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Short Communication

One-pot photocatalytic synthesis of quinal dines from nitroarenes with Au loaded ${\rm TiO}_2$ nanoparticles

K. Selvam, M. Swaminathan *

Department of Chemistry, Annamalai University, Annamalainagar 608 002, India

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ABSTRACT

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1. Introduction

A great variety of chemical transformations in the presence of semiconductor particles (CdS and TiO₂) have been reported in the recent review article [1]. In spite of several semiconductor mediated reactions, examples of combined redox reactions are rather limited in literature [2–6]. The integrated use of reductive and oxidative sites of semiconductor catalyst makes a sophisticated multi-step synthesis in 'one pot'.

In TiO₂-photocatalyzed reactions, reduction and oxidation take place concurrently at adjacent reaction sites on the surface. But the drawback in these reactions is the recombination of photogenerated charge carriers. Therefore the major challenge in heterogeneous photocatalysis is to improve the catalytic activity by restricting the recombination. For this purpose, the excited electrons in the conduction band of TiO₂ must be separated spatially from the holes in the valence band. Furthermore the time required for reduction (~1 ms) is longer than that for oxidation (~100 ns) by a factor of as much as 10 000 [7]. A very promising approach is the incorporation of noble metal nanoparticles with a large work function (i.e., high electronegativity) on TiO₂, [8] which enhances the charge separation by the interfacial electron transfer from semiconductors to metals [9]. This improves product selectivity and photoactivity of the catalysts. Selectivity is of great importance in organic synthesis.

Synthesis of quinoline and its derivatives has been the subject of focused research due to their importance in various applications and to their widespread biochemical significance. A large variety of

One-pot photocatalytic synthesis of quinaldines from nitroarenes using $Au-TiO_2$ nanoparticles is reported. Au-TiO₂ on irradiation induces a combined redox reaction with nitroarene and alcohol and the products undergo condensation–cyclization process to give quinaldines.

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quinoline derivatives have been used as antimalarial, anti-inflammatory, antiasthmatic, antibacterial, antihypertensive and tyrokinase PDGF-RTK inhibiting agents [10]. Hence great efforts have been made to develop efficient synthetic routes to quinoline derivatives in both synthetic organic and medicinal chemistry.

Photocatalysts such as TiO₂, TiO₂ with a co-catalyst (*p*-toluenesulfonic acid) and others have been reported for the synthesis of quinoline and tetrahydroquinolines [11-13]. Some of the modified semiconductor photocatalysts developed in our laboratory have been used for organic transformations [14–16]. Recently we reported the synthesis of quinaldines by oxidation-cyclization of anilines in ethanol using Au–TiO₂ nanoparticles [17]. Now we found that this catalyst could also effect a combined redox-cyclization reaction in the conversion of nitroarenes to guinaldines. In the present study, we investigated photocatalytic conversion of nitrobenzene and its derivatives in absolute ethanol to quinaldines using TiO₂ or Au-TiO₂. It was reported earlier that UV irradiation of nitrobenzene in nitrogen saturated ethanol with TiO₂ resulted in the formation of 4ethoxy-1,2,3,4-tetrahydroquinoline [11]. We discovered an interesting fact, that our reaction conditions provided selective formation of quinaldines in one reaction step with the moderate to good yield. To our knowledge this paper describes the synthesis of quinaldines from nitroarenes under mild conditions using UV light for the first time.

2. Experimental

2.1. Materials and methods

All chemicals used were of the highest purity available. HAuCl₄·4-H₂O (Aldrich) was used as Au source. Nano TiO₂ was prepared by sol-

^{*} Corresponding author. Tel.: +91 4144 225072; fax: +91 4144 238145. *E-mail address:* chemres50@gmail.com (M. Swaminathan).

