Dye-Sensitized TiO2 as Heterogenous Visible Light Photocatalyst for the Hydroxylation of Aryl Boronic Acids

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Herein, we report the preparation of a variety of dye-sensitized TiO2 and its application as a heterogeneous photocatalyst for the oxidative hydroxylation of boronic acids and esters to synthesize phenols. Several organic dyes, namely eosin Y, rose bengal, purpurin, alizarin blue, fluorescein and riboflavin were combined with TiO2. The nanohybrid TiO2-eosin Y showed the best results. Furthermore, we demonstrated a synergistic association between dyes and TiO2 that improves its photocatalytic properties. This methodology resulted compatible for aryl boronic acids with both electron-withdrawing and electron donor groups on the aromatic ring. Thus, the reactions were performed under heterogeneous photocatalytic conditions, employing visible light, saturated oxygen atmosphere, short reaction time, acetonitrile and water as environmentally friendly solvents, to produce the corresponding phenols in very good to excellent isolated yields. Finally, we proposed a mechanism where the selective excitation of EY associated with TiO2 using visible light and the formation of the superoxide anion play a main role in this reaction.

Keywords: phenol, photocatalysis, nanohybrid, hydroxylation, TiO2

Introduction

Catalysis is a fundamental pillar of green chemistry since it is directly or indirectly involved in most of its 12 principles.[1] In recent years, visible light-driven photo-redox catalysis has achieved sustained growth as a standard procedure.[2-6] Additionally, it is a fundamental tool in organic synthesis and in the chemical, pharmaceutical, and agrochemical industries. In this sense, visible light is capable of generating useful reactive species under safe and cost-effective conditions, enabling the use of the sun as a renewable energy source and avoiding the production of waste.[7]

Heterogeneous catalysis is widely used due to its main advantage where the ease of separation and the re-use of the catalyst from the reaction crude can be highlighted.[8,9] However, it is well known that its selectivity and reproducibility are sensitive to experimental conditions. The opposite is observed in homogeneous catalysis, which efficiently performs highly selective reactions; however, its main drawback lies at the time of isolation and reuse

of the catalyst. The combination of these two concepts leads to new procedures that combine the advantages of homogeneous and heterogeneous catalytic systems to improve synthetic processes at bench and industrial scale.[10]

Certainly, TiO2 is the most important metal oxide used as a heterogeneous photocatalyst. This semiconductor is widely used due to its strong redox properties.[11] Among its more extensive applications, the photodegradation of organic pollutants[12] and energy conversion and storage are the most explored.[13] Nevertheless, its use in organic synthesis has become more frequent due to its chemical and photochemical stability, durability, harmlessness, low cost, and visible light transparency (UV active).[14,15] This last property means that this robust material is non-reactive when visible light is employed. However, several strategies have emerged[16] where its combination with other semiconductors,[11] metallic nanoparticles,[12] transition metal complexes,[17] or even organic molecules[18] allows the formation of new hybrid materials, extending its absorption spectra into the visible region, improving its photocatalytic properties.

Moreover, phenols can be found in numerous natural molecules as well as biologically active compounds. They are key synthetic intermediates in organic synthesis and can be obtained from aryl halides, diazonium salts, benzyne intermediate, and C_{sp}^2–H activation. These methodologies are not compatible with functional groups sensitive to

the presence of strong basic or oxidizing reagents. For this reason, the photocatalytic oxidative hydroxylation of aryl boronic acids has become a convenient procedure for the obtention of phenols.[19] In this methodology, the key intermediate responsible for the hydroxylation of boronic acid is the superoxide anion ($O_2^{\bullet-}$) coming from oxygen.[20] In this context, homogeneous photocatalysts based on Ir[21,22] or Ru[23] transition metal complexes and organic dyes such as eosin Y (EY),[24] rose bengal (RB),[25] flavin derivatives,[26] as well as thioxanthones,[27] acridones[28] and boron-dipyrromethene (BODIPY) were reported.[29] In addition, other protocols employing heterogeneous photoactive materials such as g-C_3N_4,[30-32] metal-organic frameworks (MOFs)[33,34] and covalent organic frameworks (COFs)[35,36] were also reported. Furthermore, non-photoactive materials have also been used as support coated with photoactive molecules such as perylenediimide (PDI) on SiO_2,[37] Ru complexes on glass wool,[38] EY on Amberlite[39] and anthraquinones on poli(2-hidroxietil methacrilato) (PHEMA) polymer[40] were used. In the last years, materials based on semiconductors such as quantum dots (QDs),[41] and TiO_2 coated with Cu_2O[42] or QDs[43] have also been reported.

