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Thermo-electrochemical coupling for room temperature thermocatalysis in pyroelectric ZnO nanorods

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ABSTRACT

A strong thermo-electrochemical coupling in solvothermally-synthesized ZnO nanorods is achieved by combining pyroelectric effects and electrochemical oxidation, and is employed for room temperature thermocatalysis. Under 22–62 °C heating–cooling cycles, ZnO nanorods are shown to possess high thermocatalytic activity for Rhodamine B, resulting in ~98.15% decomposition. The active species are shown to be hydroxyl and superoxide radicals generated from the reaction between pyroelectrically-induced charges and the hydroxyl ions/oxygen gas in solution. After being recycled six times, the ZnO shows no decrease in thermocatalytic activity. Thermocatalysis offers a non-toxic, highly efficient, recyclable approach for utilization of thermal energy at room temperature.

1. Introduction

Photocatalysis has attracted substantial interest in the research community for > 50 years due to its potential application in dye wastewater purification [1,2]. However, there are some important factors that prohibit commercial application of photocatalytic decomposition, including low efficiency of solar energy use, lack of response in the dark, and failure to penetrate deeply colored or turbid dye wastewater due to their poor transmission of light [3–5]. It is therefore necessary to develop new environmentally friendly methods for treatment of pollutants. Like sunlight, environmental temperature fluctuations can be considered as a naturally occurring source of energy. It would be highly desirable to design thermocatalysts to harness this thermal energy. Some thermocatalysts based on the pyrolysis of organic materials at > 400 °C have been reported, but there are few reports of room temperature thermocatalysis [6].

In photocatalysis, the generation of electron–hole pairs upon irradiation promotes the formation of powerful oxidizing agents on the surface of the catalyst that favour the decomposition of organic compounds and pollutants [2–5]. In general, thermoelectric or pyroelectric materials are able to convert thermal energy to electrical energy and can also create positive and negative electric charges (q^+ and q^-) [7,8], which it is hoped will generate strong oxidant active species, resulting in thermocatalytic decomposition of dyes. Thermoelectric materials produce a voltage when there is a different temperature on each side of the material. However, it is difficult to maintain such a temperature difference at the nanoscale [7,8]. Pyroelectricity is the ability of pyroelectric materials to generate an electrical potential when there is an external temperature change. Thus pyroelectric materials are more suitable for use as thermocatalysts than thermoelectric materials. Moreover, pyroelectric conversion efficiency (> 40%) [8,9] is much higher than the photovoltaic conversion efficiency of photocatalysts.

ZnO has been extensively used in a range of applications including photocatalysis, piezoelectric nano-generators and pyroelectric sensors. Hexagonal wurtzite ZnO possesses a pyroelectric coefficient of $\sim -9.4\ \mu C\cdot m^{-2}\cdot K^{-1}$, a relative permittivity of ~11 and a Curie temperature of ~127 °C [10–13].

In this work we achieved a strong thermo-electrochemical effect in pyroelectric ZnO nanorods by thermal cycling between 22 °C and 62 °C, the resulting thermocatalysis producing ~98.15% decomposition of Rhodamine B (RhB) solution.

2. Experimental

All the chemicals from commercial sources were reagent grade. ZnO nanorods were synthesized via a solvothermal method [14]. 1.1 g $Zn(CH_3COO)_2\cdot 2H_2O$ and 4.0 g NaOH were dissolved in 30 mL CH_3CH_2OH and 7.5 mL PEG400. The mixed solution was then transferred into a 50 mL Teflon-lined stainless steel autoclave and heated in an oven at 120 °C for 12 h. Finally ZnO was obtained and rinsed several times

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alternately with absolute ethanol and deionized water.

X-ray diffraction (XRD) was carried out using a Philips PW3040/60 analyzer. Scanning electron microscopy (SEM) was performed using a Phenom ProX desktop analyzer. The thermocatalytic effect was evaluated by studying the absorbance change at $\lambda_{max} = 554$ nm of RhB using a Hitachi U-3900 UV–vis spectrophotometer.

