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Photodegradation of 4BS DyeOver Pd-doped TiO_2 Synthesized By EDTA-Glycol Method

M.J. Pawar*, V.B. Nimbalkar, A.D. Khajone, M.D. Gaonar
Laboratory of Materials Synthesis, Smt. Narsamma ACS College, Kiran Nagar, Amravati M.S. India

Abstract
We report in this chapterphotocatalytic activity of Pd-doped TiO_2 nanoparticles under visible light irradiation synthesized by using anEDTA-Glycol method. Structural, morphological, and basic optical properties of these samples were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-Vis reflectance. Room temperature X-ray diffraction analysis revealed that Pd-doped TiO_2 has both anataseand brookite phases, but TiO_2sample doped 2wt% Pd only have the anatase phase. The morphologies of TiO_2were influenced by doping with Pd, as shown from the SEM images. UV-Vis reflectance results show decreased band gap energy of Pd-doped TiO_2 in comparison to that of pure TiO_2.The present research work is mainly focused on the enhancement of degradation efficiency of Fast Scarlet4BS by doping of Pd inTiO_2 matrix using UV-light(365nm).A99.5%photodegradation ofmethylene blue wasachievedbyutilizing0.25mol% Pd-doped TiO_2 (1 g/L) at pH = 3 within70min.

Keywords*: TiO_2: Pd-doped TiO_2: Photodegradation: 4BS Dye*

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I. Introduction

The semiconductors TiO_2, ZnO, $SrTiO_3$, CeO_2,WO_3, Fe_2O_3,GaN, Bi_2S_3, CdS and ZnS can all act as photoactive materials forredox/charge-transfer processes due to their electronic structureswhich are characterized by a filled valence band and anempty conduction band. Among the simple oxides (e.g. TiO_2, ZnO, WO_3, Fe_2O_3),anatase phase of TiO_2 is the dominant structure employed for sunlightapplications mostly due to its charge carrier handling properties and exhibit the adequate conversion values [1-12].However, in spite ofits high conversion values, the calculated quantum yield for thereactions studied is appreciably low: certainly well below 10% formost degradation and synthesis processes [12].The catalytic activity of TiO_2 isdependent on its crystal structure, crystal size distribution,surface roughness, surface hydroxyl group density, and so on [13].

However, the TiO_2 photocatalyst is known to have limitations for practical applications. One of these limitations is that the TiO_2 has activity only under light of wavelength shorter than 388 nm because of its wide band gap (Eg = 3.2 eV) [14-16]. The wide band gap limits the use of sunlight as excitation energy and the high rate of recombination of photo-generated electron-hole pairs in TiO_2 results in low photocatalytic efficiency. To overcome these two difficulties, many efforts have been made to modify TiO_2 nanoparticles [17-19]. One of the promising approaches is based on the metal loading. Various metals, such as Pt, Au, Pd, Rh and Ag, have been used as electron acceptors to separate the photo-induced hole/electron pair andpromote interfacial charge-transfer processes [20-24]. Therefore, the aim of the present work is to study the effect of palladium on the properties and activity of the TiO_2 photocatalyst prepared by the EDTA-Glycol method. To investigate the photocatalytic efficiency of the pure and doped TiO_2, water-soluble C.I. Direct Red 23 known also as Fast Scarlet4BS (abbreviated as 4BS in the present study) dye was used as a model pollutant.

II. Experimental

2.1 Synthesis of pure and Pd-doped TiO_2

The precursor solution was prepared by dissolving titanium tetraisopropoxide (TTIP) in the glacial acetic acid (AA), followed by the addition of double distilled water. Then the solution of salt of ethylene diamine tetraacetic acid (EDTA) was added to this mixture and the mixture was stirred for 60 min at 60°C. After 60 min, to the stirred mixture, ethylene glycol (EG) was added and stirring was continued for further 60 min at 60°C. The mol ratio of TTIP:EGmustbekeptat1:1 and 1:2.The obtained material was calcined at 500°C to get pure TiO_2 coded as TiO. Then,1MPdsolutionwasadded drop wise into the precursor solution for a few minutes in order to get the samples Pd1TiO and Pd2TiO with Pd wt% of 0.1 and 0.2 respectively.Thesolutionwasdriedatthetemperatureof80°Covernight.Thedried gel was grinded and calcined in a muffle furnace at 500°C for 4 h. To study the effect of fuel quantity on the TiO_2, the volume of EG was doubled

and the similar method was adopted for the sample preparation.