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gel method from titanium tetraisopropoxide (Himedia 98.0%). Sol was formed by the addition of distilled water to titanium tetraisopropoxide in isopropanol (1.6 M) and it was stirred for 4 h. The gel obtained was filtered, washed and dried in an air oven at 100 °C for 12 h. The sample was calcined at 400 °C in a muffle furnace for 1 h. Au (*x*)–TiO₂ samples, containing different gold loadings [*x* (wt.%) = Au/(TiO₂ + Au)100; *x* = 0.5, 1, 1.5, 2] were prepared by photodeposition method [16], in which photoirradiation of an aqueous solution of homemade TiO₂ with HAuCl₄· 4H₂O afforded grey colored Au–TiO₂ catalyst.

2.2. Apparatus

Powder X-ray diffraction patterns of TiO₂ and Au–TiO₂ samples were obtained using X'Pert PRO diffractometer equipped with a CuK_{α} radiation (wavelength 1.5406 Å) at 2.2 kW Max. Peak positions were compared with the standard files to identity the crystalline phase. High resolution TEM (HR-TEM) measurements were carried out using a JEOL-JEM-2010 UHR instrument operated at an acceleration voltage of 200 kV with a lattice image resolution of 0.14 nm. Diffuse reflectance UV-Vis spectra of the catalysts were recorded using a Cary 500-8.01 spectrophotometer. Perkin-Elmer GC-9000 with a capillary column of DB-5 and flame ionization detector was used for product analysis. GC/MS analysis was carried out using Varian 2000 Thermo with the following features: capillary column VF5MS (5% phenyl-95% methyl polysiloxane), 30 m length, 0.25 mm internal diameter, 0.25 µm film thickness, temperature of column range from 50 to 280 °C (10 °C/min), and injector temperature 250 °C, attached with mass spectrometer model SSQ 7000. Atomic force microscope JSPM-5200TM, JEOL model was used to study the morphology of the catalyst. This AFM uses a silicon tip with a radius of 20 mm and a lowresonance frequency cantilever with a spring constant of 35-65 N/m. Scans of $1.8 \times 1.8 \,\mu\text{m}$ were obtained for each sample. The images were recorded in the non-contact mode. All recordings were made in air under ambient conditions to produce 2 and 3D images. X-ray photoelectron spectra (XPS) of the catalysts were recorded in an ESCA-3 Mark II spectrometer (VG scientific Ltd., England) using Al Ka (1486.6 eV) radiation as the source. The spectra were referenced to the binding energy of C(1s) (285 eV).

2.3. Photocatalytic synthesis of quinaldines

In the experiment, 50 mg TiO₂ was suspended in 25 mL of an absolute ethanolic solution containing 25 mM of the nitroaromatic compound. Suspension was irradiated by a 365 nm medium-pressure mercury lamp (Sankyo Denki, Japan; intensity $l=1.381 \times 10^{-6}$ Einstein L⁻¹ s⁻¹) after purging with N₂ for 30 min. N₂ bubbling (flow rate = 6.1 mL s⁻¹) and magnetic stirring of the suspension were continued throughout the reaction while the temperature was maintained at 30 ± 1 °C. Product analysis was carried out with GC and GC/MS. The product isolation was performed by column chromatography on a silica gel column by eluting with a co-solvent of hexane and ethyl acetate (volume ratio; 8:2). The yield was determined by comparison with the retention times of those of authentic samples and by co-injection with the authentic compounds.

3. Results and discussion

3.1. Catalyst characterization

The Au loaded TiO_2 catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Atomic Force microscopy (AFM), High Resolution Transmission electron microscopy (HR-TEM) and diffuse reflectance spectroscopy (DRS). Fig. 1 shows X-ray powder diffraction (XRD) patterns of TiO_2 and Au-TiO₂ samples. The 2 θ peak at 25.5° (anatase 101) revealed that the gold deposition did not affect the anatase phase of TiO_2 No other crystal phase is detected in XRD. Deposition of Au is responsible for a new less intense peak at 44.4° [18]. The average crystalline size of Au–TiO₂ was calculated using the Scherrer equation. The average size of pure TiO₂ is 11.3 nm whereas Au loaded TiO₂ has an average size of 12.1 nm. Au–TiO₂ has a larger size than pure TiO₂ at the same calcination temperature.

