatalysis is a phenomenon which requires charge separation of electron and holes which is favored by formation of core-shell nanostructures as charge separation occurs at the interface due to difference in band alignment of the two materials. Transition metal oxides are good photocatalytic materials due to large surface area. Now a days, typical composite nanostructures like core-shell nanostructure are fabricated inside nanorods with outside covered layers e.g. TiO₂/ZnO, ZnO/MgO and ZnO/Er₂O₃ [4]. Also it is reported on enhanced photocatalytic activity of core-shell TiO₂/MgO nanostructures by H.S.Jung and his co workers where Mg(OH)₂ gel was topoactically decomposed on TiO₂ particle surface resulting in highly nanoporous MgO coated TiO₂ particles.[5]. In our work, we prepared core-shell TiO₂/SnO₂ nanoparticles via a simple sol-gel method and studied their photocatalytic activity for phenol under UV light illumination which is found to be enhanced than TiO₂ nanoparticles.

I. Materials and methods

Titanium iso Propoxide, 2-Propanol, Stannous Chloride and

ethanol were used as the main reactant. For all washing and cleaning purpose, double distilled water was used. For the synthesis of core TiO₂ nanoparticles, we followed a standard procedure[6] where titanium isopropoxide, Ti{OCH(CH₃)₂}₄, was mixed with 2-propanol in a 2:5 ratio and stirred for 30 min for homogenous mixing. Then a few drops of water were added for hydrolysis. SnO₂ nanoparticles were synthesized following[7] only with an increment of the pH to 11. By this procedure, SnO₂ solutions of three different concentrations were prepared namely 0.2 M, 0.4 M and 0.6 M. To the prepared TiO₂ nanoparticles, SnO₂ solutions were added dropwise followed by stirring for 4-5 hours then centrifuging and drying to obtain the three core-shell TiO₂/SnO₂ nanostructures named as TS₂, TS₄ and TS₆.

The UV-Visible DRS spectra of the samples were recorded in the range 300-700 nm using Shimadzu UV-2550 UV-Visible spectrophotometer. The photoluminescence spectra were recorded by a Perseus-Eloven fluorescence spectrophotometer. Powder X-Ray diffraction (XRD) study was performed by a Rigaku Miniflex X-Ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 30 kV and 15 operating at with 2θ ranges from 10-70 degree. TEM characterization was done by a JEOL 2100 200 KV TEM instrument and EDX spectra was recorded with JEOL JSM SEM Model 6390 LV under liquid nitrogen environment

II Results and Discussion

Fig 1(a) shows the XRD pattern for core TiO₂ and the corresponding three core-shells TS₂ (0.2 M Sn²⁺), TS₄ (0.4 M Sn²⁺), TS₆ (0.6 M Sn²⁺). The XRD pattern clearly shows the formation of anatase phase of core TiO₂ in all the four

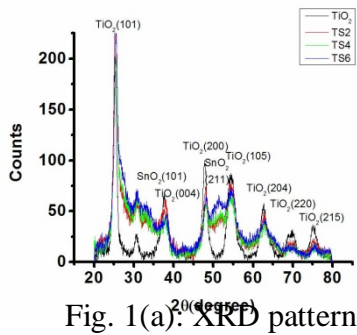


Fig. 1(a): XRD pattern

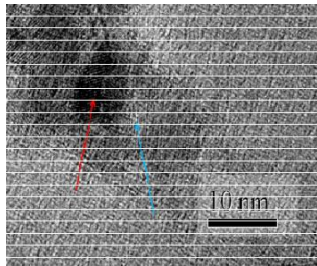


Fig. 1(b): TEM image

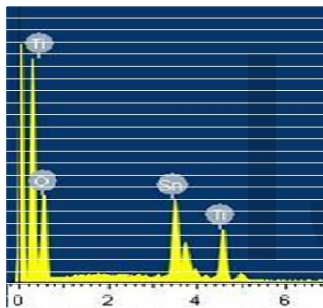


Fig.1(c): EDX pattern

samples. The diffraction peaks of TiO₂ for different values of $2\theta = (25,38,48,54,63,69,75)$ from different crystal planes $\{(101),(004),(200),(105),(204),(220),(215)\}$ respectively are found in the pristine TiO₂ nanoparticles as well as all the three core-shell structures. Also two peaks of SnO₂ are found in the core-shell nanostructures indicating the presence of SnO₂ in the core-shell sample. The presence of all the constituent elements in the sample are also confirmed via EDX spectra at Fig 1(c). Fig 1(b) shows the TEM image of the core-shell TiO₂/SnO₂ nanostructure where the core portion is the darker regime that is indicated by red colored arrow and the surrounding lighter regime is the shell portion which is indicated by the blue colored arrow. The core has a size of 15 nm with a shell thickness of 20 nm.