2.3 Photocatalytic Decolorization of 4BS

The photocatalytic reactivity of pure and Pd-doped TiO_2 was evaluated by the decolorization of 4BSunder visible light irradiation. A LED lamp of 15 W was used as a light source for testing. Different amounts of the pure and Pd-doped TiO_2 powder was added into 25 ml of 20 mg/L MB solution. Before open LED light, the suspension was put in the reactor and stirred until dye adsorption was completed. After that, the LED light was turned on. The concentration of 4BS dye solution was evaluated at given time intervals of every 30 min by using UV-vis spectrophotometry at wavelength of 650 nm (λ_{max}).

III. Result and discussion

3.1 XRD analysis

The X-ray diffraction patterns of the undoped and 0.0%, 0.1%, and 0.2% palladium doped TiO_2 calcined at 450˚C is presented in Figure 1. This figure indicates that the sample calcined at 450˚C consists of both anatase and brookite phases. The XRD patterns didn't show any Pd phase even for the 0.2% Pd doped TiO_2. This may reveal that Pd ions are uniformly dispersed in TiO_2 matrix. The shape of diffraction peaks of the crystal planes of pure TiO_2 is quite similar to those of Pd-doped TiO_2 of different Pd concentrations.Substantially, the enlarged peaks at (101) plane(JCPDSnumber-21-1272)and(121)planefor thesamplesFigures1b and 1c showed a slight shift to smaller angleswithPdincorporation.ItindicatesthatPdioncouldenterintoTiO$_2$latticeorinterstitialsite.Weknowthatthedeferen ceinionic radius between palladium ion (Pd^{2+} = 0.11nm)andtitanium ion (Ti^{4+} = 0.064 nm) is large.The average crystal sizes of TiO_2 and Pd doped TiO_2 nanoparticles were calculated and also, were presented in Table 1. It was observed that, the average crystal size of the synthesized samples was significantly changed due to the addition of the Pd.

Table 1 Average crystallite size, specific surface area and pore size of pure and Pd-doped TiO_2 calcined at 450˚C (TTIP:EG 1:1).

Sample	Pd wt%	Average crystallite size (nm)[a]	BET surface area (m^2g^{-1})	Pore size (nm)[b]
TiO	0.0	24.30	64.44	3.24
Pd1TiO	0.1	22.23	65.43	3.85
Pd2TiO	0.2	20.25	72.54	4.33

a = calculated form Scherrer equation; b = Calculated from S_{BET}

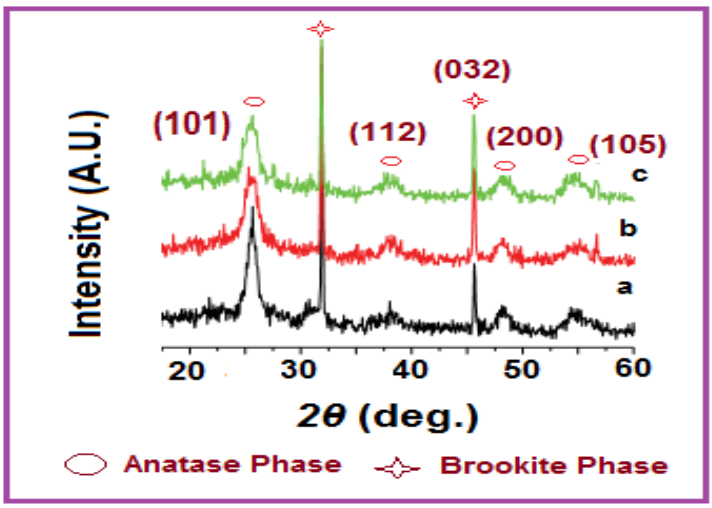

Figure 1. XRD patterns of pure and Pd-doped TiO_2 calcined at 500˚C.