Herein, we report the preparation of dyes-sensitized TiO_2 as a heterogeneous photocatalyst applied to the visible light-assisted hydroxylation reaction of aryl boronic acids, under mild reaction conditions to produce the corresponding phenols from good to excellent yields.

Results and Discussion

Synthesis and characterization of dye-sensitized TiO₂

The synthesis of the heterogeneous photocatalyst was carried out as previously described.[44] The preparation of the photocatalyst involved the combination of TiO_2 Aeroxide P25 with different organic dyes, namely eosin Y (EY), rose bengal (RB), purpurin (PP), alizarin blue (AB), fluorescein (FL) and riboflavin (RF). These organic dyes were selected due to their photo-redox properties and their absorption in the visible region of the electromagnetic spectrum.

The UV-Vis diffuse reflectance of all dye-sensitized TiO_2 prepared was measured (see Figure S1 in Supplementary Information (SI) section). The TiO_2 semiconductor showed absorption below 400 nm, being inactive in the visible region of the electromagnetic spectrum. Photocatalysts sensitized with organic dyes showed the presence of both components, TiO_2 together with an absorption band in the visible region which agrees with the absorption reported for the corresponding dyes in solution.[45] In particular, the heterogeneous photocatalysts containing FL and RF showed their absorption maximum in the blue region

centered at 482 and 436 nm, respectively; nanohybrids containing RB, PP and AB showed their maximum in the green region at 555, 524 and 546 nm, respectively. Finally, EY containing photocatalyst showed a maximum centered at 528 nm and a shoulder at 485 nm; hence, two irradiation channels can be used: the blue or the green regions of the electromagnetic spectrum.

Hydroxylation of aryl boronic acids with TiO₂-dye

In order to optimize the reaction conditions, TiO_2-EY was selected as a photocatalyst and phenyl boronic acid (**1a**) as a model substrate. The hydroxylation reaction of 0.1 mmol of **1a** was carried out in the presence of TiO_2-EY (10 mg), an oxygen atmosphere, triethyl amine (TEA, 5 equiv.) as the sacrificial donor, and water as solvent under blue light emitting diode (LED) irradiation for 1 h. Under these conditions, the only product obtained was phenol (**2a**) in 26% yield (Table 1, entry 1). When the reaction time was increased to 4 h, **2a** was obtained in 39% yield (Table 1, entry 2). Various mixtures of $CH_3CN:H_2O$ have been used as solvent (Table 1, entries 3-4) in order to improve reaction yields and extend their use in organic synthesis. Acetonitrile was chosen due to its low toxicity and higher oxygen solubility.[46] When a mixture of $CH_3CN:H_2O$ (4:1) was used as solvent, phenol was obtained in 95% yield. At this point, irradiation time was decreased from 4 to 1, 0.5 and 0.25 h (Table 1, entries 5-7). Under these conditions, **2a** was produced in 99, 95 and 90%, respectively. From this result, it can be concluded that the reaction is completed after 30 min. Also, the amount of TiO_2-EY used in the reaction was reduced from 10 to 5 and 2.5 mg (Table 1, entries 6, 8-9), giving 95, 65, and 59% yield of **2a**, respectively. The amount of sacrificial donor was also investigated, by reducing the TEA from 5 to 3 and 1 equivalents (Table 1, entries 10-11), resulting in the formation of **2a** in 83, and 81% yields, respectively. In the absence of TEA, no phenol was observed (Table 1, entry 12), indicating that the presence of the sacrificial donor is crucial for the formation of the desired product. Also, the degradation of the organic dye was noticed under this condition since a white suspension was obtained at the end of the reaction. In order to use a more environmentally friendly solvent, acetonitrile was replaced by ethanol. However, after 30 min of irradiation the formation of **2a** dropped to 59% yield (Table 1, entry 13). At this point, 1 h of 5 W blue LED irradiation in $CH_3CN:H_2O$ (4:1) and 10 mg of photocatalyst were selected as the best conditions to continue the study (Table 1, entry 5).

