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Synthesis and Characterization of A Novel Ternary Photoactive Chitosan-Polypyrrole-TiO_2 System for Visible Light Photocatalytic Application

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ABSTRACT

A series of novel three component photocatalytic system consisting of bio-polymer chitosan (Chit), organic conducting polymer polypyrrole (Ppy) and UV active TiO_2 were designed and synthesized by varying the proportions of Chit and Ppy with respect to TiO_2. The synthesized materials were characterized for their elemental and morphological behaviour using different instrumental techniques like FTIR, XRD, CHN, diffuse reflectance spectra and SEM analysis. The ternary catalysts exhibit enhanced photodegradation efficiency in methylene blue dye degradation under visible light than the binary counterparts (Chit-TiO_2 and Ppy-TiO_2) and bare anatase TiO_2, the efficiencies being 86.4%, 67.2%, 72.8% and 58.6% respectively. Ppy photosensitizes TiO_2 in the visible region while Chit enhances the photoactivity of TiO_2 by adsorbing more dye molecules and thus inhibiting e^--h^+ recombination. Synergism exists between the roles of Chit and Ppy and as a result the ternary system exhibits remarkably higher photoactivity in visible region.

1. Introduction

TiO_2 is an attractive catalyst in photocatalysis due to its low cost, high photocatalytic activity, stability in aquatic systems and low environmental toxicity [1,2]. The use of bare TiO_2 phases in the industrial treatment of dyestuffs is limited as i) only small amount of photons are absorbed in the visible region (upto 380 nm) with the consequent need to irradiation with UV light, ii) there is high recombination rate for the photoproduced electron-hole pairs, etc. [3]. So the research direction is now focused on modification of electronic and morphological properties of TiO_2 for the enhancement of its photoefficiency under visible light [4,5].

Supporting materials such as silica, ZrO_2, zeolites, chitosan and activated carbon were used for the preparation of TiO_2 based photocatalysts to avoid the recombination of e^--h^+ pair via increasing the possibility of adsorption of reacting species and providing them continuously to the TiO_2 surfaces. Sensitizers such as polymers, metal ions were added to TiO_2 to shift the light absorption toward intense visible region [6–8]. A variety of ternary and quaternary compounds in oxide and oxyhalide forms was reported for the degradation of different pollutants [3]. Ternary system graphene–(CdS nanowire)–TiO_2 nanocomposite has been investigated for various photo-redox processes including reduction of nitro organics, heavy metal ions and oxidation of alcohols [9]. Rutile particles doped with Cr and Sb were shown to be active for photocatalytic production of O_2 from $AgNO_3$ solution under visible irradiation [10]. TiO_2 modified with Fe^{3+}, Ni^{2+} and Au nanoparticles has been reported for the selective oxidation of cyclohexane in the presence of O_2 under sunlight irradiation [11]. Ternary composites based on conducting polymer have been successfully used in electrochemical sensing of different analyte compounds [12]. However, conducting polymer based ternary catalysts are very less in the field of photocatalysis. Ternary composite of poly(3-hexylthiophene), carbon nitride and graphene was applied as an efficient photocatalyst for the degradation of methylene blue under visible light [13]. Recently Pandiselvi et al. [14] prepared ternary system chitosan-polyaniline/ZnO hybrid composites and studied their UV light degradation of reactive orange 16.

The main objective of the present work is to design a novel conducting polymer based three component photocatalyst involving an adsorbent, a visible light sensitizer and TiO_2. Chitosan (Chit) is a biopolymer that enhances adsorption-photocatalytic process of dye species with the help of pendant hydroxyl and amino groups in its backbone [15]. Chit as a supporting material in Chit–modified–TiO_2 adsorbs dye molecules and supplies them to TiO_2 continuously [4]. The synergic role of Chit with TiO_2 was also observed in the adsorptive removal of organic dyes [5]. Polypyrrole (Ppy) has attracted much commercial applications due to its greater conductivity, good environmental stability and facile synthesis [16]. Ppy facilitates nanocomposites to absorb more visible light and generate more e^--h^+ pairs, which could result in a greater photocatalytic activity of TiO_2 nanoparticles [6,7]. The existence of Ppy units along with polyaniline greatly improves the photoactivity of TiO_2 [8]. So the combination of salient features of Chit and Ppy with TiO_2 is expected to deliver an enhanced visible light photocatalytic efficiency. The resulting ternary system Chit-Ppy-TiO_2 could thus function without any notified drawbacks of TiO_2. The results of the present work explicitly show that the newly developed catalysts fulfil this anticipation with improved photocatalytic functionality.