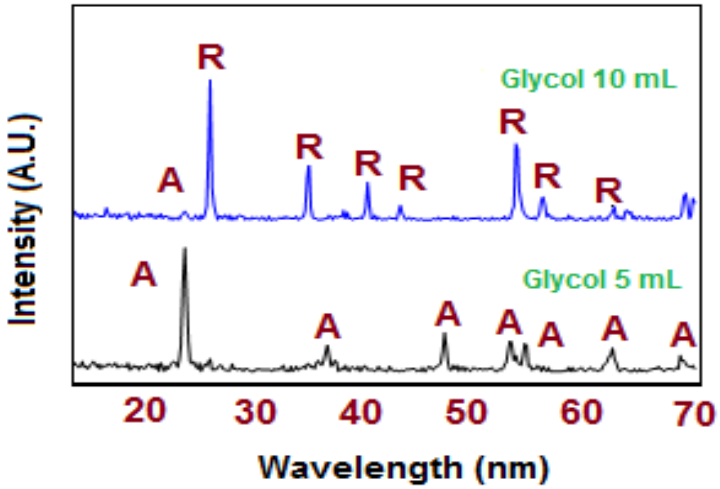

Figure 2 XRD patterns of pure and Pd-doped TiO_2 calcined at 500˚C.

Further, we have synthesized Pd2TiO sample by EDTA-Glycol method using the double volume of EG to investigate the influence of the amount of the fuel during combustion on the structure and the synthesized TiO_2 materials. The role of fuel quantity was also found to be crucial in determining the photocatalytic efficiency of TiO_2. XRD results are presented in Figure 2. From XRD results, it was observed that, on doubling the volume of glycol the drastic change in phase of TiO_2 was observed from anatase to rutile phase.

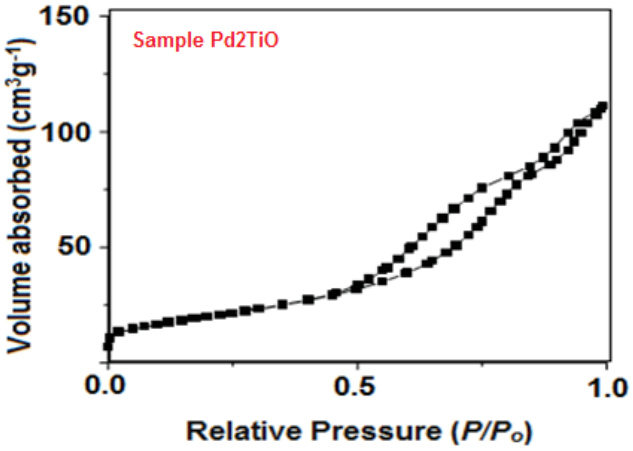

Figure 2. N_2 adsorption/desorption isotherm of Pd2TiO sample calcined at 500˚C.

3.2 N_2 adsorption studies

The surface textural characteristics of pure and Pd-doped samples are derivedfromN_2adsorptionanalysis. Specific surface area (S_{BET}) by BET method, total pore volumecalculatedatP/P_0=0.99,andaverageporediameter values are presented in Table 1. Figure 3 presents the adsorption isotherms of pure and Pd-doped samples. The samples showed type IV behaviour with the typical hysteresisloop.Thishysteresisis a characteristicof mesoporous materials [25,26].It can be seen in Table 1, that the doped sample had larger surface area and smaller average crystallite size than the undoped one. This might be due to the slight decrease ofcrystallinesizeforthePd-dopedTiO_2as mentionedinXRDpattern.

3.3 UV–vis spectroscopy

Optical properties were observed by UV–vis spectroscopy. Figure 4demonstrates the optical absorption spectra of pureand Pd-doped TiO_2samples. The absorption edge of TiO_2nanoparticles at 387 nm moved to a longer wavelength after doping with Pd-doping, showing the absorption edge at 432nm for Pd1TiO sample and 450 nm for Pd2TiO sample. After doping with Pdthe response of TiO_2nanoparticles to visible light was increased and showed red shift. The red shift of the absorption curve results in a reduction of the band gap energy and also the recombination rate, and hence, enhanced photocatalyticactivity.

