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Greater Sensitizing and Catalytic Role of Nano-Gold Compared To Conductive Polypyrrole in Visible Light Activation of TiO_2

E. Subramanian*, G.I. Adlin Sheeba, J.V. Anusha

Department of Chemistry, Manonmaniam Sundaranar University, Tirunelveli – 627 012, TN, India.

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ABSTRACT

In the present work TiO_2 is chemically modified by loading with conductive polypyrrole (Ppy). Using $FeCl_3$ as the oxidizing agent Ppy was synthesized and loaded *in situ* on TiO_2 at various wt% (0.5, 1, 2 and 5 wt%) forming organic-inorganic hybrid (OIH) material. In addition, TiO_2 and OIH material were further modified using Au metal nanoparticle. FTIR, XRD, DRS and SEM characterizations revealed the formation of hybrid material, Au-TiO_2 and the ternary system Au-Ppy-TiO_2. All the materials were applied for the visible light photodegradation of rhodamine 6G in aqueous medium. The dye was degraded by 45%, 57%, 68% and 69% with bare TiO_2, 1 wt% Ppy-TiO_2, Au-TiO_2 and Au-Ppy-TiO_2 in 2 hour respectively. Ppy-TiO_2 OIH material and Au-TiO_2 have higher efficiency than bare TiO_2 and prove that the present chemical modification is a facile route to activate TiO_2 under visible light. Au-TiO_2 has exceeding efficiency (68%) than Ppy-TiO_2 (57%) and thus nano gold exhibits a greater sensitizing and catalytic role than Ppy in visible light activation of TiO_2. However, when both Au and Ppy are present together on TiO_2 (ternary system), the efficiency is not much improved (69%) by Ppy loading.

1. Introduction

Titanium dioxide is a well-known metal oxide material in many fields of science and technology such as water splitting, hydrogen production, solar cells, paints, pigments, etc. TiO_2 is a prominent photocatalyst because of its chemical stability, non-toxicity, cheap cost and its efficient photocatalytic characteristic particularly under UV irradiation [1]. TiO_2 has Eg value of 3.2 eV and it absorbs light with wavelength $\lambda \leq 380$ nm. In order to increase the photo efficiency of TiO_2 under visible light, chemical modification of TiO_2 is essential [2].

The photocatalytic efficiency of TiO_2 can be modified by photosensitizers. Sensitizers such as polymers, metal ions and C, N, S etc., were added to TiO_2 to shift the light absorption towards intense visible region [1]. Among the various polymers, polypyrrole (Ppy) is extensively studied because of its higher environmental stability, non-toxic nature, reversible redox activities, charge/discharge process, catalytic activity, ease to synthesize and appropriate band position for electron transfer to TiO_2 [3-5]. Huang et al [6] reported various metal oxide particles coated with polypyrrole using aerial oxygen as an effective oxidant. Some reported publications show that Ppy/TiO_2 is a good nanocomposite under visible light than bare TiO_2 [7, 8]. Iron (III) chloride is used as an oxidant in the preparation of polypyrrole since the oxidizing potential of $FeCl_3$ (E^0 = +0.77V) is matchable to the oxidation potential of pyrrole. $FeCl_3$:pyrrole of 2:1 molar ratio in neutral/acidic medium is applied in the synthesis of Ppy [3].

The main aim of the present work is to design an organic-inorganic hybrid (OIH) material using conducting polypyrrole as visible light sensitizer. It was found that semiconductor nanoparticles undergo charge equilibration with noble metal nanoparticles when they are in contact with each other [9]. The gold nanoparticle loaded on TiO_2 exhibits excellent catalytic activity in many oxidation reactions [10]. Hence, in the present work gold nanoparticle is also supported on Ppy-TiO_2 OIH material to enhance the chemical activity of the OIH material.

Rhodamine 6G dye (R6G) is used to assess the photocatalytic activity because of its photostability at different pH and environmental pollution [11]. The degradation experiment was repeated by changing parameters like pH, volume of H_2O_2 and photocatalyst dosage.

The result of the present work shows that the Ppy-TiO_2 OIH materials and Au-TiO_2 have efficient photocatalytic activity and the ternary system has higher efficiency than OIH materials.