2. Experimental Methods

2.1 Materials

Pyrrole (99.5%) was obtained from Merck and it was distilled over zinc dust before its use. TiO_2 (99.8% anatase) from Sigma-Aldrich was used as-received. Chitosan was prepared from chitin (Sigma–Aldrich) following base hydrolysis. Methylene blue (Ranbaxy), anhydrous $FeCl_3$ (96%, Merck) and other chemicals of reagent grade and were used without further purification. Distilled water was used throughout the work.

2.2 Synthesis of Chitosan-Polypyrrole-TiO_2

The ternary photocatalyst chitosan–polypyrrole–TiO_2 (Chit-Ppy-TiO_2) was developed via a typical two stage consecutive process. A known amount of Chit was added to 3% acetic acid solution and stirred overnight for the complete dissolution. TiO_2 was added to the above acidified solution and stirred for further 30 min and ultrasonicated for 10 min to get a homogeneous dispersion of TiO_2 particles. Pyrrole was added to the above solution and stirring was continued for further 30 min to facilitate pyrrole monomer adsorption onto TiO_2 surface. Anhydrous $FeCl_3$ was added to the above solution (pyrrole: $FeCl_3$ = 1:2). Pyrrole was completely polymerized over TiO_2 particle for 2 h at room temperature (~ 30 °C). The

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pH of the acidic solution was brought to 9 using 1 M NaOH for the deposition of Chit over Ppy/TiO_2. The formed ternary photocatalyst was filtered, washed thoroughly with deionised water and finally dried at 80 °C for overnight. The dried catalyst was ground into a fine powder and stored in zip-lock polythene cover. The catalytic systems with the proportions of the three components 1:1:1, 1:1:5, 1:1:20, 1:1:50 and 1:1:100 were synthesized. The catalyst samples were labelled as Chit–Ppy–TiO_2 with the weight % inside parenthesis. The binary photocatalysts Chit–TiO_2 and Ppy–TiO_2 were also prepared keeping wt% ratio of Chit or Ppy to TiO_2 as 1:100.

2.3 Characterization of Chitosan-Polypyrrole-TiO_2

The synthesized photocatalysts were characterized using Fourier transform infrared spectroscopy (JASCO FTIR-410), X-ray diffraction (PANalytical Expert Pro-MPG), diffuse reflectance spectroscopy (DRS; Shimadzu UV 2700 instrument), and scanning electron microscope (VEGA3-TESCAN) techniques. The band gap energy of the photocatalysts was obtained from diffuse reflectance spectroscopy (DRS) using Kubelka-Munk function [17]. CHN elemental analysis was carried out (Vario Micro Cube) to find the carbon, hydrogen and nitrogen content of the synthesized photocatalysts using Sulfanilamide as a standard reference.

2.4 Photocatalytic Activity Test

The preliminary photocatalytic activity of the synthesized catalysts was evaluated using methylene blue (MB; Ranbaxy) as a model dye at natural pH (6.8) with 200 mL of 50 ppm MB aqueous dye solution, 2 mL H_2O_2 and 100 mg catalyst. The degradation reaction was conducted in an immersion type (Heber photoreactor, model HIPR LC-150) photoreactor fitted with 150 W tungsten-halogen lamp ($\lambda \geq 400$ nm: intensity = 14.79 mW/cm^2 at 555 nm). The degradation reaction was monitored after 1 h by withdrawing 2 mL sample solution followed by its dilution, centrifugation and absorbance measurement at 650 nm (UV-vis Spectrophotometer; Perkin Elmer Lambda 25). The % degradation of MB was calculated from Eq. (1) using absorbance value.

$$\%\ \text{degradation} = \frac{[\text{MB}]_o - [\text{MB}]_t}{[\text{MB}]_o} \times 100 \quad \text{-----}\ (1)$$

where, $[\text{MB}]_o$ = initial concentration of MB and $[\text{MB}]_t$ = concentration of MB after t time.