The absorption is calculated by Kubelka-Munk plot $F(R) = (1-R)/2R$, where R is the reflectance of the sample and it is found from the reflectance spectra. The band gap of the nanomaterials were calculated from a plot of the modified Kubelka-Munk function $[F(R) E]^{1/2}$ vs the energy of absorbed light $E (=h\nu)$ where $R=R_{\text{sample}}/R_{\text{BaSO}_4}$.

After plotting the graphs and fitting linear, we get the band gaps as:

Band gap of TiO₂ nanostructure=3.25 eV, Band gap of TS2 = 2.9 eV, Band gap of TS4 = 2.75 eV, Band gap of TS6 = 2.6 eV

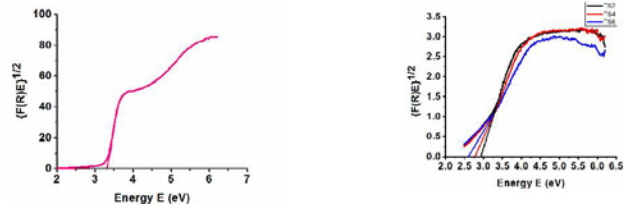


Fig. 2(a): Band gap determination of TiO₂ nanoparticles and (b) Band gap determination of the corresponding three core-shell nanoparticles.

Which shows the electrons at core-shell nanostructures can get excited even at visible light making them more practically applicable for photo catalysis purpose. Fig 2(c) depicts the photoluminescence spectra of core TiO₂ nanoparticles as well as the corresponding three core-shell nanostructures excited at a wavelength of 320 nm. We can see from the graph that the intensity of the band edge emission peak of core TiO₂ nanoparticles is lowered in the core-shell TS2 and TS4 nanostructures which signifies that the recombination is very less in the core-shell nanostructures than the core structure. That means the electron hole overlap integral in these type of core-shell nanostructures is very less indicating pronounced charge separation in the samples which is one of important factors contributing to photocatalysis phenomenon. But in case of TS6 sample we can see that the intensity of the band edge peak is far more enhanced than in the core structure signifying less charge separation and more recombination of electron and holes in the sample which makes it unfavorable for photocatalysis purpose. Thus both band gap calculation and photoluminescence spectra provide sufficient proof of TYPE 2 core-shell nanostructures. The peak around 425 nm corresponds to Ti³⁺ defect states and other peaks correspond to oxygen vacancy related states. Fig 2(d) represents the photocatalytic degradation of phenol under UV light illumination (365 nm) for all the four samples i.e TiO₂, TS2, TS4 and TS6 and it is found that core-shell TS2 and TS4 show much better degradation than the core TiO₂ nanoparticles.