The performance of the photocatalysts was further studied under conditions where **2a** formation was not quantitative, reducing the reaction time to 30 min and 5 mg

Table 1. Optimization of reaction conditions for the hydroxylation of phenyl boronic acid (**1a**) to phenol (**2a**)

$$\text{1a } (B(OH)_2) + O_2 \xrightarrow[\text{5W blue LED}]{\substack{\text{TiO}_2\text{-EY} \\ \text{TEA (5 equiv.)}}} \text{2a (OH)}$$

entry[a]	time / h	TiO₂-EY / mg	Solvent	Yield 2a[b] / %
1	1	10	H₂O	26
2	4	10	H₂O	39
3	4	10	CH₃CN:H₂O (1:1)	77
4	4	10	CH₃CN:H₂O (4:1)	95
5	1	10	CH₃CN:H₂O (4:1)	99
6	0.5	10	CH₃CN:H₂O (4:1)	95
7	0.25	10	CH₃CN:H₂O (4:1)	90
8	0.5	5	CH₃CN:H₂O (4:1)	65
9	0.5	2.5	CH₃CN:H₂O (4:1)	59
10[c]	0.5	10	CH₃CN:H₂O (4:1)	83
11[d]	0.5	10	CH₃CN:H₂O (4:1)	81
12[e]	0.5	10	CH₃CN:H₂O (4:1)	0
13	0.5	10	EtOH: H₂O (4:1)	59

[a]Reaction conditions: phenyl boronic acid (**1a**, 12.2 mg; 0.1 mmol); TiO₂-EY as photocatalyst, TEA (5 equiv.), O₂ saturated atmosphere, 25 °C and 5 W blue LED irradiation; [b]yields determined by ¹H NMR using the internal standard method; [c]TEA (3 equiv.); [d]TEA (1 equiv.); [e]no TEA was added. EY: eosin Y; TEA: triethyl amine.

of the photocatalyst. In addition, the irradiation source was selected according to the maximum absorption of each nanohybrid (blue or green LED irradiation, see Figure S1 in SI section). When TiO₂-EY was irradiated with 5 W green LEDs instead of blue LED, the reaction yield of **2a** decreased from 65 to 26%, respectively (Table S1 (SI section), entries 1-2). In both cases, phenyl boronic acid was observed to account for the mass balance.

When the reaction was performed using both TiO₂-AB and TiO₂-PP under green light irradiation, phenyl boronic acid remained unreactive and only traces of **2a** were found (Table S1, entries 3-4). In the case of TiO₂-RB under green LED irradiation, complete conversion of **1a** was observed but only 67% yield of phenol was obtained. For TiO₂-FL and TiO₂-RF, only 7 and 9% of **2a** was formed, respectively, when the reaction was performed under blue LED irradiation. Summing up, the nanohybrid TiO₂-EY resulted the best photocatalyst under blue LED irradiation for the hydroxylation of aryl boronic acids.