3. Results and Discussion

3.1 FTIR and PXRD Analyses

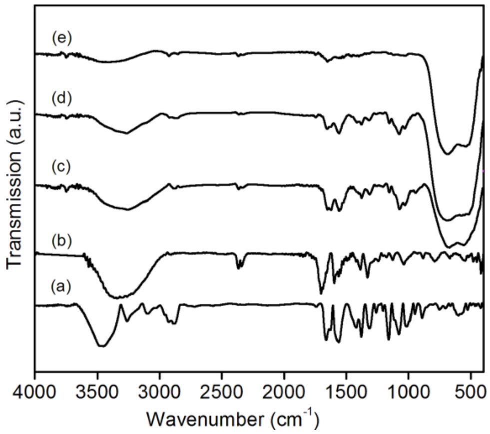

Fig. 1 FTIR spectra of (a) Chit, (b) Ppy, (c) Chit-Ppy-TiO_2 (1:1:1), (d) Chit-Ppy-TiO_2 (1:1:5) and (e) Chit-Ppy-TiO_2 (1:1:100)

Fig. 1 shows the FTIR spectra of Chit, Ppy and the synthesized photocatalysts. Chit has the characteristic peaks at 1661 cm^{-1} (C=O absorption of –NHC=O structure), 1077 cm^{-1} (C–O stretching of primary alcohols), 2876 cm^{-1} (asymmetric stretching of –CH group), 1379 cm^{-1} (COO– in carboxylic acid salt), 1558 cm^{-1} (N–H deformation of amide) and a broad band at 3250-3450 cm^{-1} (–OH and –NH groups). Ppy shows the characteristic peaks at 1529 cm^{-1} (C=C), 1419 cm^{-1} (C–N), and 1127 cm^{-1} (N=Q=N vibrational mode; Q refers to quinoid-type pyrrole rings). The broad peak in the range from 400 cm^{-1} to 800 cm^{-1} indicates the presence of TiO_2 [18]. The characteristic peaks of both Chit and Ppy in the IR spectra of the photocatalysts confirm their presence and also the formation of ternary photocatalyst Chit-Ppy-TiO_2. The merged O–H and N–H band appearing with a red shift in Chit-Ppy-TiO_2 (1:1:1) suggests a stronger interaction between Chit and Ppy with TiO_2. The intensity of the characteristic peaks of Chit and Ppy decreases with decrease in their content in the photocatalysts (spectra d and e). The characteristic peaks of Chit and Ppy appear in the photocatalyst even at the very low concentration of 1 wt%. This further suggests the formation of ternary photocatalysts.

XRD patterns of Chit and the prepared photocatalysts are given in Fig. 2. Chit shows the diffraction peaks at 2θ = 9.29° and 19.38° representing respectively the reflection planes 0 2 0 and 1 1 0 [19]. The appearance of peaks at 2θ = 25.3°, 37.8° and 48.1° in respect of the planes 1 0 1, 0 0 4 and 2 0 0 confirms the preservation of anatase TiO_2 phase (JCPDS card no. 21-1272) in all the synthesized photocatalysts [4,6]. However, there is contribution from amorphous phase Chit at 2θ = ~ 9.3° as a band (in b-d patterns) but it is visibly seen as subdued with increase in TiO_2 content in the photocatalysts.

