Electrochemical Oxidation Degradation of Azobenzene Dye Self-powered by Multilayer-Linkage Triboelectric Nanogenerator

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Keywords

Multi-layer Linkage; Triboelectric Nanogenerator, Azobenzene dye, Self-power, Degradation

Abstract

A pre-charge injected multilayer-linkage triboelectric nanogenerator (PMLL-TENG) with all its friction layers ganged, contacted and separated simultaneously, has been designed. It features adjustable size and number of friction layers to yield desired voltage and power density. Using the electric power generated by such a PMLL-TENG, high toxic and carcinogenic 4-dimethylaminoazobenzene can be indirectly degraded to CO₂ as promoted by the active oxygen species generated at the anode interface. The oxidation degradation mechanism is tentatively proposed based on the cyclic voltammogram, GC-MS and ¹H NMR of the degraded intermediates. This work suggests that PMLL-TENG with multilayer-linkage structures, sustainable energy, can be reasonably tailored to self-power practical electrochemical treatment of dyeing wastewater by harvesting vibration energy.

1. Introduction

Azo dyes have been studied extensively owing to their versatile optical and redox properties. Over 0.7 million tons of them are produced annually worldwide to be used in pharmaceuticals, cosmetics, textiles and printing [1-6]. However, about 15% of them are released into the environment waters with typical concentration of 10-200 mg L⁻¹, which and whose incomplete degradation products (for example, aniline) are toxic, carcinogenic, mutagenic and

non-biodegradable [7-17], thus posing a major threat to humans and animals. Increasing efforts have therefore been devoted to the degradation technology of azo dyes, however, traditional methods of absorption [18], photocatalysis [19-21], coagulation [22] and biological process [23,24] may be shadowed by limitations of sophisticated instruments, complex procedures and possibly producing secondary pollutants. Consequently, thorough degradation of azo dyes are desired, and the typical example is electrochemical technology, which can oxidize a broad range of organic pollutants with nontoxicity, environmental compatibility and high efficiency [25-27]. But reported electrochemical systems are often driven by external power provided by fossil fuels, which is associated with new geo-political problems and limited in availability of large-scale and sustainable supply. Hence self-powered systems harvesting universally available and renewable mechanical energy is expected to be a good substitute.

Four years ago, Wang's group creatively invented triboelectric nanogenerator (TENG) to harvest mechanical energy [29]. Rapidly, such technology has been widely used to self-powered digital clock [30], sensor for detecting toxic Hg^{2+} ions [31], and electrochemical reactions including metal anticorrosion [32], oxidation of toxic gases [33], water splitting [34] and organic matter eliminations [35,36]. To the best of our knowledge, the self-powered electrochemical degradation of azo dyes, especially the degradation mechanism, is rarely investigated [37,38]. Herein, we first design a pre-charge injected, multilayer-linkage enhanced TENG (PMLL-TENG) and then apply it to self-powered electrochemical degradation system (SPEDS) to degrade carcinogenic azo dye of 4-dimethylaminoazobenzene (DAB) to CO_2 . Systematical study via cyclic voltammogram (CV), GC-MS, ^1H NMR and UV-vis spectra indicates that DAB can be indirectly degraded by reactive oxygen species such as $\text{O}^\bullet$ and $\text{HO}^\bullet$ radicals generated at the anode interface [39-41] self-powered by PMLL-TENG. In double-compartment cell (D-cell), DAB can be self-powered to be degraded to CO_2 at the anode interface, which takes advantage over (1) electrochemical reduction degradation at the cathode interface with producing the carcinogenic and hard degradable intermediates, aniline and its derivatives, and (2) electrochemical redox degradation in single-compartment cell (S-cell) with generating more toxic degraded product, 4, 4'-dihydroxybiphenyl.

2. Experimental sections

2.1 Materials

Al foil (thickness, 110 μm) and polytetrafluoroethylene films (PTFE, 500HN; thickness, 50 μm) are purchased from DuPont. DAB, sulfuric acid and sodium bicarbonate (NaHCO_3) are purchased from Alfa Aesar. All the materials are used as received.

