

Article

Pyroelectrically Induced Pyro-Electro-Chemical Catalytic Activity of BaTiO₃ Nanofibers under Room-Temperature Cold–Hot Cycle Excitations

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Abstract: A pyro-electro-chemical catalytic dye decomposition using lead-free BaTiO₃ nanofibers was realized under room-temperature cold–hot cycle excitation (30–47 °C) with a high Rhodamine B (RhB) decomposition efficiency ~99%, which should be ascribed to the product of pyro-electric effect and electrochemical redox reaction. Furthermore, the existence of intermediate product of hydroxyl radical in pyro-electro-chemical catalytic process was also observed. There is no significant decrease in pyro-electro-chemical catalysis activity after being recycled five times. The pyro-electrically induced pyro-electro-chemical catalysis provides a high-efficient, reusable and environmentally friendly technology to remove organic pollutants from water.

Keywords: pyroelectric effect; BaTiO₃ nanofibers; pyro-electro-chemical catalysis; dye decomposition

1. Introduction

Organic dyes from printing, textile, and tanning industries are one of the most harmful pollutants in wastewater [1,2]. To decompose those organic dye pollutants, various methods have been developed, such as physical technologies, biological processes and semiconductor-based photo-catalysis. However, there still exist many defects in such technologies. Physical technologies such as adsorption on activated carbon, flocculation and reverse osmosis can only transfer dyes from liquid phase to solid phase apart from the secondary pollution problem [3–5]. Most dyes dissolved in water are stable and toxic, which creates difficulties for biological processes [6,7]. Semiconductor-based photo-catalysis using TiO₂ was widely studied, whereas it is still limited in practical application due to slow reaction rate and usage limitation [8–10]. It is necessary to develop a new environmentally friendly and efficient catalytic process.

Similar to photovoltaic effect, pyro-electric materials can convert temperature oscillation to electrical energy by pyro-electric effect with high thermal-to-electric energy conversion efficiency of 45%–55% [11,12], compared to that of photovoltaic materials (<20%) [13,14]. Therefore, analogy to classical photo-catalysis, a new catalytic process depending on the product of pyro-electric effect and electrochemical redox reaction under cold–hot cycle excitations, was designed on the basis of the principle of product effect [15], which can be called pyro-electro-chemical catalysis.

One of the most popular pyro-electric materials, BaTiO₃, was selected to realize pyro-electro-chemical catalytic dye decomposition because of its non-toxic nature and strong pyro-electric response with a pyro-electric coefficient of $\sim 1 \times 10^{-7} \text{ C}\cdot\text{cm}^{-2} \text{ K}^{-1}$ [16]. In this work, hydrothermally prepared BaTiO₃ nanofibers exhibit remarkable pyro-electro-chemical catalytic activity in dye decomposition with $\sim 99\%$ efficiency under room-temperature cold-hot cycle excitations.

2. Materials and Methods

First, 1.88 g titanium dioxide was added into 60 mL 10 M sodium hydroxide solution. Then, the mixture was sealed in 100 mL Teflon-lined stainless steel autoclave heating at 200 °C for 24 h to obtain sodium titanate (Na₂Ti₃O₇). The obtained Na₂Ti₃O₇ powder was soaked in 0.2 M aqueous hydrochloric acid solution for 4 h to obtain hydrogen titanate (H₂Ti₃O₇) nanofibers. The H₂Ti₃O₇ nanofibers were then washed with deionized (DI) water until the PH reached about 7, and subsequently dried at 80 °C for 12 h. The resultant H₂Ti₃O₇ powder was dispersed in 60 mL of 0.05 M Barium hydroxide aqueous solution to fully transfer H₂Ti₃O₇ nanofibers to BaTiO₃ nanofibers. The mixture was set in 100 mL Teflon-lined stainless steel to react at 200 °C for 2 h. The obtained precipitate was washed with ethanol and DI water before drying at 60 °C for 12 h.