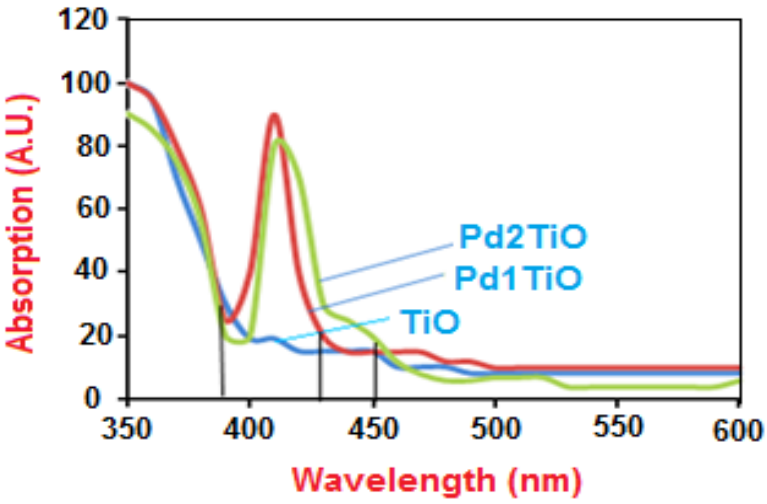

Figure 3.UV visible absorption spectra of pure and Pd-doped TiO_2 samples.

3.4 SEM and TEM studies

The micrographsofthe TiO, Pd1TiO and Pd2TiO samplesareshowninFigure5. One can see the change in morphology and the surface structure of the pure and Pd-doped TiO_2 samples with increasing wt% of Pd.Figure5alsoshows the TEM result of the pure and Pd-doped TiO_2nanoparticles calcined at 500˚C. The TEM images also confirm the decrease in crystallite size with Pd doping in TiO_2 structure. The result of the TEM agrees with the XRD results concerning the particle size range.

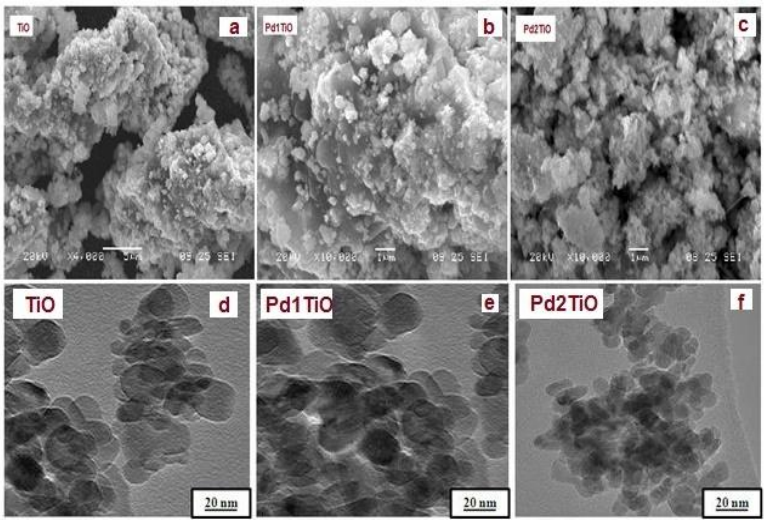

Figure 4 SEM and TEM images of pure and Pd-doped TiO_2.

3.5 Effect of Operating Parameters on the Photodegradation of 4BS

3.5.1 Effect of catalytic dose

Experiments were performed to study the variations in therate of decolorization at different concentrations of catalyst,ranging from 1.0 to 3.0 g/L, at pH 12.0. It was observed that thephotocatalyticdecolorization efficiency of 4BS increased withan increasing amount of the photocatalyst, and reached the highestvalue when the concentration of pureand Pd-doped TiO_2sample was 2 g/Land finally decreased, as shown in Figure 5. This phenomenon issimilar to that found in the study of other photocatalysts, suchas TiO_2 and ZnO [27]. The enhancement of the removal ratemay be due to the increase in the availability of active sites,which increases the number of dye molecules adsorbed, andthe increase in the density of particles in the area of illumination.At higher catalyst loading, the percentage of degradationdecreases because of the deactivation of activated moleculesby agglomeration, whichdecreasesthe radiation penetration and increasesthe radiation scattering in dye the solution. The best amount of catalyst must be added in order to avoid unnecessary excess catalyst andto ensure the maximumphotodegradation of dye.