Then, the reaction scope and photocatalytic potential of TiO₂-EY were further studied. A wide range of aryl boronic acids were tested under the best reaction conditions (Table 1, entry 5). As a result, aryl boronic acids, with both electron-withdrawing and electron donating substituents, were converted to the corresponding ArOH from good to excellent isolated yields (50-94%, Scheme 1).
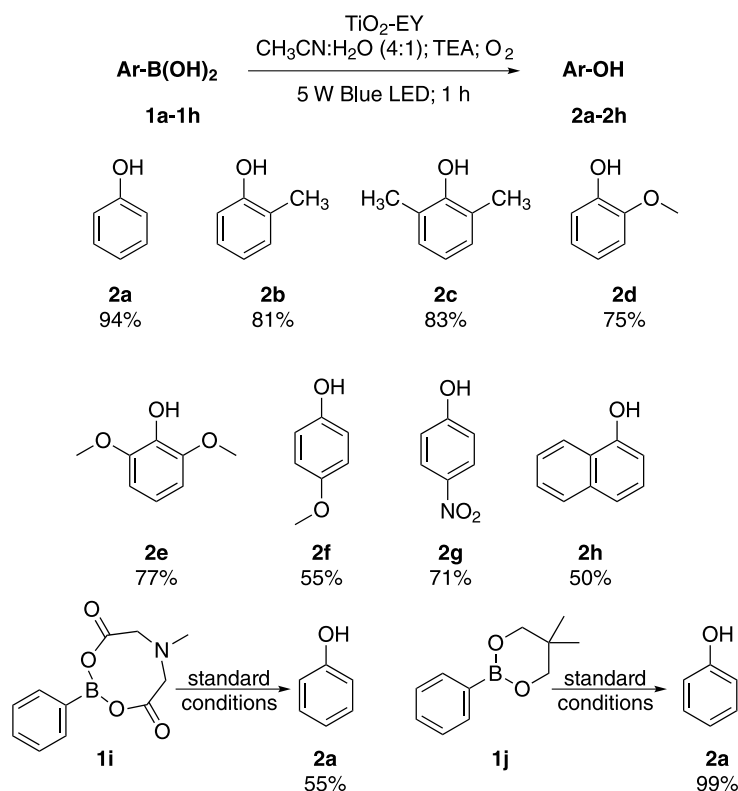
Scheme 1. Reaction scope for the hydroxylation of aryl boronic acid and esters. Standard reaction conditions: aryl boronic acid (**1**, 0.2 mmol), TiO₂-EY (20 mg), TEA (5 equiv.) 4 mL of CH₃CN:H₂O (4:1), oxygen saturated atmosphere irradiated with 2 × 5 W blue LED at 25 °C. Isolated yields are reported.

When aryl boronic acid-bearing methyl groups in the *ortho* position were used, the yields of the corresponding phenols **2b** and **2c** slightly decreased to 81 and 83%, respectively. The inclusion of the strong electron donating methoxy group in **1d**, **1e** and **1f** boronic acids, resulted in a significant decrease of its corresponding phenols **2d** (75%) and **2e** (77%) substituted in the *ortho* positions and 55% in the case of *p*-methoxy phenol (**2f**). Substrate **1g** with a strong electron withdrawing nitro as substituent produces the corresponding *p*-nitrophenol in good yield (**2g**, 71%). When exploring an extended π system such as 1-naphthyl boronic acid, the yield of the corresponding 1-naphthol (**2h**) decreases to 50%. Moreover, the scope of the methodology can be extended to aryl boronic esters; the reaction carried out with phenyl boronic acid *N*-methyliminodiacetate (MIDA) (**1i**) and phenyl boronic acid neopentylglycol (**1j**) esters, produced **2a** in good to excellent yields, 55 and 99%, respectively (Scheme 1).

To get a better insight into the reaction mechanism, control reactions were carried out (Table 2). When the reaction was performed under a nitrogen atmosphere, product **2a** was not observed, and the decomposition of the organic dye was evidenced by a change of its characteristic

Table 2. Mechanistic control reactions for the oxidative hydroxylation of boronic acids

entry[a]	Photocatalyst	Atmosphere	Irradiation	Yield **2a**[b] / %
1	TiO₂-EY	N₂	blue LED	0
2	TiO₂-EY	air	blue LED	44
3	TiO₂-EY	O₂	dark	traces
4	TiO₂	O₂	blue LED	traces
5[c]	EY	O₂	blue LED	70
6[d]	TiO₂ + EY	O₂	blue LED	64
7	SiO₂-EY	O₂	blue LED	45
8	–	O₂	blue LED	traces
9[e]	TiO₂-EY	O₂	blue LED	14