The electronic state of Au in the catalysts was verified by XPS. The XPS survey spectrum (Fig. 2) of the Au–TiO₂ indicates the peaks of elements Ti, O, C and Au (trace). The carbon peak is attributed to the residual carbon from the sample and adventitious hydrocarbon from XPS instrument itself. The Ti2p peak at 461 eV, O1s peak at 534 eV and Au 4f peak at 84 eV reveal the presence of Ti, O and Au elements in Au–TiO₂. High resolution XPS spectrum (inset in Fig. 2) from 80 to 90 eV confirms the existence of Au. Fig. 2 shows the binding energies of Au 4f7/2(84.0 eV) and Au 4f5/2(87.3 eV) and the splitting of the 4f doublet (3.3 eV). These binding energies indicate that gold is present in metallic state.

AFM 3D image of a dense Au loaded TiO_2 nanoparticle is shown in Fig. S1. Au–TiO₂ particles are well dispersed without any trace of coalescence. Consequently we assure that Au particles in TiO_2 layer either overcoated or sandwiched. In AFM, a cross section through a single particle reveals almost quite flat and non-spherical shape despite the close packing of the particles. The target nanoparticle sits about 20 nm×20 nm above the surrounding matrix. The apparent width and height of Au loaded TiO_2 nanoparticle are found to be 0.50 nm (Fig. S1b). Analysis of the diffuse reflectance spectra of TiO_2 and Au–TiO₂ reveals that the loading of Au on TiO_2 results in increased absorbance from 400 nm to an entire visible region (Fig. S2). There is no significant change in UV region (see supplementary data for Figs. S1 and S2).

High resolution transmission electron microscope images at two different regions permit easy differentiation of Au loading in TiO_2 crystallites (Fig. 3a and b). Au nanocrystals are seen on the surface of the TiO_2 particle as dark dots. Sizes of Au– TiO_2 nanoparticles have also been analyzed by HR-TEM and the results are shown in Fig. 3c. It can be seen that the Au– TiO_2 particle sizes are in the range from 5 to 35 nm with an average size of 19.8 nm. Au metal particles are randomly dispersed on the TiO_2 surface. Further observations from high resolution TEM micrograph show that the Au particles diameters are in the range of 3–15 nm and they are randomly located on the crystal surface. The results confirmed the conclusion gained from the XRD analysis. Fig. 3d and e shows the lattice fringes of Au and TiO_2 and SAED pattern of Au– TiO_2 . The distance between the fringes was



Fig. 1. XRD patterns of a) TiO₂ and b) Au-TiO₂.



Fig. 2. XPS survey spectra of $\mbox{Au-TiO}_2$ and high resolution XPS spectrum (inset) of Au element.

measured by an analysis soft attached on the instrument. The statistical *d*-values for Au particles and TiO_2 crystals are 0.25 and 0.35 nm respectively. These values indicate that the observed fringes are for the Au (111) plane and TiO_2 (101) anatase facets.

3.2. Photocatalytic synthesis of quinaldines

The catalytic activity of $Au-TiO_2$ for the synthesis of quinaldine **2** was investigated for the reaction of nitrobenzene (**1**) with ethanol. The changes in the concentrations of **1** and the product, quinaldine (**2**)



Fig. 3. HR-TEM analysis: (a and b) images of 1% Au-TiO₂, (c) particle size distribution of Au-TiO₂, (d) lattice fringes of Au-TiO₂ and (e) SAED pattern of Au-TiO₂.