To investigate the pyro-electro-chemical catalytic activity of BaTiO₃ nanofibers, dye decomposition experiments were carried out with rhodamine B (RhB) as model organic pollutant. In the process, 50 mg of as-prepared BaTiO₃ nanofibers were added into 50 mL RhB dye solution with initial concentrate of 5 mg/L. Before performing cold-hot cycle excitations, the mixture was stirred for 2 h in darkness to achieve equilibrium adsorption. Then, after finishing the physical absorption in advance, the solution was put into a glass beaker placed in the water bath container for pyro-electro-chemical catalysis experiment. The temperature variation (30–47 °C) was applied via water bath container with a slow magnetic stirring (RCT-B-S25, IKA, Königswinter, Germany) in a dark environment to avoid photo-degradation. At regular intervals, 3 mL of solution sample was collected and centrifuged to determine RhB concentration using a U-3900 UV-Vis spectrophotometer (Hitachi, Tokoy, Japan). For comparison purposes, decomposition experiment without BaTiO₃ nanofibers was thus carried out.

Radical trapping experiment was performed to explore the mechanism of pyro-electro-chemical catalysis. The hydroxyl (•OH) radicals were detected via fluorescence method employing terephthalic acid for selectively reaction with the generated •OH radicals to produce 2-hydroxyterephthalic acid, which can be detected via a fluorescence spectrometer [17]. Fifty mg of BaTiO₃ nanofibers was added into 50 mL, 1 mM of terephthalic acid and NaOH solution to perform the same cold-hot cycle excitations. At regular intervals, 3 mL of mixture was collected and centrifuged to determine the concentration of •OH radicals.

To determine the reusability of the as-prepared BaTiO₃ nanofibers, dye decomposition experiment was repeated five times. After performing 72 cold-hot cycle excitations, the mixture was centrifuged to separate out BaTiO₃ nanofibers. Then, the obtained nanopowder was washed with DI water and dried at 70 °C for 4 h for the next recycling utilization.

The structure of BaTiO₃ nanofibers was investigated using an X-ray diffractometer (PW3040/60, Philips, Eindhoven, the Netherlands). Scanning electron microscopy (S-4800, Hitachi, Tokyo, Japan) was applied to characterize the surface morphology of the as-prepared nanopowder. Pyro-electro-chemical dye decomposition results were investigated through absorption spectra using a UV-Vis spectrophotometer (U-3900, Hitachi, Tokoy, Japan). Fluorescence spectra were obtained via a fluorescence spectrometer (F-4500, Hitachi, Tokoy, Japan).

3. Results

The X-ray diffraction (XRD) pattern of the as-prepared nanopowder is shown in Figure 1. The XRD pattern displays strong peak intensity, which means high crystallites of the as-prepared powder. It can be seen that this XRD pattern can be indexed to the pure tetragonal phase of BaTiO₃ (JCPDS, 05-0526) having no other impurity peaks.

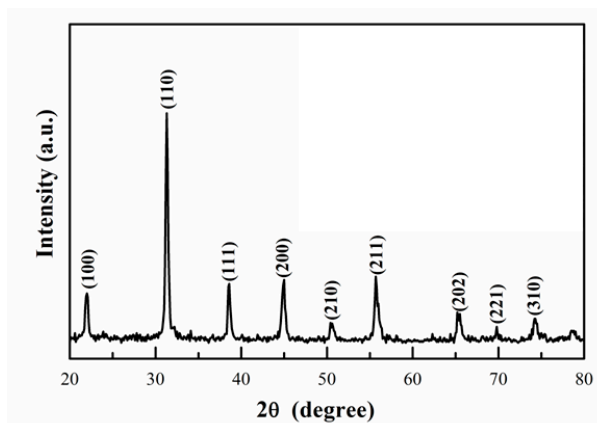


Figure 1. The X-ray diffraction pattern of BaTiO₃ nanofibers.