2. Experimental Methods

2.1 Materials

TiO_2 (99.8%) anatase of Sigma-Aldrich make was used as such. Pyrrole (98%) of Alfa Aesar make was obtained and it was distilled before its use. $HAuCl_4$ (49% LOBA Chemie), Hydrochloric acid (30% Merck), R6G (S.d fine chemicals), Hydrogen peroxide (30% SD Fine chemicals), Ferric chloride (Merck) and other chemicals were used without further purification. Distilled water was used throughout the work.

2.2 Photocatalyst Preparation

2.2.1 OIH Material Preparation

Anatase TiO_2 was dispersed in 100 mL of 0.2 M HCl solution and sonicated using ultrasonicator for about 15 minutes for the monodispersion of TiO_2. Then pyrrole of required volume was added to the above mixture. Anhydrous $FeCl_3$ was added to the mixture in the ratio of 1:2 (pyrrole:$FeCl_3$). The above mixture was continuously stirred for 2 h and thus pyrrole was polymerized *in situ* over TiO_2 particles. After the completion of polymerization, the slurry was filtered and washed with distilled water and dried at 80 °C overnight. The dried OIH material was finely ground to fine powder and stored in zip-lock polythene covers. The yield was noted and the sample was studied further. The synthesis was repeated with different wt% of Ppy (0.5 wt%, 1 wt%, 2 wt% and 5 wt%) with respect to TiO_2.

2.2.2 Ternary Hybrid Preparation

The ternary catalytic system was synthesized by loading gold nanoparticles on OIH material by the given procedure. Anatase TiO_2 was suspended in water and 1 wt% of Au was added to it. The mixture was then kept in the oven at 80 °C for about 4 hours with frequent shaking for every 30 min. The slurry was then filtered, washed with distilled water and calcinated at 300 °C in muffle furnace for about 4 hours. The dried photocatalyst was finely ground and stored.

*Corresponding Author
Email Address: esubram@yahoo.com (E. Subramanian)

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2.3 Characterization of the Synthesized Materials

Fourier-transform infrared spectra (FTIR) of the powdered synthesized samples were obtained by mixing few mg of the samples with dry and spectral grade KBr and grinding it. The spectrum was recorded on a FTIR spectrometer (JASCO FTIR-410) in the region 4000-400 cm^{-1}. Powder X-ray diffraction (XRD) patterns for the synthesized samples were recorded for 2θ = 10 - 80° in a step of 0.05° in a continuous scanning mode using the instrument, PANanalytical Expert Pro-MPG with CuK_a radiation (λ = 1.5406 Å) with a generator set at 30 mA and 40 KV. From XRD data, the crystallite size (D) of the particles was determined using Debye-Scherrer's formula given in Eq. (1).

$$D = k\lambda / \beta \times \mathrm{Cos}\theta \quad (1)$$

where k is known as Scherrer's constant (shape factor), ranging from 0.9 to 1.0, λ is the wavelength of the X-ray radiation which is 1.5406 Å, β is the width of the maximum intensity XRD peak at half height and θ is Bragg angle [12]. Diffuse reflectance spectra (DRS) of the synthesized samples were obtained by mixing few mg of the sample with dry and spectral grade $BaSO_4$ and grinding it thoroughly. The spectrum was recorded on DRS spectrophotometer (Schimadzu UV-Visible Spectrophotometer-2700) in the region 200-850 nm. From DRS the band gap energy Eg values were calculated. The Scanning Electron Microscope images were recorded using Carl Zeiss EVO 18.