In the thermocatalytic experiment, 0.1 g ZnO nanorods were suspended in 50 mL RhB solution (5 mg/L) in a glass vessel. After the adsorption–desorption equilibrium had been established, thermal cycling between 22 °C and 62 °C was carried out. In general, temperature change can be provided via conduction, convection or radiation. In this work the mixture of ZnO and dye solution was heated or cooled in a water bath with mechanical stirring in the absence of light. The temperature was monitored using a thermometer placed in the middle of the solution. Every 3 cycles, 3 mL of RhB solution was extracted for absorbance spectra measurement. Terephthalic acid solution was employed for $\cdot$OH trapping and its photoluminescence (PL) was measured on a FLS920 spectrofluorometer with an excitation wavelength of 315 nm [15].

3. Results and discussion

The XRD patterns of the solvothermally synthesized ZnO are shown in Fig. 1. All of the peaks can be indexed to hexagonal ZnO (JCPDS No. 36-1451) [16], with no impurity peaks detected. An SEM image of the ZnO nanorods, which have an average length of ~4 µm and an average diameter of ~300 nm, is shown in the inset of Fig. 1.

Spontaneous polarization (P_s) of ZnO induces bound polarization charges in the material with equivalent compensating charges on the surface [11–13]. For a given temperature change (ΔT), the induced electric potential (V) can be expressed as follows [17]:

$$V = (p \cdot h \cdot \Delta T)/(\varepsilon^{T}{}_{33} \cdot \varepsilon_0) \tag{1}$$

where the pyroelectric coefficient p is defined as the change in P_s with temperature (T) ($p = \partial P_s/\partial T$). ΔT, h, $\varepsilon^{T}{}_{33}$ and ε_0 represent temperature change, particle size, and relative and vacuum permittivity, respectively. Thermodynamically, the oxidation potentials of $\cdot O_2{}^-$ and $\cdot$OH are respectively at least ~1.9 V and ~1.7 V [2–5]. Knowing the values of the pyroelectric coefficient and relative permittivity of ZnO (see Section 1), Eq. (1) can be used to calculate the length of the ZnO rod required to generate sufficient V to induce $\cdot O_2{}^-$ and $\cdot$OH for a 40 °C temperature variation. The required size is evaluated as > 0.44 µm. Therefore our ZnO rods with an average length of ~4 µm should be suitable for thermocatalysis.

Fig. 2 shows a schematic mechanism for pyroelectrically-induced thermocatalysis. At thermodynamic equilibrium ($\Delta T = 0$), the compensating charges on the surface completely screen the polarization charges, as shown in (I) [18]. When ZnO is heated, as shown in (II), the polarization density decreases ($\Delta P_s < 0$) and ZnO has uncompensated electric charges on its surface, which can be expressed as follows:

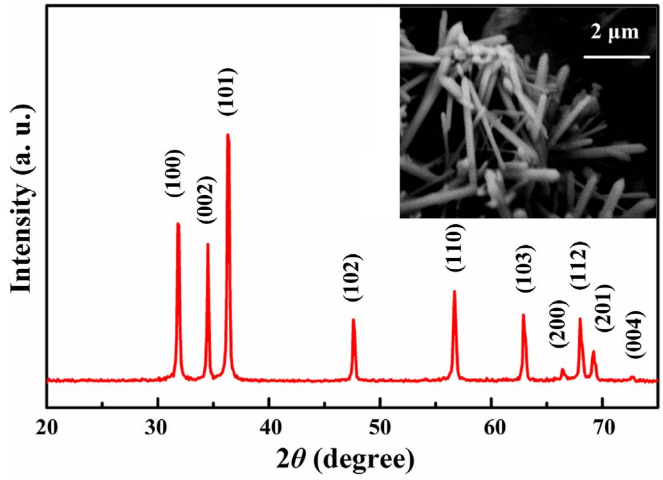

Fig. 1. XRD pattern of solvothermally synthesized ZnO. Inset: SEM image.