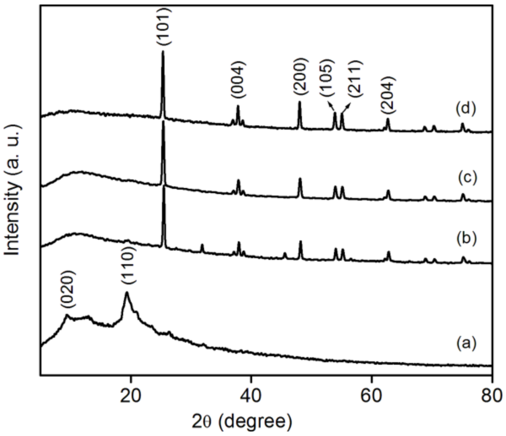

Fig. 2 XRD patterns of (a) Chit, (b) Chit-Ppy-TiO_2 (1:1:1), (c) Chit-Ppy-TiO_2 (1:1:10) and (d) Chit-Ppy-TiO_2 (1:1:100).

3.2 CHN Analysis

The data given in Table 1 represents the carbon, hydrogen and nitrogen contents of Chit, Ppy and the three component photocatalysts. The obtained C H N values suggest that the original organic contents present in three component catalysts are somewhat closer to the calculated values (given in parenthesis in Table 1) and hence confirm the formation of ternary photocatalysts. The higher than the expected H values at lower polymer content in Chit-Ppy-TiO_2 (1:1:50) and (1:1:100) suggests the formation of some hydroxyl groups on the surface of the catalyst.

Table 1 CHN analytical data of chitosan, Ppy and the prepared photocatalysts

Catalyst	C H N content (%)		
	C	H	N
Chitosan	41.5	6.14	6.1
Polypyrrole	52.3	4.16	11.07
Chit-Ppy-TiO_2 (1:1:1)	26.68 (31.23)	3.09 (3.43)	4.69 (5.72)
Chit-Ppy-TiO_2 (1:1:10)	4.39 (7.8)	0.56 (0.86)	ND (1.43)
Chit-Ppy-TiO_2 (1:1:50)	1.80 (2.28)	0.42 (0.20)	ND (0.33)
Chit-Ppy-TiO_2 (1:1:100)	0.82 (1.16)	0.24 (0.10)	ND (0.17)

ND = not detected. Values in the parenthesis shows the calculated one.

3.3 Bandgap Energy

The band gap energy (Eg) values given in Table 2 are the average of both direct and indirect band gap energies. This method well suits for anatase TiO_2 with the value of 3.21 eV and therefore it is adopted for all other materials.

Table 2 Band gap energies of the photocatalysts

Catalyst	E_g (eV)	Catalyst	E_g (eV)
TiO_2	3.21	Chit-Ppy-TiO_2 (1:1:1)	2.89
Chit-TiO_2 (1:100)	3.20	Chit-Ppy-TiO_2 (1:1:50)	3.14
Ppy-TiO_2 (1:100)	3.16	Chit-Ppy-TiO_2 (1:1:100)	3.17

Ppy sensitizes TiO_2 tuning E_g to 3.16 eV at 1%. This supports the visible light sensitizing property of Ppy in the composite Ppy-TiO_2 [6]. The E_g value of the ternary system gradually decreases with increase in the amount of Ppy present in the system. The catalyst with maximum (~ 33 wt%) Ppy content has E_g 2.89 eV among the material studied.

3.4 SEM Analysis

SEM image of TiO_2 (Fig. 3, image a) shows smooth-surfaced uniform spherical particles of size ~ 100 nm. This original spherical nature of TiO_2 is retained in the photocatalysts with higher TiO_2 content (image d). However, at lower level, for instance in Chit-Ppy-TiO_2 (1:1:1) (image b) which has equal content of the three components, agglomeration predominates forming irregularly shaped clumps of secondary particles. Thus a strong interaction exists among the three components.