Fig. 4. Time-dependent change in the concentrations of substrate and products during photoirradiation of nitrobenzene in neat EtOH with a) TiO_2 and b) Au– TiO_2 catalyst. Reaction conditions: 25 mM of nitrobenzene in ethanol, $TiO_2 = 50$ mg.

during the photocatalytic reaction were determined at different times (Fig. 4). With pure TiO₂ (Fig. 4a), 6 h photoirradiation of **1** gave only 60% yield of the product **2**. In contrast, 75% product **2** yield was obtained in 5 h with Au–TiO₂ (Fig. 4b). This reveals the selectivity of Au–TiO₂ in the reaction. The higher efficiency and selectivity of Au–TiO₂ were also shown by the formation of quinaldine from 3-nitrotolune and 4-methoxynitrobenzene. Au–TiO₂ produced 80 and 60% of quinaldine but bare TiO₂ gave only 68, 41.5% of quinaldine from 3-nitrotolune and 4-methoxynitrobenzene respectively (data not given Table 1). This indicates that Au–TiO₂ promotes rapid and selective quinaldine production.

 Table 1

 Photocatalytic synthesis of various substituted quinaldines using Au-TiO₂.

Run	Conditions	Products yield [%]	Byproduct [%]	Conversion [%]
1	Nitrobenzene	Quinaldine (75)	24	99
2	3-Nitrotoluene	2,7-Dimethylquinoline (80)	19	99
3	4-Nitrotoluene	2,6-Dimethylquinoline (70)	29	99
4	4-Methoxynitrobenzene	6-Methoxy-2- methylquinoline (60)	20	80
5	3,5-Dimethylnitrobenzene	2,5,7-Trimethylquinoline (70)	19	89
6	4-Chloronitrobenzene	6-Chloro-2- methylquinoline (16)	83	99
7	4-Fluoronitrobenzne	6-Fluoro-2- methylquinoline (8)	91	99

All reactions were performed with a 25 mM alcoholic solution of a reactant 50 mg of Au–TiO₂ suspension, I_{UV} = 1.381×10⁻⁶Einstein L⁻¹s⁻¹, irradiation time–5 h.



Fig. 5. GC-MS chromatograms at different reaction times for the photocatalytic conversion of nitrobenzene.

The higher conversion of nitrobenzene with $Au-TiO_2$ (Fig. 4b) is due to the trapping of electrons by Au on the excited TiO_2 . This increases the charge separation and facilitates a combined redox reaction. Control experiments demonstrated that nitrobenzene did not undergo any reaction in the absence of TiO_2 or without irradiation. GC-MS chromatograms recorded at different reaction times of the photocatalytic conversion of nitrobenzene in ethanol are presented in Fig. 5. GC–MS chromatograms reveal the formation of nitrosobenzene, aniline, N-hydroxyaniline, 2-methyl-*N*-phenyl-1,2,3,4-tetrahydroquinolin-4-amine as intermediates during the quinaldine formation. The formation of byproducts aniline and 2-Methyl-1,2,3,4-tetrahydroquinoline is indicated by GC–MS chromatogram obtained after 6 h.

This process is tolerant for the synthesis of various substituted quinaldines. Photoirradiation of alcohol solutions of different nitroarenes with Au-TiO₂ catalyst successfully afforded the corresponding quinaldines (Table 1). 3-Nitrotolune gave 80% yield of 2,7-dimethylquinoline but 4-nitrotolune resulted in 70% yield of 2,6-dimethylquinoline. Quinaldine yield for 3-nitrotolune is higher than for 4nitrotolune. In the synthesis of quinaldine, the initial step is the reduction of nitro group, which is followed by condensation with aldehyde and cyclization. It seems that the electron-releasing group at para-position inhibits the condensation of amino group with aldehyde. This is also revealed by 60% quinaldine formation by 4methoxynitrobenzene, which has a strong electron-releasing group at para-position. In the case of 3,5-dimethylnitrobenzene, the cyclization reaction is hindered due to steric effect and this decreases the product yield (70%) when compared to 3-nitrotolune (80%). In the case of 4chloro- and 4-fluoronitrobenzenes, the yield of guinaldines was very low. This is attributed to photoinduced dehalogenation. Dehalogenated anilines have been identified in GC-MS analysis.