2.2 Characterization

The output voltage and current of the TENG are measured using a digital oscilloscope from Agilent with its inner impedance of 100 $\text{M}\Omega$ and an SR570 low noise current amplifier from Stanford Research Systems, respectively. GC-MS is measured with an Agilent 6890/5973N Trace GC/MS system. UV-Vis spectra are recorded on TU-1810 spectrometer. The ^1H NMR spectra are performed using a AVANCE III HD 600 in ppm downfield from Me_4Si . CV is performed on a CHI660D electrochemical workstation.

2.3 Fabrication of PMLL-TENG

The structure of the PMLL-TENG is shown in **Figure 1a**, which illustrates that each PMLL-TENG pair has two friction layer parts, the PTFE part and Al part. The Al layer part: a piece of commercial Al foil (width: 6 cm, length: 6 cm, thickness: 110 μm) is adhered on an acrylic sheet. The PTFE layer part: a piece of Al foil as charge collector (width: 6 cm, length: 6 cm, thickness: 110 μm) is adhered onto an acrylic plate as the substrate. In turn, a piece of PTFE film with the same size of Al foil is adhered onto the Al foil with no uncoated side exposed.

Pre-charge injected surface modification [42,43]: The PTFE film on Al foil is connected to a high voltage DC power, with the positive end connected with the charge collector on the acrylic sheet with Al foil, and the negative end connected with the other end on the PTFE film with a vertical distance of 1 cm. The voltage of 5 kV (25 $\text{V}/\mu\text{m}$) is applied on the device. Two pieces of PTFE films with Al foil bellow are released and the voltage is removed in 10 min.

2.4 Electrochemical measurements

The electrochemical degradation of DAB in acidic electrolyte is self-powered by PMLL-TENG in a glass beaker, with platinum foil as the counter and the working electrodes. CVs are tested in 0.1 M H_2SO_4 solution at a scan rate of 100 mV s^{-1} from -0.1 V to +1.2 V at CHI660D electrochemical workstation with a three-electrode system, the platinum disk electrode and Pt electrode as the working and counter electrodes, and $\text{Hg}/\text{Hg}_2\text{Cl}_2$ as the reference electrode. Before measurement, the electrolyte (0.1 mol L^{-1} H_2SO_4) is pretreated with N_2 for 30 min, and the working electrode is polished using alumina powder and

sonicated in deionized water for 20 min. For the D-cell, anode and cathode are separated by an airtight anion exchange membrane with electrolyte in each chamber, and the reference electrode is put in cathode chamber. For the S-cell, three electrodes are fixed in a glass beaker. A constant 2V voltage is applied for a predefined period.

The solutions collected at different electrochemical degradation time are neutralized with Na_2CO_3 , filtered and extracted with CH_2Cl_2 , and then washed three times with deionized water. The obtained organic layers are dried with Na_2SO_4 , filtered, and concentrated under atmosphere at room temperature to give the degraded product, which is dissolved in 1 ml CH_2Cl_2 and 0.6 ml DMSO- d_6 for detection by GC-MS and ^1H NMR, respectively.

3. Results and discussions

It is well known that a typical TENG often has high output voltage but low current, despite the state-of-art progress, more endeavors are still highly desired to further improve its current output. Generally there are two means of enhancing the performance of TENG, structure design improvement and friction layer modification [44]. Based on the former, a multilayer-linkage structure with all its friction layers ganged, contacted, and separated simultaneously is designed to optimize the performance of all the friction layers, which is schematically shown in Figure 1a. In order to further improve its performance and ground on the latter concept, pre-charge injection technique is introduced here on PTFE layer to enhance the charge density of the PTFE layer on charge collector, Al [45]. A photograph of the as-fabricated PMLL-TENG is shown in Figure 1b. A cycle of electricity generation process (Figure 1c) and potential distribution by COMSOL is schematically illustrated in Figure 1d (the angle between connector and acrylic sheet ranges from 0° to 30° in a cycle). With an external vibration source, the PMLL-TENG acts as an electron pump that drives electrons back and forth between charge collectors. Figure 2a, b shows the output performance of PMLL-TENG, and the peak open circuit voltage V_{oc} and short circuit current I_{sc} of one unit of the PMLL-TENG reach 793 V and 0.56 mA respectively at a vibration frequency of 3 Hz, corresponding to a peak power density of 30.8 W m^{-2} . Here, a home-made motor was used to introduce a periodical impact onto the PMLL-TENG. The Q_{tr} of one single unit reaches the highest value of $1.2 \mu\text{C}$ at a vibration frequency of 3 Hz (Figure S1). The PMLL-TENG can be applied to light up 400 commercial LEDs simultaneously as shown in Figure S2 and Video S1. In addition, the performance of simple multilayer-linkage TENG without pre-charge injection (MLL-TENG) with different number of friction layers is studied. Figure 2c shows a nearly