Figure 2 is the scanning electron microscope (SEM) result of BaTiO₃ nanofibers, which has an average diameter of 200 nm and an aspect ratio of ~50.

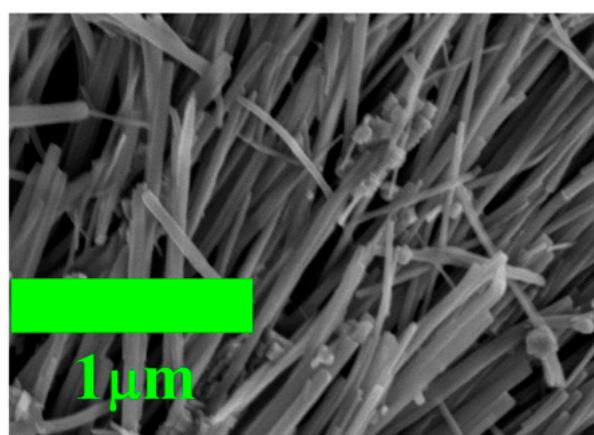


Figure 2. The scanning electron microscope image of BaTiO₃ nanofibers.

Our pyro-electro-chemical catalysis is originated from the ferro-/pyroelectric effect. In general, the ferro-/piezoelectric performance of the aligned nanofiber ferroelectric arrays can be characterized through Piezoresponse Force Microscopy (PFM) [18–20]. However, unlike arrays, our as-prepared BaTiO₃ nanofiber powders are orderless. It is difficult to directly measure ferro-/piezoelectric performance. During the growth, the sub-crystal grows in a certain crystallographic direction and the resultant as-prepared pyroelectric nanofibers are in single-crystalline form [21–23], which means that the electric dipoles that exist in pyroelectric nanofibers are monotonous. Therefore, hydrothermally prepared pyroelectric nanofibers behave as ferro-/pyroelectric effect without undergoing poling process [24]. It has been reported that BaTiO₃ nanofiber has a high piezoelectric coefficient (d_{33}) of ~45 pC/N [16,25].

Figure 3 shows the temperature curve of one cold-hot cycle excitation. Every cold-hot cycle includes 5 min heating time, 5 min cooling time and 5 min hot/cold temperature keeping time.

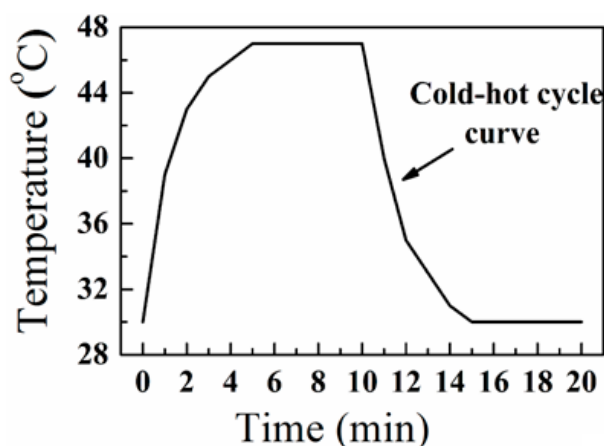


Figure 3. The temperature curve of a single cold-hot cycle excitation.

In pyro-electro-catalysis, the pyroelectrically induced electric potential difference between the anode and cathode is critical for electrochemical catalytic process and the necessary potential difference is thermodynamically at least 1.7 V and 1.9 V for the generation of $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ radicals, respectively [26,27]. Both the temperature alternation range and the size of pyroelectric particle can affect the output electric potential. In general, the pyroelectric BaTiO_3 nanofiber with $\sim\mu\text{m}$ length can generate 0.4 V for 1 °C temperature change [28]. In our experiment, cold-hot cycle excitation range varies from 30 to 47 °C. Therefore, the estimated electric potential (~ 6.8 V) is enough to drive our pyro-electro-chemical catalysis. Generally, the size of nano-catalyst materials will obviously influence the catalytic oxidation degradation efficiency [29]. Decreasing the sizes of nano-material is helpful for electric charges' quick migration between catalyst and pollutants, resulting in a high degradation efficiency. However, taking the lowest electric potential demand for generation of some strong oxidation actives into account, it is better to adopt pyroelectric nanofibers, not nanoparticles, to design pyro-electro-chemical catalysis.

