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Synthesis of nitrocarbazole compounds and their electrocatalytic oxidation of alcohol

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ABSTRACT

Three compounds with nitrocarbazole frameworks were synthesized and their electrochemical reversibility as organic electrocatalysts was studied by cyclic voltammetry. The electrochemical reversibility and oxidation-reduction potential of the compounds were greatly affected by their substituents. The oxidation-reduction potential of the compound with an electron-donating group was negative, while that of the compound with an electron-withdrawing group on the carbazole framework was positive. The electrocatalytic oxidation activities of the nitrocarbazole compounds were investigated through cyclic voltammetry and controlled potential electrolysis at room temperature. The electrocatalysts showed excellent selectivity for *p*-methoxybenzyl alcohol, converting it to the corresponding aldehyde through electro-oxidation with just 2.5 mol% of the electrocatalysts maintained their excellent electroredox activity following recycling.

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1. Introduction

The catalytic oxidation of small organic molecules is an important research area in the field of catalysis. Selective oxidation of alcohols to the corresponding aldehydes and ketones is important in the synthesis of fine chemicals and organic intermediates [1,2]. Many catalysts with high selectivity, stability and low cost have been developed to improve the conversion and selectivity in the oxidation of alcohols to the corresponding aldehydes. For instance, gold-copper bimetallic catalysts [3], and nitrogen-doped carbon nanosphere-supported palladium catalysts [4] have been prepared and used in the catalytic oxidation of benzyl alcohol. Jia et al. [5] reported the selective oxidation of benzyl alcohol to benzaldehyde using alkali-treated ZSM-5 zeolite as a catalyst and H_2O_2 as an oxidant. Many re-

searchers have also devoted effort to the study of organic catalysts. For example, the organic sulfonate [6], immobilized 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) [7] and Lewis acid-activated TEMPO have been studied as catalysts for the oxidation of alcohol. These approaches are limited by the use of either noble metals or high temperature.

Organic electrocatalysis is recognized as an environmentally compatible methodology because it avoids using toxic and dangerous oxidizing or reducing reagents, and most of the reactions can be carried out under mild conditions [9,10]. However, in direct electro-oxidation synthesis, the working electrode is easily passivated by the formation of a polymer film on the electrode surface, which can sharply decrease current efficiency. Indirect electro-oxidation with an electron transfer mediator is a good way to avoid passivation of the electrode

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[11,12]. Triarylamines have received extensive attention from researchers as a new type of electro-redox mediator because of their broad range of redox potentials. The oxidation potential of triarylamines can become positive after introduction of an electron-withdrawing group [13-18]. Compared with the triarylamine framework, the carbazole framework has better planarity and the substituents have a greater effect on the redox properties [19]. Carbazole compounds have been widely used as fluorescent materials [20], but have not been employed as an electro-redox mediator in electrocatalytic oxidation, especially carbazole compounds with nitro groups. Based on the intrinsic properties of the carbazole framework and strong electron-withdrawing nature of nitro groups, in this paper, nitrocarbazole compounds were synthesized and used as organic electrocatalysts in the mediated electro-oxidation of alcohols at room temperature.

2. Experimental

2.1. Preparation of the organic electrocatalysts [21–25]

The route used to synthesize carbazole compounds with different substituents is shown in Scheme 1.

3,6-Dibromo-9H-carbazole (1), a solution of *N*-bromosuccinimide (0.21 mol) in DMF (80 mL) was slowly added to a solution of carbazole (0.1 mol) in DMF (20 mL) in an ice bath. After reaction for 30 min, the mixture was poured into ice water (1 L), and the crude product was collected by filtration to give a blue powder. Recrystallization from EtOH/H₂O afforded blue crystals with a yield of 68%. ¹H NMR (500 MHz, CDCl₃): δ 8.14 (d, *J* = 1.9 Hz, 2H), 8.12 (s, 1H), 7.53 (d, *J* = 8.6, 1.9 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H).