constant V_{oc} output of around 640 V and an increasing I_{sc} output from 16 μ A to 61 μ A for MLL-TENG with friction layer of $n = 1-4$, which is attributed to the electrically parallel connection among them, and other performance can be seen in Figure S3a-c. The I_{sc} output with a ball dropping vertically at height of 1, 5, 10, and 20 cm is shown in Figure 2d, the evolution of Q_{tr} is displayed in Figure S3d. It can be seen that the I_{sc} increases almost linearly to be 9, 46, 109, and 124 μ A as Q_{tr} . Comparison with that of MLL-TENG without pre-charge injection, several-fold performance improvement of PMLL-TENG demonstrates a successful pre-charge injection into the PTFE.

Electrochemical degradation of azo dyes has been established to be a very effective technology with the advantages of simple equipment, flexible modulation, moderate temperature operation and no sludge formation [46-49]. As discussed above and shown in Figure S4, the designed PMLL-TENG has a high performance, especially, the I_{sc} output increases with increased friction layer numbers but a constant V_{oc} . The output performance of PMLL-TENG is greatly improved from V_{oc} of 70 V and I_{sc} of 1.8 μ A [37] (insufficient for the thorough degradation of azo dye) to V_{oc} of 793 V and I_{sc} of 0.56 mA, respectively. The latter corresponds to a peak power density of 30.8 W m⁻². Such advantages of constant V_{oc} and controllable I_{sc} output of the PMLL-TENG are beneficial to more efficiently electrochemically degrade azo dyes using nature mechanical energy, even to thoroughly degrade them to CO₂. Herein, we tried the DAB degradation self-powered by PMLL-TENG in acidic condition by pre-connecting with a rectifier to ensure a constant current and voltage and the electrolytic cell to form a SPEDS (Figure 3a). Figure 3b shows the CV plots in the absence and presence of DAB, indicating no evident oxidation and reduction processes of DAB in the voltage range of -0.1 to 1.2 V vs. SCE. A discernible reduction reaction at ~0.4 V vs. SCE accompanied by oxygen evolution happens. With narrowing the voltage windows, their current densities progressively decrease and even their peaks vanish (Figures S5), suggesting that the reduction reaction at ~0.4 V vs. SCE can be ascribed to one of the active oxygen species, i.e. O[•]- and HO[•] radicals generated during oxygen evolution (Eqs. 1, 2). The similar CV curves in the absence and presence of DAB demonstrate that DAB does not involve in the direct Faradic process (Figure 3b). The active oxygen species are believed to indirectly degrade DAB [50,51], as shown in Figure 3c that DAB experiences a color change from red to colorless self-powered by PMLL-TENG. Both the characteristic absorption peak intensities decrease with increasing the degradation time. The decoloration percentage of DAB is up to 99.9 % after 800 min, as shown in Figure S6. The two bands at 316 and 516 nm

of UV-vis spectrum (above 300 nm) of DAB belong to DABHa and DABHb respectively (Eq. 3 and Figure S7) [52-56]. The progressive decoloring and UV-vis absorption fading in the visible region of DAB (Figures 3d and S6) suggest the loss of chromophoric group $-N=N-$.