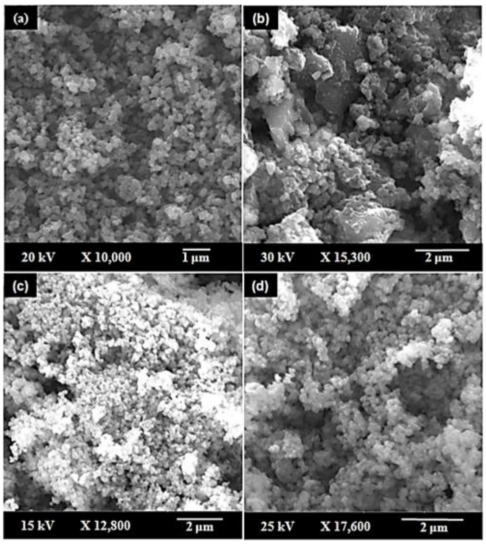

Fig. 3 SEM images of (a) TiO_2, (b) Chit-Ppy-TiO_2 (1:1:1), (c) Chit-Ppy-TiO_2 (1:1:50) and (d) Chit-Ppy-TiO_2 (1:1:100).

3.5. Visible Light Photodegradation of MB

The photocatalytic activity of bare TiO_2, binary and ternary catalytic systems of varying proportion of the three components was studied by MB dye degradation under visible light irradiation. Table 3 represents the results. The anatase phase bare TiO_2 exhibits only 58.6% degradation efficiency. When Chit/Ppy is coated in very low amount on TiO_2 (1:100), the resulting binary core-shell catalysts, Chit-TiO_2 and Ppy-TiO_2 show considerably higher efficiencies (Table 3). The photocatalyst with equal amount of the three components (1:1:1), nevertheless, exhibits a lower degradation activity even below bare TiO_2. This is due to the lesser exposure of TiO_2 particles and hence their active sites, as they are hidden in the agglomerated secondary particles (SEM image b in Fig. 3). However, the catalytic activity of the ternary systems is enhanced with increase in TiO_2 content because of the exposure of more number of TiO_2 active sites.

Table 3 Visible light degradation of MB over different catalysts

Catalyst	D* (%)	Catalyst	D* (%)
TiO_2	58.6	Chit-Ppy-TiO2 (1:1:5)	46.2
Chit-TiO_2 (1:100)	67.2	Chit-Ppy-TiO2 (1:1:20)	76.3
Ppy-TiO_2 (1:100)	72.8	Chit-Ppy-TiO2 (1:1:50)	79.3
Chit-Ppy-TiO_2 (1:1:1)	34.6	Chit-Ppy-TiO2 (1:1:100)	86.5

Reaction condition: [MB] = 50 ppm (200 mL), Catalyst amount = 100 mg, reaction time = 1 h, H_2O_2 = 2 ml. D = MB degradation.*

The presence of Chit and Ppy in very low amounts in the active catalyst Chit-Ppy-TiO_2 (1:1:100) greatly improves the dye degradation efficiency to 86.5%, which is nearly 48% higher than the value for bare TiO_2. Not only that, this catalyst's efficiency is certainly greater than those of binary counterparts. That means the combined effect of Chit and Ppy operates on TiO_2. Chit being a good adsorbent [15] uptakes dye molecules from solution phase and provides them to the active sites of TiO_2. While Ppy, being dark-coloured, helps in the absorption of visible light [6,7] and the consequent e^--h^+ pair formation. Since dye molecules are readily available at TiO_2 sites, they are acted upon by $OH^•$ radicals formed from H_2O_2. Thus e^--h^+ separation is made easier and efficient. The individual roles of Chit and Ppy operate concurrently, in other words, synergism exists in the catalytic performance of Chit-Ppy-TiO_2 (1:1:100) leading to a remarkable improvement in the photocatalytic activity of the ternary system.

4. Conclusion

In the present work a novel ternary visible light active photocatalyst Chit-Ppy-TiO_2 was designed and has been successfully synthesized by varying the proportion of Chit, Ppy and TiO_2. FTIR and XRD results confirm the formation of ternary system. SEM images suggest nanospheres and agglomerated secondary particles for TiO_2 and its catalysts. Photodegradation of MB study shows enhanced visible light activity of the ternary system. From the present study it emerges that Chit and Ppy individually and synergically could enhance the visible light photocatalytic functionality of TiO_2.