2.4 OIH Materials Efficiency Evaluation

Visible light photocatalytic efficiency of OIH materials was examined by the photocatalytic degradation of R6G dye. The photocatalytic reactor is a cylindrical pyrex-glass cell with 500 mL capacity. A 150 W tungsten-halogen lamp was used as the visible light source (Haber photoreactor model HIPR-LC-150; considerable intensity above 400 nm; intensity = 14.79 mW/cm^2 at 555 nm measured with Kusem-Meco Lux meter, model KM Lux 200k and converted into Watt). The temperature of the reactor solution was uniformly maintained throughout the experiment by using water circulation equipment. The cylindrical pyrex-glass cell was filled with 200 mL of 50 ppm R6G solution and 50 mg of photocatalyst at natural pH 6.8. The suspension was magnetically stirred for about 1 h to establish the adsorption/desorption equilibrium between dye and catalyst. Then, a certain amount of H_2O_2 (2 mL of 30%) was added to the above suspension. Analogous control experiments were performed without the photocatalyst (dye alone) and also in the absence of H_2O_2. The degradation of R6G was monitored by taking 2 mL of the supernatant dye solution at the time interval of 30 min. Each time the dye solution was centrifuged to separate the photocatalyst particles from the R6G solution. The % of degradation of R6G was estimated from the Eq. (2),

$$E(\%) = \frac{[D_0 - D]}{D_0} X\,100 \quad (2)$$

where D_0 and D are the initial and final concentrations of R6G.

3. Results and Discussion

The present work is the synthesis of various weight percent of Ppy-TiO_2 OIH materials, Au-TiO_2 and Au-Ppy-TiO_2 ternary hybrid and photodegradation of R6G using the synthesized photocatalysts. Wt% variation of Ppy in Ppy-TiO_2 (0.5, 1, 2, 5 wt%), pH variation (4, 6.8, 10), H_2O_2 volume variation (0.4, 1, 2, 4 mL) and dosage variation of photocatalyst (10, 50, 100 mg) were done and their impact on photodegradation of R6G was also investigated.

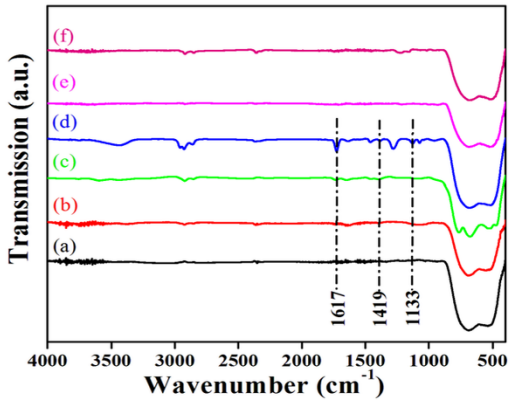

Fig. 1 FTIR Spectra of (a) Bare TiO_2 (b) Ppy-TiO_2 (0.5 wt%) (c) Ppy-TiO_2 (1 wt%) (d) Ppy-TiO_2 (2 wt%) (e) Au-TiO_2 and (f) Au-Ppy-TiO_2 (1 wt%)

3.1 FTIR Spectral Characterization

The FTIR spectra of the samples are shown in Fig. 1. The broad band/peak at lower wavenumber side (684 and 529 cm^{-1}) represents the characteristic vibration of Ti–O–Ti bond of anatase TiO_2. Ppy shows characteristic peaks at 1133 cm^{-1} (N=Q=N vibrational mode; Q refers to quinoid-type pyrrole rings), 1419 cm^{-1} (C-N) and 1617 cm^{-1} (C=C). The weak peak around 3400 cm^{-1} in the spectra (b)-(d) corresponds to –NH group [2]. The presence of the characteristic peaks of Ppy appearing in (f) also confirms the presence of Ppy in ternary hybrid. The characteristic peaks of Ppy and TiO_2 are present in the ternary hybrid at low intensity compared to Ppy-TiO_2 (2 wt%) and bare TiO_2. These results indicate the interaction between Ppy and TiO_2, suggesting the formation of OIH materials and ternary hybrid.

3.2 XRD Characterization

XRD patterns for the synthesized materials are shown in Fig. 2 and the data in Table 1. The XRD patterns of Ppy-TiO_2 hybrid material displays many sharp signals, because TiO_2 powder was used in the synthesis. The appearance of peaks could be indexed to the respective (hkl) planes. The XRD patterns of Ppy-TiO_2 and the ternary system confirm the crystal phase of anatase TiO_2 (JCPDS card no. 21-1272) in all the synthesized photocatalysts [2]. Further, these patterns do not contain any signal for Ppy. Absence of such signals reveals that the crystalline TiO_2 contributes to the major absorption and reflection of X-rays and also TiO_2 is accessible to incident X-rays. The characteristic peaks of Ppy and TiO_2 appear in the spectrum (e) at lower intensity and this result suggests the formation of ternary hybrid and also that the anatase crystal did not undergo any modification during ternary hybrid formation. The data obtained from XRD patterns and the calculated D values are given in Table 1. As evident from the D values in last column, the materials have more or less similar crystallite sizes and there is no much deviation. However, in the d space values, there is subtle shifting to higher side as wt% of Ppy is increased or as Au is loaded.