[a]Reaction conditions: phenyl boronic acid (**1a**, 12.2 mg; 0.1 mmol); 10 mg of photocatalyst, TEA (5 equiv.), 25 °C, 30 min and 5 W blue LED irradiation, using CH₃CN:H₂O (4:1) as solvent; [b]yields determined by ¹H NMR using the internal standard method; [c]0.3 mol% of EY (0.2 mg); [d]10 mg of TiO₂ and 0.3 mol% of EY were added separately to the reaction mixture; [e]2 equiv. of TIRON were added. EY: eosin Y; LED: light emitting diode.
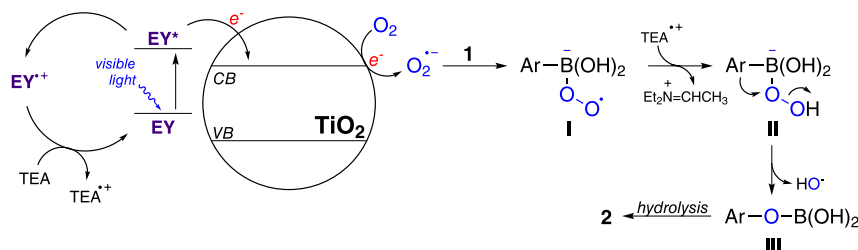
color (Table 2, entry 1). When an air atmosphere was used instead, the yield of **2a** decreased to 44% yield (Table 2, entry 2). This indicates that the presence of a high concentration of oxygen is necessary for the reaction to occur. This is consistent with the fact that a solvent with higher oxygen solubility renders higher yields of phenols. Under dark conditions, only traces of **2a** were formed which indicates the photoinduced nature of the reaction.

The efficiency of the synthetized photocatalyst, TiO₂-EY, was also compared with TiO₂ nanoparticles and organic dye EY (Table 2, entries 4-5). When only TiO₂ was used as the photocatalyst, traces of **2a** were observed, while in the case of EY, only 70% of **2a** was found and a poor mass balance was noticed since no phenyl boronic acid was detected. EY in the presence of TEA and in the absence of TiO₂ promotes reductive quenching of ¹EY*. This would generate EY•⁻, which is responsible for oxygen reduction. However, ³EY* does not participate in the formation of the reduced photocatalyst since this process is endergonic (Table 2, entry 5).[47] When a physical mixture of TiO₂ and EY was used, 64% of **2a** was detected while full conversion of **1a** to **2a** was obtained for TiO₂-EY (Table 2, entry 6, and Table 1, entry 6). In order to study the role of the semiconductor in the nanohybrid, non-photoactive support SiO₂ was used. Employing SiO₂-EY under standard conditions, **2a** was obtained in 45% yield (Table 2, entry 7). This result shows that TiO₂ not only plays the role of support, like SiO₂ but also improves the charge separation process to produce superoxide anion. Based on these last results, the association between EY and TiO₂ is necessary to ensure charge separation and avoid wasting energy processes, which show a synergic effect in TiO₂-EY. In the absence of photocatalyst, traces of **2a** were formed (Table 2, entry 8). Finally, sodium 4,5-dihydroxybenzene-1,3-disulfonate (TIRON, 2 equiv.) was used as a superoxide radical anion scavenger. Under this condition, only 14% of phenol was obtained (Table 2, entry 9), indicating that this intermediate is crucial in the reaction mechanism. According to these results, we propose the mechanism shown in Scheme 2. First, selective excitation of EY associated with TiO₂ by visible light generates the electronically excited EY*. Then, EY* transfers an electron

Scheme 2. Proposed mechanism for the oxidative hydroxylation of aryl boronic acids with TiO₂-EY.

to the semiconductor conduction band (CB) ensuring an efficient charge separation in the nanohybrid. Afterward, the electron migrates from the CB to the surface to generate the superoxide anion radical ($O_2^{\bullet-}$). To close the catalytic cycle, TEA reduces the $EY^{\bullet+}$ intermediate by electron transfer to regenerate EY. Finally, $O_2^{\bullet-}$ reacts with aryl boronic acid to generate the intermediate peroxydihydroxy(aryl)borate (**I**), which abstracts a hydrogen atom from $TEA^{\bullet+}$ to form the intermediate **II**, and through rearrangement generates **III**, which after hydrolysis, produces the corresponding phenol (**2**).[23]