Earlier it was reported that the irradiation of nitrobenzene (2 mmol) and TiO_2 (0.5 g) in nitrogen saturated ethanol solution for 8–12 h gave ethoxy-tetrahydroquinolines as the major product. We obtained a different product with continues purging of nitrogen during the reaction. Our results reveal that the oxidation power of TiO_2 is well controlled under these experimental conditions.

Scheme 1 provides a tentative overview of plausible reaction mechanisms leading to the cyclization products identified by GC–MS. The nitroaromatic compound is first reduced to aniline by



Scheme 1. Schematic overview of the possible reaction pathways.

Table	2				
Effect	of water	content o	n photod	atalytic	synthesis.

Run	Conditions ^a	Yield of quinaldine [%]	Conversion [%]
1	Neat ethanol	75	99
2	Ethanol-H ₂ O (99/1)	24	99
3	Ethanol $-H_2O(98/2)$	14	99
4	Ethanol-H ₂ O (96/4)	6	85

All reactions were performed with a 25 mM alcoholic solution of a reactant 50 mg of Au–TiO₂ suspension, I_{UV} = 1.381×10⁻⁶ Einstein L⁻¹s⁻¹, irradiation time–5 h.

photogenerated conduction band electron on the Au-TiO₂ surface. Simultaneously the alcohol is oxidized to the corresponding aldehyde consuming the photogenerated valance band holes on TiO₂. The photocatalytic formation of aldehyde from alcohol was well established [19]. These initial steps of oxidation and reduction are more facilitated with Au-TiO₂ when compared to pure TiO₂. Pathways A and B (Scheme 1) suggest the formation of an imine (Schiff base) via the reaction between the aniline and acetaldehyde, whereas pathway C requires the formation of crotonaldehyde, the product of an aldol condensation of two acetaldehyde units. These pathways are proposed on the basis of earlier report on the conversion of nitroarene to tetrahydroquinoline using TiO_2 with a co-catalyst *p*-toluene sulfonic acid [12]. Crotonaldehyde was produced in low concentration and consumed readily. Hence it could not be detected by GC-MS under the experimental conditions of this work. In fact, when crotonaldehyde was made to react with N-ethylideneaniline thermally, the reaction was completed within 4 h.

More evidence for the reaction pathway B is the formation of tetrahydroquinoline, which is also detected by GC–MS (Fig. 5). 2-Methyl-*N*-phenyl-1,2,3,4-tetrahydroquinolin-4-amine (I) can be formed *via* cycloaddition of the imine (II) to its enamine tautomer. Subsequent elimination of an aniline molecule from I yields the dihydroquinoline (III) as intermediate, which on dehydration gives quinaldine. In the reaction pathway A, titanium enolate formed on the surface of TiO₂ condenses with the aniline to give **IV**, which on further condensation and oxidation yield corresponding quinaldines. Formation of enolate with TiO₂ was reported by Chen et al. [20].

Photocatalytic experiments in different mixtures of $EtOH-H_2O$ have also been carried out. Table 2 shows that the yield of quinaldine after 5 h irradiation decreases from 75% to about 6% with the increase in amount of water. In water the photogenerated OH radicals can attack nitrobenzene or aniline in a nonselective manner. There is a possibility that water favors the hydration of the accumulated aldehyde leading to the corresponding acid and water can also react with imine intermediate.

In conclusion, Au-TiO₂ enables efficient quinaldine production from nitroarenes through a combined photoredox reaction. This process has significant advantages when compared with other methods (i) a cheap and stable reactant (alcohol), (ii) it does not require the use of acids, oxidants or reductants, and (iii) the reaction proceeds under milder ambient conditions. Therefore, this process has the potential to enable a more sustainable quinaldine synthesis from nitroarenes. The combination of photocatalytic redox-cyclization reaction presented here may help to develop a new strategy towards the development of photocatalysis-based organic synthesis.

Supplementary materials related to this article can be found online at doi:10.1016/j.catcom.2010.11.004.

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