$$\mathrm{ZnO} \xrightarrow{\Delta T} \mathrm{ZnO} + q^+ + q^- \tag{2}$$

Meanwhile OH^- and O_2 in solution participate in charge compensation to balance the extra electric charges on the surface [19]. Positive charges q^+ in solution can produce $\cdot$OH [19,20] according to the following reaction:

$$OH^- + q^+ \rightarrow {}^{\bullet}OH \tag{3}$$

Similarly, negative charges q^- in solution can produce $\cdot O_2{}^-$ by the following reaction [19,21]:

$$O_2 + q^- \rightarrow {}^{\bullet}O_2{}^- \tag{4}$$

Strongly oxidative $\cdot O_2{}^-$ and $\cdot$OH can cause decomposition of the dye with the reaction expressed as follows:

$$\text{Dye Molecules} \xrightarrow{{}^{\cdot}OH \text{ or } {}^{\cdot}O_2^-} CO_2 + H_2O \tag{5}$$

Afterwards, when the temperature stabilizes ($\Delta T = 0$), the system returns to state (I) [7–9]. When the ZnO is cooled, the polarization density increases ($\Delta P_s > 0$) and ZnO absorbs electric charges from solution as shown in (III) [13]. The process described by Eqs. (2)–(5) is repeated and the ZnO goes back to the thermodynamic equilibrium (I).

Fig. 3(a) shows the thermocatalytic decomposition of RhB solution in the presence of ZnO nanorods. As shown in the inset of Fig. 3(a), one 22–62 °C thermal cycle comprises four steps: heating for 5 min, maintaining at a constant temperature for 5 min, then cooling for 5 min and again maintaining at a constant temperature for 5 min. It can be seen from Fig. 3(a) that the 554 nm absorbance peak of RhB gradually decreases before finally disappearing after 27 cycles, indicating nearly complete decomposition of the RhB dye solution. The decomposition ratio (D) can be expressed by Eq. (6):

$$D = (1\text{–}A/A_0) \times 100\% \tag{6}$$

where A and A_0 are the measured absorbance and the initial absorbance of RhB, respectively. The dependence of D on the number of thermal cycles is shown in Fig. 3(b), where it can be seen that D is ~98.15% after 27 cycles. No direct decomposition of RhB is observed under alternating cold–hot conditions. The inset of Fig. 3(b) is a photograph illustrating the thermocatalytic decomposition of the dye after different numbers of thermal cycles. The solution initially appears pink, but the color gradually fades as the number of thermal cycles increases, becoming transparent after 18 thermal cycles.

In photocatalysis, photo-induced electron–hole pairs generate active species, while in thermocatalysis a temperature change ΔT induces q^+ and q^- to generate active species. The band-gap of ZnO is ~3.3 eV (UV–light region) [10]. Therefore the carriers in the thermocatalysis of ZnO are electrical charges, not electron–hole pairs. Despite the different sources of energy, photocatalysis and thermocatalysis should theoretically result in the same chemical degradation reaction with the dye.

$\cdot$OH, $\cdot O_2{}^-$ and holes have been reported to be the main active species in photocatalysis [22]. In our study, $\cdot$OH radicals are monitored using terephthalic acid. It is known that 2-hydroxyterephthalic acid readily reacts with $\cdot$OH to produce a highly fluorescent product, emitting a characteristic fluorescence at ~425 nm under 315 nm excitation [15,23]. The fluorescence spectra are shown in Fig. 4(a). The peak exhibits an increase, indicating the presence of $\cdot$OH [15,23,24]. As shown in the inset of Fig. 4(a), the peak at $\lambda_{max} = 425$ nm grows nearly linearly with the number of thermal cycles, suggesting stable generation of $\cdot$OH. Fig. 4(b) shows the decomposition ratio of RhB in the presence of p-benzoquinone (an $\cdot O_2{}^-$ scavenger) and EDTA (a hole scavenger), respectively [25]. The results shown in Fig. 4 indicate that the main active species in thermocatalysis are $\cdot$OH and $\cdot O_2{}^-$.