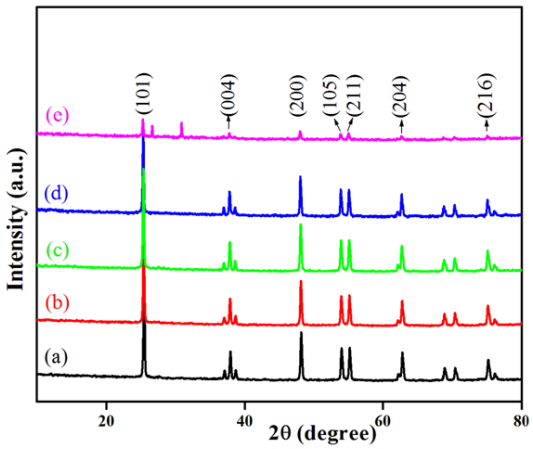

Fig. 2 XRD patterns of (a) Ppy-TiO_2 (0.5 wt%) (b) Ppy-TiO_2 (1 wt%) (c) Ppy-TiO_2 (2 wt%) (d) Au-TiO_2 and (e) Au-Ppy-TiO_2

Table 1 XRD data and crystallite size (D) values

Catalyst	Position 2θ	θ (°)	Cos θ	d-space (Å)	FWHM (°)	D (nm)
0.5% Ppy-TiO_2	25.477	12.7369	0.9754	3.4967	0.1673	54.4
1% Ppy-TiO_2	25.399	12.6993	0.9912	3.5068	0.1338	67.7
2% Ppy-TiO_2	25.359	12.6795	0.9936	3.5122	0.2007	44.2
Au-TiO_2	25.328	12.6640	0.9757	3.5165	0.1840	44.2
Au-TiO_2-Ppy	25.270	12.6350	0.9758	3.5245	0.1338	60.8

3.3 DRS Characterization

The DRS of the samples are shown in Fig. 3. In the above spectra Fig. 3a-e strong band in the range of 300 – 400 nm occurs confirming the absorption band for hybrid materials. There is slight increase in absorption with Ppy coating. The spectra of ternary hybrid (e) shows higher absorbance compared to other photocatalysts.

3.4 SEM Characterization

SEM images of the synthesized catalysts show smooth-surfaced uniform spherical particles. However, as seen in Figs. 4a-c, agglomeration predominates forming irregularly shaped clumps of secondary particles.

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Thus a strong interaction exists among the components [2]. The SEM images of the spent photocatalysts (Figs. 4d-f) do not differ much from the fresh photocatalysts suggesting the morphological stability of the catalysts during reaction.

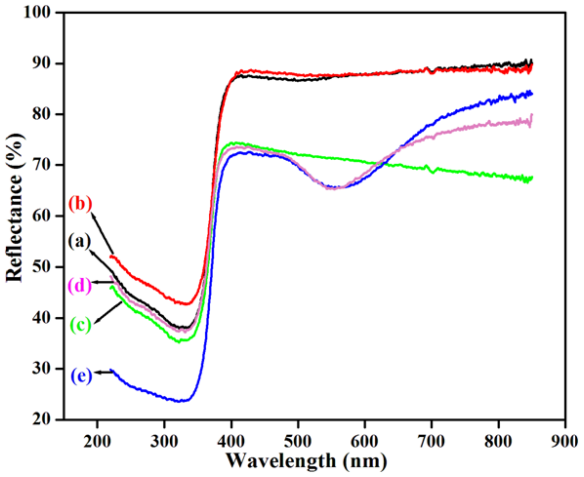

Fig. 3 DRS spectra of (a) Ppy-TiO_2 (0.5 wt%) (b) Ppy-TiO_2 (1 wt%) (c) Ppy-TiO_2 (2 wt%) (d) Au-TiO_2 and (e) Au-Ppy-TiO_2 (1 wt%)