To confirm the degradation mechanism, GC-MS and ^1H NMR of the degraded intermediates in D-cell are collected and displayed in Figures S8-S10. Table 1 summarizes their analysis results, from which, the degradation mechanism is tentatively proposed in Scheme 1, taking $HO^\bullet$ as active oxygen species. $HO^\bullet$ generated at the anode interface attacks the C–N single bond neighboring $-N=N-$, producing intermediate phenol (**1**) and 4-(dimethylamino)phenol (**2**) accompanied by the evolution of N_2 . In the presence of $HO^\bullet$, the intermediates **1** and **2** may further react to lead to hydroquinone (**3**) [52-56], which can further react with $HO^\bullet$ and form 1,4-benzoquinone (**4**). It is well-documented that **4** can easily react with $HO^\bullet$, resulting in aromatic ring degradation till it is thoroughly mineralized to CO_2 (Eq. 4). The literatures have already theoretically and experimentally verified that the active hydrogen species generated at the cathode interface in D-cell can induce indirect electrochemical reduction degradation of DAB to the final products, aniline and its derivatives [23,24,57,58], with which our result is well consistent (Table 1). Economically, the DAB degradation in S-cell is expected to effectively happen in terms of lower cell voltage and simple setup. Unfortunately, more toxic and hard degradable 4,4'-dihydroxybiphenyl is detected during electrochemical degradation progress in S-cell (Figure S11 and Table S1). Consequently, the electrochemical oxidation degradation is valid, preferable and feasible here in terms of the final degradation products in the anode and cathode compartments in D-cell and the ones in S-cell.

4. Conclusion

In summary, the designed linkage structure and pre-charge injection endow the PMLL-TENG with peak power density of 30.8 W m^{-2} . Such excellent performance is successfully tested to drive SPEDS of DAB to CO_2 based on the electrochemical oxidation degradation, which is confirmed by the CVs, GC-MS and ^1H NMR of the degraded intermediates. The electrochemical oxidation degradation of DAB to CO_2 in D-cell takes advantage over (1) electrochemical reduction degradation with producing the carcinogenic and hard degradable intermediates, aniline and its derivatives, and (2) electrochemical redox degradation in S-cell with forming more toxic degraded product, 4,4'-dihydroxybiphenyl. Extensive application of PMLL-TENG with multilayer-linkage structures, sustainable energy, is expected to be reasonably tailored to self-power practical electrochemical processes of wastewater treatment by harvesting vibration energy.

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Figure 1. Schematic fabrication process of the PMLL-TENG (a), a digital photograph of one single unit of the PMLL-TENG (b), a cycle of electricity generation process for illustrating the working mechanism of the PMLL-TENG (c), and simulated potential distributions of the PMLL-TENG at the open-circuit condition between two charge collectors on contact and separation (d) in a four-state cycle, showing the driving force for charge flow generated by the PMLL-TENG.

Figure 2. The V_{oc} (a) and I_{sc} (b) of the PMLL-TENG with different friction layer numbers. V_{oc} , and I_{sc} evolution of the MLL-TENG with different friction layer numbers (c), and I_{sc} evolution when a ball (260 g) drops from 1 cm to 20 cm onto the top substrate of the MLL-TENG (d).

Figure 3. (a) Schematic diagram of the PMLL-TENG-driven SPEDS, (b) CVs of the acidic electrolyte in the absence and presence of DAB, (c) the color change of DAB in the acidic electrolyte before and after the self-powered degradation by SPEDS with a vibrational frequency of 9 Hz, and (d) UV-vis spectra of DAB in the acidic electrolyte during degradation driven by SPEDS with a vibrational frequency of 9 Hz.

Scheme 1. Tentatively proposed mechanism of electrochemical oxidation degradation of DAB at the anode interface in D-cell.

Table 1. Intermediates tested by GC-MS in D-cell after 3 h, 5 h and 30 h of degradation of DAB.

Degradation time	Degradation Intermediates	
	Anode Compartment	Cathode Compartment
3 h
5 h
30 h

Graphical Abstract