Conclusions

In summary, a variety of dye-sensitized TiO₂ was prepared and tested as a heterogeneous photocatalyst in the oxidative hydroxylation of phenyl boronic acids. The nanohybrid TiO₂-EY showed the best performance toward various aryl boronic acids and phenyl boronic esters obtaining the corresponding phenols in good to excellent isolated yields. The synergic effect between TiO₂ and EY in the nanohybrid improves the photon efficiency of the reaction. Oxygen as a green oxidant is also required since the production of the superoxide anion ($O_2^{\bullet-}$) plays a critical role in the mechanism. Summing up, we have developed a simple methodology that uses a mixture of acetonitrile and water as a solvent, and triethylamine as a sacrificial donor, assisted by visible light at a short reaction time and compatible with electron-withdrawing and electron donor groups.

Experimental

Materials and methods

Boronic acids, triethylamine, EY, FL, RB, RF, PP and AB were all high-purity commercial samples from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. Titanium(IV) oxide Aeroxide P25 was obtained from Aldrich Chemical Co. (Milwaukee, WI, USA). Ultrapure acetonitrile, water and ethanol were used without further purification. The reaction products were isolated by flash column chromatography (silica gel, eluting with dichloromethane) from the reaction mixture. UV-Vis diffuse reflectance measurements were acquired using a StellarNet Inc spectrometer equipment. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded at 400.16 and 100.62 MHz, respectively, on a Bruker 400 spectrometer with CDCl₃ as a solvent. All spectra were reported in δ (ppm) relative to the residual solvent signal (δ_H (CHCl₃) 7.26 ppm). 1,4-Dinitrobenzene was used as the internal standard in ¹H NMR quantification. All the phenols

were isolated, and their spectroscopic data were in good agreement with the reported in the literature.

General procedure for the synthesis of dye-sensitized TiO₂[44]

All synthesis were carried out using 0.03 mmol of the corresponding dye was put into a 50 mL erlenmeyer containing 10 mL of anhydrous ethanol for 10 min of ultrasonication. Then, 1 g of TiO₂ was added to the dispersed dye for a further 10 min of ultrasonication. The mixture was then stirred for 12 h. Then, dye-TiO₂ was collected with a rotary evaporator and subsequently dried at 100 °C in a vacuum drying chamber (see Figure S2 in SI section).

General procedure for the oxidative hydroxylation of boronic acids

All reactions were carried out in a vial equipped with a magnetic stirrer, using 0.1 mmol of aryl boronic acid or aryl boronic ester (1.0 equiv), dye-sensitized TiO₂ (10 mg), TEA (5 equiv.), and 2 mL of a mixture of CH₃CN:H₂O (4:1) as a solvent. The vial was sealed, and the reaction mixture was saturated with oxygen for 10 min and then irradiated with 5 W blue LEDs for 1 h. In the reactions shown in Scheme 1, 0.2 mmol of aryl boronic acid or aryl boronic ester (1.0 equiv), dye-sensitized TiO₂ (20 mg), triethylamine (TEA, 5 equiv.), and 4 mL of a mixture of CH₃CN:H₂O (4:1) as a solvent were used. The vial was also sealed, and the reaction mixture was saturated with oxygen for 10 min and then irradiated with 2×5 W blue LEDs for 1 h. Then, the reaction mixture was filtered, and the resulting supernatant was acidified with HCl (0.1 M) up to pH 3-5 and extracted with ethyl acetate (3×20 mL). The combined organic layers were dried with anhydrous Na₂SO₄ and filtered. The solvent was removed under reduced pressure, and phenols were purified by flash chromatography using dichloromethane as an eluent.

Supplementary Information

Supplementary information includes UV-Vis diffuse reflectance spectrum, Table S1, ¹H and ¹³C NMR of all synthesized phenols **2a-2h**, and are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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