The adsorption spectra of RhB are shown in Figure 4. The adsorption peak intensity decreases continuously with the increasing cold-hot cycle times, which results in the decreases of RhB concentration. After performing 72 cold-hot cycle excitations, the adsorption peak disappears.

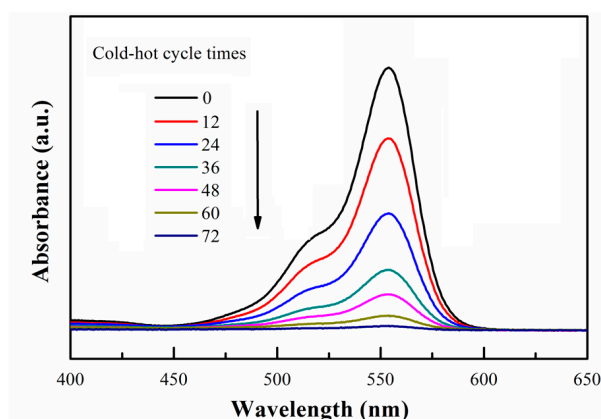


Figure 4. The adsorption spectra of RhB after performing different numbers of cold-hot cycle excitations.

The principle of pyro-electro-chemical catalysis can be described as in Figure 5: With temperature gradient (ΔT), pyro-electric materials have the ability to achieve thermal-to-electric conversion. In pyro-electric material, the spontaneous polarization (P_s) dipole moment is non-zero, which results in the existence of bound polarization charges in the two opposite sides of the inner surface. When the temperature comes to a constant, the bound polarization charges are shielded by these equal and opposite absorbed charges on the surface of pyro-electric material; the result is electrically neutral [30]. When pyro-electric material is heated, the P_s density decreases as dipole

moments begin to lose their orientation. Charge compensation occurs to balance the extra absorbed charges on the surface caused by the decrease of the P_s density [31], which results in the formation of $\bullet\text{O}_2^-$ radicals. When pyro-electric material is cooled, the negative temperature gradient leads to an increase in P_s density as dipole moments begin to regain their orientation, which causes the charges adsorption and the generation of $\bullet\text{OH}$ radicals on the surface. Chain reactions of those strong oxidative $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals occur to decompose the dye solution [32]. Based on the mechanism analysis, the chemical equations describing the pyro-electro-chemical dye decomposition can be drawn as:

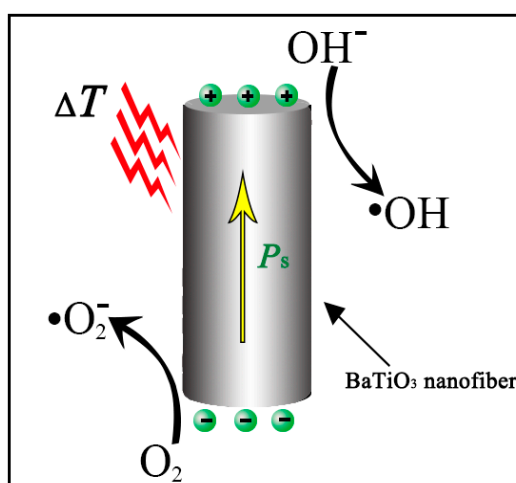
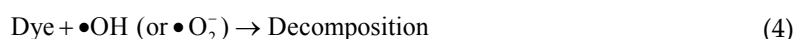


Figure 5. The principle scheme of pyro-electro-chemical catalysis of pyroelectric materials under thermal cycle excitations.