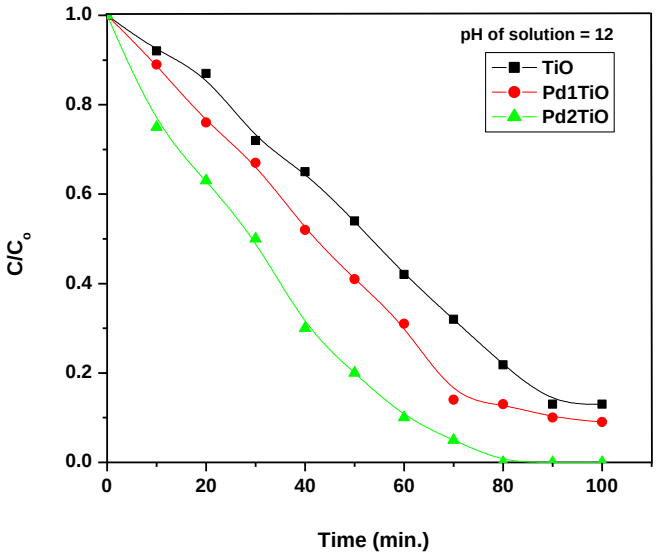

Figure 5 Effect of catalyst dose on photocatalytic degradation of 4BS over pure and Pd-doped TiO_2.

3.5.2 Effect of pH

The effect of pH from 4.0 to 12.0 on the decolorization atconstant air flux, a temperature of 25˚C with 2 g of Pd2TiO the catalystfor 90 min is illustrated in Figure 6.The worst results were obtained at pH 7.0 and acidic and alkaline pH values were favored. The photocatalytic removal of color wasobserved to be faster at alkaline pH than at acidic pH. The bestpH was 12.0.

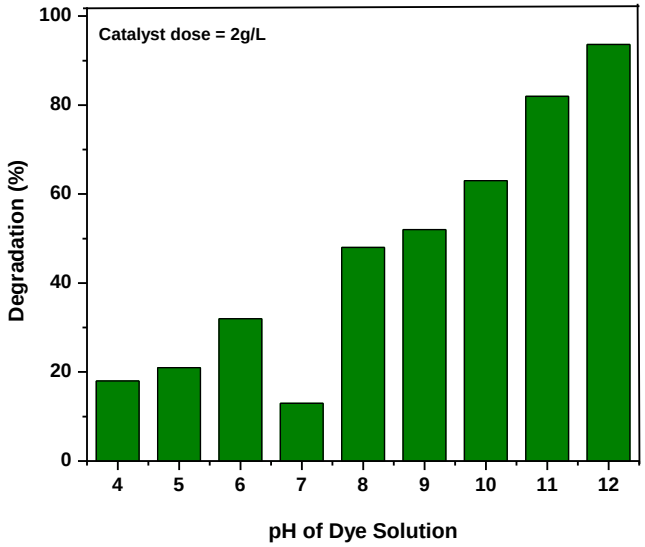

Figure 6 Effect of pH of dye solution on 4BS degradation over Pd2TiO.

3.5.3 Effect of initial concentration of dye

The effect of the initial concentration of dye on the rate ofdecolorization was studied by varying the initial dye concentrationfrom 100 to 500 mg/L at pH 12.0, with a constant intensityof 250W and a catalyst loading of 2 g/L, as shown in Figure 7. It was observed that, the photodegradation of 4BS dye decreases with increasing initial concentration of dye.Theseresults presented in Figure 7 are in good agreement with the results of the studies reportedbyNeppolian et al. [28] and Toor et al. [29]. Therate of dye degradation relates to the probability of formation ofOH radicals on the surface of the catalyst and to the probabilityof OH radicals reacting with dye molecules. As the initial concentrationincreases, the active sites of the catalyst are coveredby dye ions and the path-length of photons entering the solutiondecreases. In low concentrations, however, the

reverse effectis observed; consequently, the number of OH radicals formedon thesurface of catalyst increases, the relative numberof OH radicals attacking the compound increases, and thus thephotodegradation efficiency increases. Another possible causefor such results is the UV-screening effect of the dye itself. At ahigh concentration of dye, a significant amount of UV light maybe absorbed by the dye molecules rather than the catalystparticles, and that reduces the efficiency of the catalytic reactionbecause the concentrations of •OH and O_2•$^-$ decrease [31].