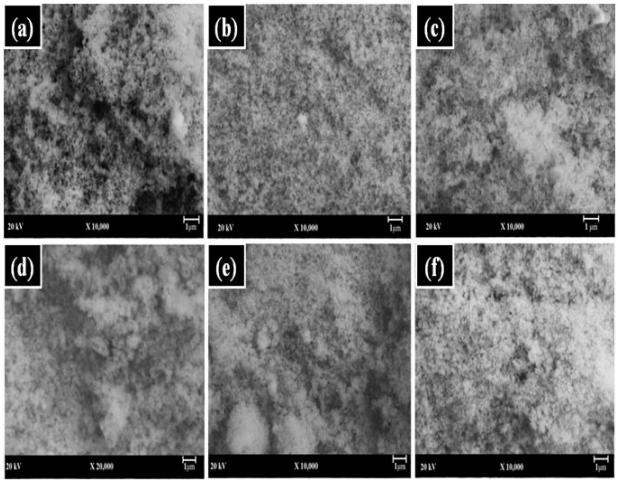

Fig. 4 SEM images of fresh photocatalysts (a) Au-TiO_2 (b) Ppy-TiO_2 (1 wt%) (c) Au-Ppy-TiO_2 (1 wt%) and spent photocatalysts (d) Au-TiO_2 (e) Ppy-TiO_2 (1 wt%) and (f) Au-Ppy-TiO_2 (1 wt%)

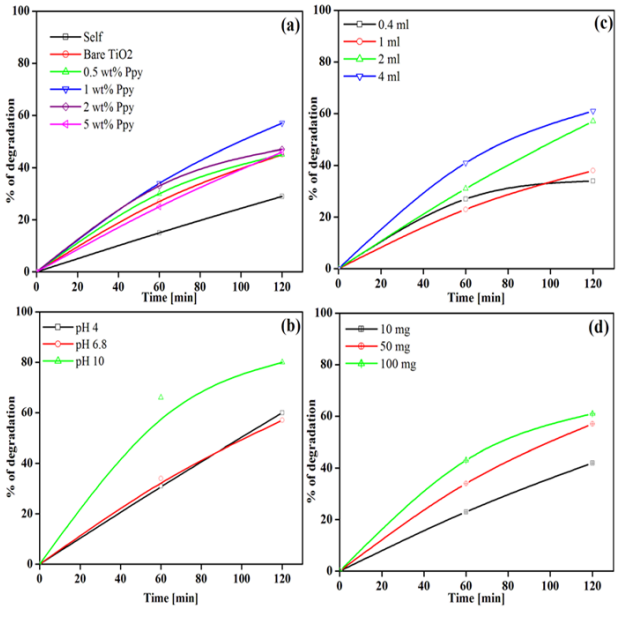

Fig. 5 Degradation of R6G using (a) catalyst variation (b) pH variation (c) H_2O_2 volume variation and (d) catalyst dosage variation