Figure 6 shows the RhB decomposition results with and without BaTiO₃ nanofibers under cold-hot cycle excitations. The decomposition efficiency (D) can be calculated as:

$$D = \frac{C_0 - C_t}{C_0} \times 100\% \quad (5)$$

where C_0 and C_t are the initial concentration and actual concentration of RhB after performing different cold-hot cycle excitations, respectively. It can be observed that BaTiO₃ nanofibers possess a remarkable pyro-electro-chemical catalytic effect in RhB decomposition with a high efficiency of ~99% after performing 72 cold-hot cycle excitations. The inset in Figure 6 shows the photograph of RhB solutions after different cold-hot cycle times. The color of RhB fades with the increasing cold-hot cycle times and finally disappeared after 72 cold-hot cycle times, which indicates the accomplishment of RhB decomposition. However, the RhB concentration changed slightly without BaTiO₃ nanofibers under cold-hot cycle excitations. These dye decomposition experimental results demonstrate that the pyro-electro-chemical catalysis should be ascribed to the pyro-electric effect of BaTiO₃ nanofibers, not the pyrolysis of organic dye occurring at high temperatures of 400–1000 °C [33]. Besides pyro-electric materials, cold-hot cycle excitations are also necessary for the achievement of pyro-electro-chemical catalysis. In general, the pyro-electric coefficient ($\alpha = \partial P_s / \partial T$) may be described as a change in the P_s with temperature. The pyro-electric effect is thus related to temperature variation, which means that without

cold-hot cycle excitations, it is difficult to realize pyro-electro-chemical catalysis of pyro-electric materials.

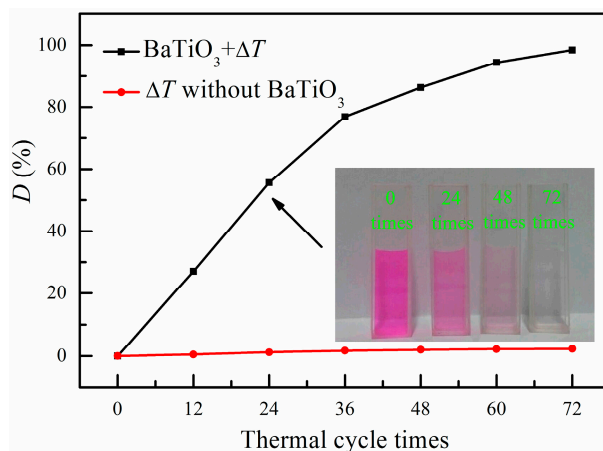


Figure 6. The decomposition efficiency of RhB with or without BaTiO₃ nanofibers. The inset is the degradation photograph.

To further investigate the role of pyro-electro-chemical catalysis, radical trapping experiment was carried out using terephthalic acid as •OH radical agent. Figure 7 shows fluorescence spectra of terephthalic acid solution after performing different times of cold-hot cycle under an excitation wavelength of 315 nm. Remarkable characteristic fluorescence emission peak signals of 2-hydroxyterephthalic acid are observed after performing cold-hot cycle excitations, which is a result of the selective reaction between terephthalic acid and •OH radicals. The intensity of characteristic peaks at ~425 nm increases almost linearly with the thermal cycles as shown in the inset of Figure 7, suggesting •OH stable production during the pyro-electro-catalytic RhB dye decomposition.

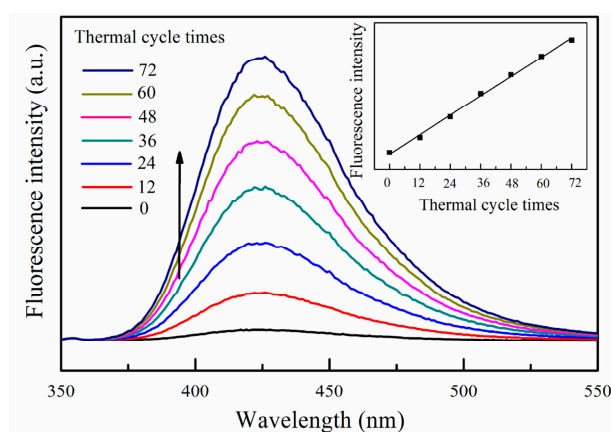


Figure 7. Fluorescence spectra for •OH trapping. The inset is fluorescence intensity peaked at 425 nm against the thermal cycle times.