3,6-Dimethoxycarbazole (2), in a 100-mL three-necked flask, a solution of sodium methoxide (0.1 mol) in methanol (15 mL) was stirred at room temperature for 30 min. CuI (0.02 mol), **1** (0.005 mol), and DMF (17 mL) were added and then the mixture was heated under reflux for 8 h under N₂ atmosphere. The solution was filtered while hot to remove CuI and the filtrate was poured into stirred water (1 L). The resulting precipitate was collected by filtration, washed thoroughly with water, and dried to afford a black powder in a yield of 88%. ¹H NMR (500 MHz, CDCl₃): δ 3.95 (s, 6H, –OCH₃), 7.00 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.53 (s, 2H), 7.79 (s, 1H, –NH).

3a–3c, a 100-mL two-necked flask equipped with a reflux condenser was charged with a carbazole compound with a –OCH₃, H or Br substituent (15.3 mmol), K₂CO₃ (76.52 mmol), *p*-nitrofluorobenzene (61.4 mmol), and DMF (80 mL). Each reaction mixture was heated under reflux for 12 h, cooled, and then poured into water (500 mL). Each precipitate was filtered, dried, and recrystallized.

3a, orange powder, yield 66%. ¹H NMR (500 MHz, DMSO-d₆): δ 8.47 (d, *J* = 8.6 Hz, 2H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.87 (d, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 6H).

3b, bright yellow powder, yield 66%. ¹H NMR (500 MHz, CDCl₃): δ 8.48 (d, *J* = 9.0 Hz, 2H), 8.14 (d, *J* = 7.8 Hz, 2H), 7.8 (d, *J* = 9.0 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.46–7.43 (m, 2H), 7.35–7.33 (m, 2H).

3c, bright yellow powder, yield 81%. ¹H NMR (500 MHz, CDCl₃): δ 8.57–8.47 (m, 2H), 8.23 (d, *J* = 1.9 Hz, 2H), 7.79–7.71 (m, 2H), 7.57 (d, *J* = 8.7, 2.0 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H).

4-(3,6-Dimethoxy-9H-carbazol-9-yl)aniline (**4a**), **3a** (0.41 mmol) was dissolved in ethanol (30 mL), and then SnCl₂·2H₂O (2.80 mmol) was added. The reaction mixture was heated under reflux for 15 h and then cooled to room temperature. Subsequently, the reaction mixture was adjusted to basic pH with saturated NaHCO₃, and then extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by silica-gel column chromatography to afford an orange powder in a yield of 75%. ¹H NMR (500 MHz, CDCl₃): δ 7.57 (d, *J* = 2.4 Hz, 2H), 7.33–7.23 (m, 4H), 7.09–7.01 (m, 2H), 6.90–6.79 (m, 2H), 3.96 (s, 6H), 3.85 (s, 2H).

4-(9H-Carbazol-9-yl)aniline (**4b**), compound **3b** (0.09 mol), 10% Pd/C (0.103 g) and ethanol (20 mL) were added to a 50-mL round-bottom flask equipped with a stirring bar. The reaction mixture was heated under reflux. Hydrazine monohydrate (3 mL) was added slowly to the mixture, and then the solution was stirred under reflux for 10 h. The solution was cooled to room temperature, filtered to remove Pd/C, and then concentrated to afford a light brown viscous liquid in a yield of 80%. ¹H NMR (500 MHz, CDCl₃): δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.34–7.26 (m, 6H), 6.88– 6.87 (m, 2H), 3.83 (s, 2H).

4-(3,6-Dibromo-9H-carbazol-9-yl)aniline (**4c**), compound **4c** was synthesized according the method used to prepare **4a**



a: R₁ = OCH₃; b: R₁ = H; c: R₁ = Br

Scheme 1. Synthesis of the organic electrocatalysts.

with **3c** instead of **3a** to afford a white powder in a yield of 92%. ¹H NMR (500 MHz, CD₃CN): δ 8.34 (d, *J* = 2.0 Hz, 2H), 7.55 (d, *J* = 9.0, 2.0 Hz, 2H), 7.25–7.23 (m, 4H), 6.92–6.90 (m, 2H), 4.74 (–NH₂, 2H).