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References

[1] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobio. C Photochem. Rev. 1 (2000) 1–21.
[2] K. Hashimoto, H. Irie, A. Fujishima, TiO_2 photocatalysis: a historical overview and future prospects, Jap. J. Appl. Phy. 44(12) (2005) 8269–8285.
[3] A.D. Paola, E.G. López, G. Marcì, L. Palmisano, A survey of photocatalytic materials for environmental remediation, J. Hazard. Mater. 211–212 (2012) 3–29.
[4] Z. Zainal, L.K. Hui, M.Z. Hussein, A.H. Abdullah, I. Hamadneh, Characterization of TiO_2–chitosan/glass photocatalyst for the removal of a monoazo dye via photodegradation–adsorption process, J. Hazard. Mater. 164 (2009) 138–145.
[5] M.H. Farzana, S. Meenakshi, Synergistic effect of chitosan and titanium dioxide on the removal of toxic dyes by the photodegradation technique, Ind. Eng. Chem. Res. 53 (2014) 55–63.
[6] Q. Luo, X. Li, D. Wang, Y. Wang, J. An, Photocatalytic activity of polypyrrole/TiO_2 nanocomposites under visible and UV light, J. Mater. Sci. 46 (2011) 1646–1654.
[7] N.D. Dimitrijevic, S. Tepavcevic, Y. Liu, S.C. Silver, D.M. Tiede, Nanostructured TiO_2/polypyrrole for visible light photocatalysis, J. Phys. Chem. C 117 (2013) 15540–15544.
[8] F. Deng, L. Min, S. Wu, S. Luo, Visible-light photocatalytic degradation performances and thermal stability due to the synergetic effect of TiO_2 with conductive copolymers of polyaniline and polypyrrole, Nanoscale 5(18) (2013) 8703–8710.
[9] S. Liu, M. Yang, Y. Xu, Surface charge promotes the synthesis of large, flat structured graphene–(CdS nanowire)–TiO_2 nanocomposites as versatile visible light photocatalysts, J. Mater. Chem. A 2 (2014) 430-440.
[10] T. Ikeda, T. Nomoto, K. Eda, Y. Mizutani, H. Kato, A. Kudo, H. Onishi, Photoinduced dynamics of TiO_2 doped with Cr and Sb, J. Phys. Chem. C 112 (2008) 1167–1173.
[11] Y. Ide, N. Kawamoto, Y. Bando, H. Hattori, M. Sadakane, T. Sano, Ternary modified TiO_2 as a simple and efficient photocatalyst for green organic synthesis, Chem. Commun. 49 (2013) 3652–3654.
[12] C. Janáky, C. Visy, Conducting polymer-based hybrid assemblies for electrochemical sensing: a materials science perspective, Anal. Bioanal. Chem. 405 (2013) 3489–3511.
[13] S. Gawande, S.R. Thakare, Ternary polymer composite of graphene, carbon nitride, and poly(3-hexylthiophene): an efficient photocatalyst, Chem Cat Chem. 4 (2012) 1759–1763.
[14] K. Pandiselvi, S. Thambidurai, Synthesis of porous chitosan–polyaniline/ZnO hybrid composite and application for removal of reactive orange 16 dye, Coll. Surf. B Biointer. 108 (2013) 229–238.
[15] W.S.W. Ngah, L.C. Teong, M.A.K.M. Hanafiah, Adsorption of dyes and heavy metal ions by chitosan composites: a review, Carbohydrate Polym. 83 (2011) 1446–1456.
[16] L. Wang, X. Li, Y. Yang, Preparation, properties and applications of polypyrroles. React. Funct. Polym. 47 (2001) 125–139.
[17] L. Yang, B. Kruse, Revised Kubelka–Munk theory I. Theory and application, J. Opt. Soc. Am. A 21 (2004) 1933–1941.
[18] C. Zhang, Q. Li, J. Li, Synthesis and characterization of polypyrrole/TiO_2 composite by in situ polymerization method, Synth. Metals 160 (2010) 1699–1703.
[19] Y. Zhang, C. Xue, Y. Xue, R. Gao, X. Zhang, Determination of the degree of deacetylation of chitin and chitosan by X-ray powder diffraction, Carbohydrate Res. 340 (2005) 1914–1917.

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