In general, thermal cycle times can affect the decomposition efficiency D . With the increase of thermal cycle times, the generation of electric charges also increases, resulting in the increase of the number of strong oxidizing hydroxyl and the increase of D as shown in Figure 7. The volume of wastewater or the content of catalyst can also affect the decomposition efficiency D . Our pyro-electro-chemical catalysis is the product of pyroelectric effect and electrochemical redox reaction. Being similar to photo-catalysis, volume of wastewater mainly affects the electrochemical redox reaction of the pyro-electro-chemical catalysis process. In theory, the dependence of volume of wastewater on dye decomposition efficiency in pyro-electro-chemical catalysis should have a similar trend with that in photo-catalysis. In general, D will decrease for the excess volume of wastewater, which has been widely reported [34,35].

To investigate the reusability and stability of pyro-electro-chemical catalysis in our as-prepared BaTiO₃ pyroelectric fibers, a recycling utilization experiment testing pyro-electro-catalytic RhB decomposition ability of the as-prepared BaTiO₃ nanofibers was performed as shown in Figure 8. It can be observed that BaTiO₃ nanofibers exhibit little reduced pyro-electro-catalytic activity in dye decomposition with a reduced efficiency of ~3% after being recycled for five dye decomposition experiments, which means that BaTiO₃ nanofibers can be repeatedly heated and cooled without losing too much catalytic activity. It reveals the outstanding recyclability and stability of BaTiO₃ nanofibers, which is beneficial for its long-term use in decomposition of organic pollutants.

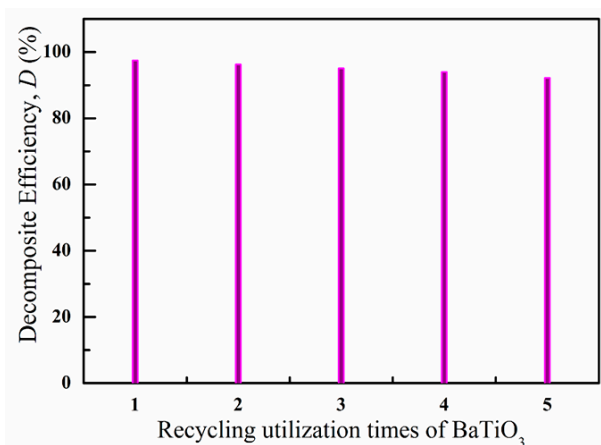


Figure 8. Recycling utilization of pyro-electro-catalytic BaTiO₃ nanofibers.

4. Conclusions

In this work, pyro-electro-chemical dye decomposition using hydrothermally prepared BaTiO₃ nanofibers has been achieved. The decomposition is high, up to ~99% within 72 cold-hot cycle excitations. The intermediate product of the pyro-electro-chemical catalysis was detected by radical trapping experiment. There is no significant decrease in pyro-electro-chemical catalysis activity after being recycled five times. The pyro-electro-chemical catalysis using lead-free BaTiO₃ nanofibers offers a high-efficient, reusable and environmentally friendly technology to decompose organic dye.

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Author Contributions: Yanmin Jia and Zheng Wu conceived and designed the experiments; Yuntao Xia and Xiaoli Xu performed the pyro-electro-chemical catalytic experiments and recycling performance; Zichen Han and Huilin You measured the XRD and SEM; Ge Bai and Liwei Wang measured the strong oxidation actives; Muhammad Ismail described the physical mechanism of pyro-electro-chemical catalysis of pyroelectric nanofibers. Weiqi Qian and Yuanling Hong analyzed the data; Yuntao Xia wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; and in the decision to publish the results.

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