2.2. Electrochemical measurements

Cyclic voltammetry (CV) was carried on a CHI 660B electrochemical workstation (Shanghai CH Instrument Company, China) equipped with a three-electrode system. All experiments were performed in an undivided electrochemical cell. Glassy carbon (3-mm diameter) served as the working electrode, a platinum sheet (1×2 cm) as the counter electrode, and Ag/AgNO₃ as the reference electrode. The electrolyte consisted of 0.2 mmol/L LiClO₄ in CH₃CN/CH₂Cl₂ (4:1 by volume). The concentration of the organic electrocatalyst was 1 mmol/L. The concentration of *p*-methoxybenzyl alcohol (*p*-MBzOH) was varied from 3 to 20 mmol. The concentration of other substrates was 5 mmol. The scan rate was 50 mV/s. All the measurements were performed at room temperature and the CV curves shown are the third stable circle.

Controlled potential electrolysis was performed in an undivided electrochemical cell equipped with a graphite rod (5-mm diameter) as the working electrode, platinum sheet $(1 \times 2 \text{ cm})$ as the counter electrode, and Ag/AgNO3 as the reference electrode. The electrolyte consisted of 0.2 mmol/L LiClO₄ in CH₃CN/CH₂Cl₂ (4:1 by volume). The concentration of the organic electrocatalyst was 1 mmol/L. The concentration of p-MBzOH in the controlled potential electrolysis measurements was varied from 20 to 200 mmol. The electrolysis process was performed for 6 h at room temperature. The major products were detected using GC-MS (Thermo Fisher). The yield of the oxidation products was determined by GC (Agilent 7890A) and calculated by the area normalization method. The organic electrocatalyst was recycled by extracting the organic phase of the reaction liquid, concentration of the organic phase and purification by silica-gel column chromatography.

3. Results and discussion

3.1. Electrochemical properties of the organic electrocatalysts

The CV curves of the nitrocarbazole-based redox catalysts with different substituents are shown in Fig. 1. The oxidation-reduction potentials of the catalyst with an electron-donating group (-OCH₃) was negative, while they became positive after introducing an electron-withdrawing group (-Br) onto the carbazole framework. Compound 3c has a positive oxidation potential of 1.282 V versus Ag/AgNO₃. Meanwhile, the introduction of a -OCH3 or -Br substituent led to better oxidation-reduction reversibility than that of the compound with H. The CVs of the substituted carbazole compounds indicate that they are suitable for use as mediators in electrochemical oxidation reactions. However, the electrochemical oxidation-reduction reversibility of the carbazole compounds disappeared when -NO2 was replaced by -NH2 (Fig. 2). A reasonable explanation for this may be that the aminocarbazole com-



Fig. 1. Cyclic voltammograms of nitrocarbazole-based redox catalysts with different substituents.

pounds tended to form stable ammonium cations after losing an electron, and the reduction increased the delocalization of the conjugated compound. The oxidation potentials (E_{ox}), reduction potentials (E_{re}) and differences between them (ΔE) of the carbazole-framework compounds are listed in Table 1.

3.2. Electrochemical oxidation of an alcohol

The CVs of *p*-MBzOH with and without **3c** are depicted in Fig. 3. The oxidation peak potential for the electro-oxidation of *p*-MBzOH exhibited a 64-mV negative shift from 1.350 to 1.286 V in the presence of **3c**. The energy consumption of the oxidation process was effectively decreased because it could be carried out at a relatively lower potential compared with the electro-oxidation process in absence of **3c**. Simultaneously, the oxidation peak current increased markedly. These results show that **3c** has excellent catalytic performance in the electro-oxidation of *p*-MBzOH.

Figure 4 presents the CV curves of different concentrations of p-MBzOH in the presence of 1 mmol/L of **3c**. The oxidation current increased obviously with increasing substrate concentration, indicating that relatively high concentrations of



Fig. 2. Cyclic voltammograms of aminocarbazole-based redox catalysts with different substituents.

Table 1

Oxidation potentials $E_{\rm ox}$, reduction potentials $E_{\rm re}$ and difference between the oxidation and reduction potentials ΔE of the carbazole-based compounds.