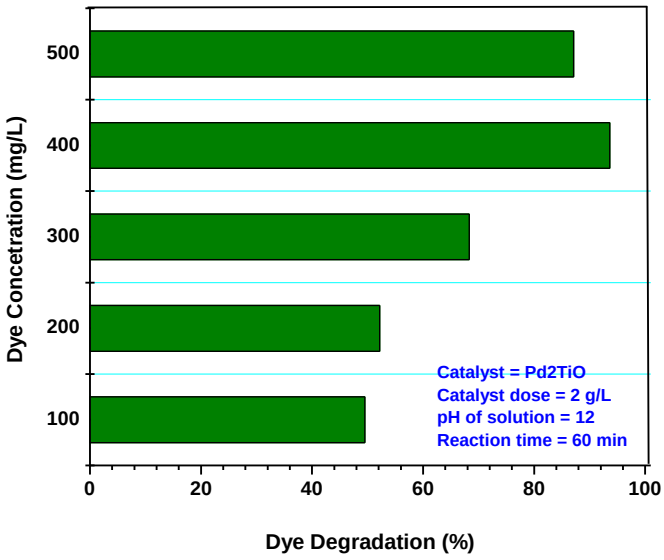

Figure 7 Effect of initial concentration of dye on 4BS degradation over Pd2TiO.

3.5.4 Effect of scavenger

Iodide ion acts as a scavenger that reacts with positive holesand surficial hydroxyl radicals, reducing the dye degrading efficiency of photocatalyst. In the present investigation, the 4BS dye solution (dose = 400 mg/L, pH of solution = pH 12.0) mixed with scavengerKI (0–40 mmol/L) was irradiated for 60 min with 2 g/Lof Pd2TiO. Figure 8showsthe change of photocatalytic decolorization of 4BS with increasingKIconcentration. Obviously, with the increase of the KIconcentration, the rate of dye degradation decreases. Since iodideion scavenged the positive holes and surface hydroxyl radicalson catalysts surface reduced the number of reactive species availablefor photodegradation the adsorbed 4BS. In addition, iodideion completed the adsorptive sites on the Pd2TiOsurface, resulting in the decreased dye degradation efficiency.

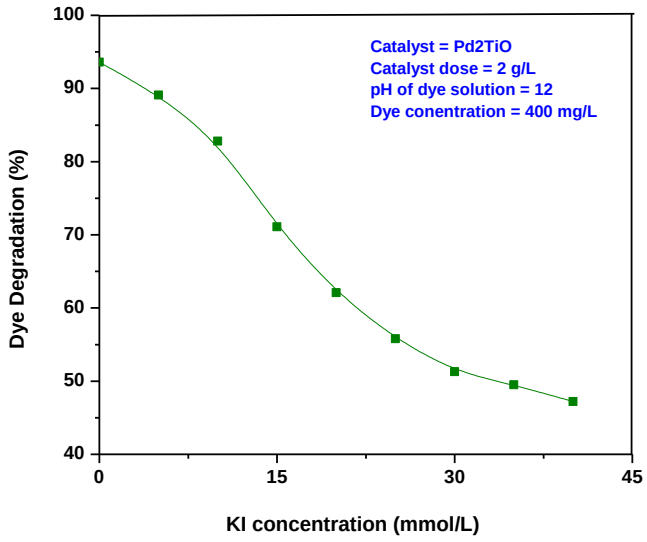

Figure 8 Effect of KI concentrations as a scavenger on 4BS dye degradation over Pd2TiO catalyst.

IV. Conclusion

The pure and Pd-doped TiO_2nanoparticles were prepared by the EDTA-Glycolmethod using ethylene glycol as a fuel. Samples prepared by calcinations at 500˚C contain anatase phase only. If the volume of ethylene glycol is doubled, the percentage of rutile phase increases dramatically. Doping TiO_2 with palladium hasno significant effect on the particle sizes and did not result in the formation of a new crystalline phase. It was confirmed that the incorporation of Pd in TiO_2 matrix shifts the onset wave length of absorption to higher values. The pure TiO_2 exhibited lower efficiency than the Pd-doped TiO_2 for 4BS dye solution and the photocatalytic efficiency increases with increasing palladium content up to 0.2wt%.At pH = 12, about 95% degradation of 4BS was with 2 g/L of Pd2TiO dose. Further studies to improve the metal loading can lead to the production of even more efficient materials for photocatalyticapplications.

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