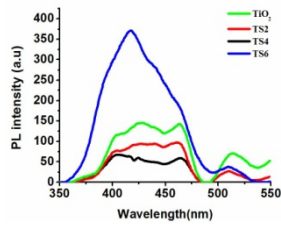


Fig. 2(c): Photoluminescence spectra

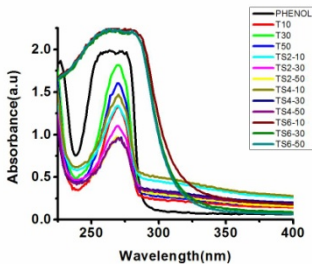


Fig. 2(d): Photocatalytic degradation

The degradation efficiency was calculated from the decrease in concentration or degradation of Phenol from its initial concentration was studied by the decrease in the absorption peak (A_t) of phenol solution irradiated for 10 min, 30 min and 50 min. The degradation efficiency of phenol solution is given by $\{(A_0 - A_t) / A_0\} \times 100\%$ [8]. For pristine TiO_2 , the maximum degradation efficiency was found as 35.35% which is at 10 min irradiation while it is decreased at 30 min irradiation time and again increased at 50 min irradiation. This is because of the fact that at 30 min irradiation, not enough charge carriers are created to excite phenol and most of the charge carriers are lost in recombination before they can reach the surface. Again with increasing time, the photocatalytic degradation again increases as with increase in time enough charge carriers are created and they get enough time to reach the surface while some of them are lost in recombination. For core-shell TS2 and TS4, we can see that degradation increases with increase of time and the efficiency is much higher than that of core TiO_2 nanoparticles because of more prominent charge separation in the samples. The highest degradation was found for TS4 core-shell nanostructures which is 52%. We could not see any kind of degradation in case of TS6 sample which is attributed to the fact that charge separation is very less in the sample and also maximum number of electrons are lost in recombination. Another reason may be the following fact that the shell thickness becomes so high, that the light source does not have enough energy to excite the electrons and those electrons that are excited they could not tunnel to the surface to take part in the reaction that yields photocatalysis.

Table 1: Photocatalytic degradation of Phenol by different prepared samples at 10, 30 and 50 minutes of UV irradiation.

Sample name	10 min	30 min	50 min
TiO_2	35.35%	8%	19%
TS2	35.35%	44.64%	51%
TS4	25%	50%	52%

Conclusion

Thus, in this report, we have shown the successful synthesis of core TiO_2 nanoparticles along with core-shell $\text{TiO}_2 / \text{SnO}_2$ nanoparticles with three different concentrations. Also this report throws light on degradation of a carcinogenic material like phenol under UV light illumination and it is found that the core-shell nanostructures show better photocatalytic activity than the core structure owing to charge separation. It is expected that lots of scope are available to work on this material $\text{TiO}_2 / \text{SnO}_2$ for further detailed study on photocatalytic degradation of other toxic materials in near future.

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References

- [1] P. Basyach and A. Choudhury, "Structural and optical properties of core-shell $\text{Ag}_2\text{S}/\text{HgS}$ nanostructures," *Mat. Res. Bulletin*, New York, vol. 48, pp. 2543-2548, 2013.
- [2] S. A. Ivanov, A. Piryatinski, J. Nanda, S. Tretiak, K. R. Zavadil and W. O. Wallace, et al., "Type-II Core/Shell CdS/ZnSe Nanocrystals: Synthesis, Electronic Structures, and Spectroscopic Properties," *J. Am. Chem. Soc.*, U.S., vol. 129, pp. 11708-11719, 2007.
- [3] L. P. Balet, S. A. Ivanov, A. Piryatinski, M. Achermann, and V. I. Klimov, "Inverted Core/Shell Nanocrystals Continuously Tunable between Type-I and Type-II Localization Regimes," *Nano. Lett.*, U.S., vol. 4, pp. 1485-1488, 2004.
- [4] C. W. Zou¹ and W. Gao, "Zinc oxide, Vanadium pentoxide, Titanium dioxide, Processing of composite oxides, Nanostructure, Photoluminescence, Photocatalysis, TEEM South Korea, vol. 11, pp. 1-10, 2010.
- [5] H. S. Jung, J. K. Lee, M. Nastasi, J. R. Kim, S. W. Lee and J. Y. Kim et al., "Enhanced photocatalytic activity by using TiO_2 - MgO core-shell structured nanoparticles," *Appl. Phys. Lett.*, U.S., vol. 88, pp. 013107-013109, 2006.
- [6] S. Mahshid, M. S. Ghamsari, M. Askari, N. Afshar and

S.Lahuti, "Synthesis TiO₂ nanoparticles by hydrolysis and peptization of titanium isopropoxide solution," Semiconductor Physics, Quantum Electronics & Optoelectronics, vol.9, pp. 68, 2006

[7] P.Chetri and A.Choudhury, "Investigation of optical properties SnO₂ nanoparticles," Physica E, New York, vol.47, pp.257- 263, 2013.

[8] B.Choudhury, B.Borah and A.Choudhury, "Extending Photocatalytic Activity TiO₂ Nanoparticles to Visible Region of Illumination by Doping of Cerium", Ph chemistry and Photobiology, U.S., vol.88, pp.257-264, 2012

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