3.5 Visible Light Degradation of R6G

The photocatalytic activity of the bare TiO_2, Ppy-TiO_2 OIH materials, Au-TiO_2 and Au-Ppy-TiO_2 was studied by the visible light degradation of R6G (Fig. 5). The self-degradation was only 8% and 29% without and with oxidant (H_2O_2) respectively. In order to determine the optimal condition several preliminary experiments were carried out. The photocatalytic activity using variations such as catalyst variation, pH variation, H_2O_2 volume variation and catalyst dosage variation were done and the results are shown in Figs. 5a-d respectively. Fig. 5a shows that 0.5 wt%, 2 wt% and 5wt% Ppy-TiO_2 degrade the dye by 45%, 47% and 46% respectively. All the OIH photocatalysts increase the degradation of R6G than that of bare TiO_2 (45%). The presence of Ppy-TiO_2 (1 wt%) degrades the dye by 57% whose efficiency is higher than other OIH materials. Thus the catalyst variation shows that 1 wt% Ppy-TiO_2 OIH material has the highest efficiency. The pH variations at 4, 6.8 and 10 show (Fig. 5b) 60%, 57% and 80% of degradation. The degradation of R6G increases with increasing pH and the maximum efficiency is obtained at alkaline pH of 10 (80%). This observation can be explained on the basis that as the pH of the solution increases more OH^- ions are available and they will generate more $^{\bullet}OH$ radicals by combining with the catalyst. These $^{\bullet}OH$ radicals are responsible for greater photocatalytic degradation of R6G [13]. Fig. 5c shows the degradation of R6G in different volumes of H_2O_2 (optimal condition: 50 ppm dye, catalyst = 50 mg, pH = 6.8). The increasing volume of H_2O_2 in the suspension significantly increases dye degradation under visible light irradiation. The maximum degradation efficiency is obtained at 4 mL of H_2O_2 (61%). The various catalyst dosages of 1 wt% Ppy-TiO_2 (10, 50 and 100 mg) for R6G dye (optimal condition: 50 ppm dye, pH 6.8, H_2O_2 = 2 mL) increase gradually the percentage of photocatalytic degradation. It seems that increasing the catalyst mass increases the number of hydroxyl radicals formed and hence the dye degradation. The presence of increasing amount of H_2O_2 and catalyst lead to more electron-hole generation and produce more $^{\bullet}OH$ radicals and causes greater dye degradation [13].

From the foregoing results on the study of R6G dye degradation with OIH material catalysts and the parametric variation, the summarizing points are: 1) Ppy-TiO_2 catalysts perform better than bare TiO_2, 2) 1 wt% Ppy-TiO_2 is the best catalyst among OIH materials, 3) alkaline pH is the optimum condition, 4) increase in degradation of R6G dye with increase in H_2O_2 volume and catalyst dose.

Apart from visible light sensitization of TiO_2 with conducting Ppy, it was also our interest to investigate the sensitization by gold nanoparticles (AuNP) separately on TiO_2 and Ppy-TiO_2 OIH materials. The presence of AuNP in the photocatalyst permits the visible light sensitization of catalysts due to Localized Surface Plasmon Resonance (LSPR) [14]. The dye degradation experiment was done under the optimal condition of 50 ppm dye, pH 6.8, catalyst dose 50 mg and H_2O_2 2 mL. Table 2 compiles the data. Au-TiO_2 has better efficiency (68%) than bare TiO_2 (45%). The higher efficiency of TiO_2 with AuNP definitely points out the sensitization and catalytic role of AuNP. However, when AuNP is loaded on Ppy-TiO_2 OIH material, the efficiency is not much improved (69% only), perhaps due to the absence/meagre sensitization and catalytic role of Ppy.

Table 2 Visible light photodegradation of R6G using different photocatalysts

Photocatalyst	D_{R6G} (%)	Photocatalyst	D_{R6G} (%)
Ppy-TiO_2 (0.5 wt%)	45	Self (R6G)	29
Ppy-TiO_2 (1 wt%)	57	TiO_2 (bare)	45
Ppy-TiO_2 (2 wt%)	46	Au-TiO_2	68
Ppy-TiO_2 (5 wt%)	46	Au-Ppy-TiO_2	69

Reaction condition: [R6G] = 50 ppm (200 mL), Catalyst amount = 50 mg, Reaction time = 2 hr, natural pH = 7, H_2O_2 = 2 mL. D_{R6G} = R6G degradation.

4. Conclusion

In order to make TiO_2 visible light active it was chemically modified with the loading of conducting polypyrrole and/or Au nanoparticle. All the hybrid materials formation was confirmed by various instrumental characterizations. The photocatalytic activity assessment under visible light with R6G dye degradation shows that all the Ppy-TiO_2 OIH materials and Au-TiO_2 have higher efficiency than bare TiO_2 and prove that both Ppy and Au have sensitizing effect. Among various Ppy-TiO_2 OIH materials, 1 wt% Ppy-TiO_2 emerges as the optimum catalyst with 57% efficiency and Au-TiO_2 with 68% efficiency. A comparison clearly indicates that AuNP exhibits a greater sensitizing and catalytic role in visible light activation of TiO_2. Since the ternary system Au-Ppy-TiO_2 has only 69% degradation efficiency, just 1% higher than that for Au-TiO_2, Ppy exhibits either meager/nil role in activation of Au-TiO_2 system.

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