R_1 R_1 R_1					
R ₁	R ₂	Compound ·	Carbazoles		$\Delta E/mV$
			$E_{\rm ox,1}/{\rm V}$	$E_{\rm re,1}/{\rm V}$	$\Delta E/\Pi V$
OMe	NO_2	3a	0.717	0.644	73
Н	NO_2	3b	1.051	0.905	146
Br	NO_2	3c	1.282	1.203	79
OMe	NH_2	4a	_	_	_
Н	NH_2	4b	1.086	_	_
Br	NH_2	4c	1.709	_	_

p-MBzOH could be electrochemically oxidized and the electrolysis efficiency was improved by **3c**. To expand the applicability of **3c** to different substrates, the electrocatalytic performance of the nitrocarbazole compound toward benzyl alcohol with different *para*-substituents was investigated, as shown in Fig. 5. Even for the substrates with high oxidation potentials, **3c** still showed good catalytic oxidation properties.

In an electrolysis system with a volume of 10 mL and keeping the electrocatalyst concentration at 1 mmol/L, controlled potential electrolysis was conducted using different concentrations of *p*-MBzOH at the oxidation potential of the electrocatalyst **3c** (1.28 V) for 6 h. The yields of 4-methoxybenzaldehyde (*p*-MBA) obtained with different starting concentrations of *p*-MBzOH are illustrated in Fig. 6. When the concentration of *p*-MBzOH was under 40 mmol/L, it was completely transformed to the target product *p*-MBA after 6 h. The yield of *p*-MBA decreased when the concentration of *p*-MBzOH was above 80 mmol/L. This is attributed to the low stoichiometric ratio of **3c** to the substrate (\leq 1:80) at high substrate concentration. The controlled potential electrolysis equation of *p*-MBzOH is shown in Eq. 1 and a possible indirect electro-oxidation mechanism for the nitrocarbazole organic cata-



Fig. 3. Cyclic voltammograms of *p*-methoxybenzyl alcohol (*p*-MBzOH) with and without **3c**. (1) blank; (2) 1 mmol/L of **3c**; (3) 5 mmol/L of *p*-MBzOH; (4) 1 mmol/L **3c** + 5 mmol/L *p*-MBzOH.



Fig. 4. Cyclic voltammograms of different concentrations of *p*-MBzOH in the presence of electrocatalyst **3c** (1 mmol/L).



Fig. 5. Cyclic voltammograms of different substrates (5 mmol/L) in presence of 1 mmol/L **3c**. (1) *p*-MBzOH; (2) *p*-tolylmethanol; (3) phenylmethanol.

lyst is provided in Scheme 2.

3.3. Recycling of the organic electrocatalyst

The organic electrocatalyst **3c** was recycled after its first use in controlled potential electrolysis, and the electrochemical properties obtained after recycling are depicted in Fig. 7. E_{ox} of



Fig. 6. Yields of *p*-MBA obtained by controlled potential electrolysis of different concentrations of *p*-MBzOH using **3c** as a catalyst.



Scheme 2. Proposed indirect electrolysis mechanism of p-MBzOH.

the recovered **3c** was 1.281 V, $E_{\rm re}$ was 1.203 V and ΔE was about 78 mV, indicating that the recycled electrocatalyst **3c** still retains excellent electrochemical reversibility and could be used again as the mediator in the indirect electro-oxidation of alcohols.

4. Conclusions

Nitrocarbazole compounds showing good electrochemical reversibility were synthesized by introducing a nitro group onto the carbazole framework. The redox potential of the electrocatalysts could be tuned through modification with different substituents. The oxidation potential of the electrocatalysts became positive after introducing a strongly electron-withdrawing nitro group, which meant that this kind of electrocatalyst was suitable for mediating the electro-oxidative process of different substrates with high oxidation potentials. The nitrocarbazole compounds displayed excellent electrocatalytic oxidative activities in the electro-oxidation of alcohols to the corresponding aldehydes, and the electrocatalysts could be recovered.

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Fig. 7. Cyclic voltammogram of recycled electrocatalyst 3c.

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