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ZnO based thermopower wave sources

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Exothermic chemical reactions from nitrocellulose are coupled onto thermoelectric zinc oxide (ZnO) layers to generate self-propagating thermopower waves resulting in highly oscillatory voltage output of the order of 500 mV. The peak specific power obtained from ZnO based sources is approximately 0.5 kW kg⁻¹.

The development of miniaturized power sources with efficient energy storage capabilities is still one of the greatest technological challenges. There are fundamental limits in scaling down the size of rechargeable energy sources to the micro realm and smaller dimensions. Problems such as disruption of ionic flow near electrodes and plasma discharges impede the effective size reduction for sources such as batteries and fuel cells.^{1,2} Additionally, elements such as supercapacitors are incapable of holding charges for a long time, due to their high self-discharge rates.³ The development of many fascinating applications such as “cardiac micro-defibrillators” and “smart dust” are currently hampered by lack of suitable sized power sources.⁴ Also, micro/nano-sized energy sources could potentially be used for precisely targeting cancer cells by exerting localised, highly directional pulses of energy.⁵ Hence, in order to achieve true miniaturization and the realization of the aforementioned applications, we need to look beyond the conventional methods of energy generation.

New thermopower wave-based energy sources are particularly attractive as they are capable of generating higher specific power (power-to-mass ratio) in comparison to many of the conventional sources such as batteries and fuel cells, especially at small dimensions.^{6,7} Additionally, they are capable of producing alternating currents (AC), which is desirable for practical applications unlike batteries and fuel cells that are only capable of producing direct current (DC).⁸

Chemically driven thermopower waves guided by multi-walled carbon nanotubes (MWNTs) have been shown to generate specific powers as large as 7 kW kg⁻¹.⁹ In such devices the electrically conductive MWNT core allows the transportation of free electrical carriers that are generated as a result of a large temperature gradient across the device. This temperature gradient is attained as a result of an exothermic reaction of a highly reactive solid fuel covering the MWNTs.

One of the main limitations of the MWNT based thermopower devices is the low voltage and oscillation

amplitudes. We have recently demonstrated thermopower wave generation using bismuth telluride (Bi₂Te₃) and antimony telluride (Sb₂Te₃) as the core thermoelectric materials.¹⁰ These devices produced highly oscillatory voltages (100–150 mV) and specific powers of up to 1 kW kg⁻¹. In order to make such systems practically suitable, higher output voltages are desired. In order to achieve this, materials with a high Seebeck coefficient, electrical conductivity and thermal conductivity are required. A high thermal conductivity is essential for sustaining the propagation of the thermopower waves.

Zinc oxide (ZnO), an N-type semiconducting oxide, appears as an outstanding candidate as the core thermoelectric material for thermopower based energy sources. ZnO exhibits a relatively high Seebeck coefficient (approximately –360 μ V K⁻¹ at 85 °C) which increases with temperature, a high electrical conductivity at elevated temperatures of above 300 °C (ZnO film resistance of 250 Ω at 300 °C) hence suitable for operation in thermopower wave sources), high thermal conductivity (15 W m⁻¹ K⁻¹ at 300 °C) and good chemical stability.¹¹ The temperature dependence of the Seebeck coefficient and electrical conductivity will be discussed later in the manuscript.

In this work, we show that ZnO based thermopower devices are capable of generating significantly larger voltages and oscillation amplitudes than previously reported systems utilising MWNTs, Bi₂Te₃ and Sb₂Te₃ as the core thermoelectric materials.

The ZnO films were deposited on alumina (Al₂O₃) substrates using RF magnetron sputtering (see ESI†, S1) for details). Previous work carried out on RF sputtered ZnO films shows that their resistivity can vary up to 8 orders of magnitude depending on the sputtering power and the substrate temperature.¹² Consequently, in this work we used a high sputtering power (160 W) and no substrate heating in order to synthesise crystalline and electrically conductive ZnO thin films (~1.2 μ m). Nitrocellulose [C₆H₈(NO₂)₂O₅] was used as the fuel, due to its large enthalpy of reaction (4.75×10⁶ J kg⁻¹).¹³ Sodium azide (NaN₃) in aqueous solution (50 mg mL⁻¹) was then added to serve as a primary igniter to lower activation energy (40 kJ mol⁻¹ for NaN₃, compared to 110–150 kJ mol⁻¹ for nitrocellulose, (see ESI†, S1). A schematic of the fuel/ZnO/Al₂O₃ is shown in Figure 1.

Fig. 1 Schematic of a fuel/ZnO/Al₂O₃ thermopower wave generation system (not to scale).

Ignition was initiated at one end using a blow torch with a fine tip resulting in self-propagating reaction waves that travels at a rapid pace to the opposite end.^{9,10} This accelerated reaction wave entrains a simultaneous wave of electrical carriers resulting in an oscillatory voltage output.

The optical photos of the samples before and after the reaction are shown in Figure 2a. A typical thermopower voltage signal obtained across a sample of the fuel/ZnO/Al₂O₃ system is shown in Figure 2b. The voltage profile exhibits two distinct regions: an initial phase during the wave propagation and a cooling down phase until the temperature across the ZnO film reaches equilibrium. The initial reaction phase is a region of rising voltage as the wavefront spreads across the sample until all the combustion fuel is consumed. This is followed by a region of exponential decay. The moving temperature gradient results in voltages with peak magnitudes of up to 500 mV and oscillations with peak-to-peak amplitude of up to 400 mV. The power obtained from these devices can be as large as 1 mW (see ESI†, S2&S3).

We have previously adapted the theory of combustion waves to describe coupled thermal waves in fuel/Bi₂Te₃/Al₂O₃ and fuel/Sb₂Te₃/Al₂O₃ systems.¹⁰ Using the model presented by Mercer *et al.* and McIntosh *et al.* we were able to predict the oscillatory behaviour and the propagation velocity of the thermopower waves.¹⁴ The theoretical analysis concluded that the oscillatory behaviour and wave front velocities strongly depend on the thermal conductivity. A change in thermal conductivity affects the heat loss parameters of the system. It was demonstrated that a higher thermal conductivity enhances the heat transfer through the thermoelectric core, resulting in a proportional increase in combustion velocities. Consequently, Sb₂Te₃ based systems exhibited combustion velocities that were almost 2.5 times faster than the Bi₂Te₃ based devices reflecting the difference in the thermal conductivities of the two materials.^{10b}

Hence, based on the aforementioned analysis we expect that a higher thermal conductivity of ZnO (~15.0 W m⁻¹ K⁻¹) compared to Bi₂Te₃ (1.0 W m⁻¹ K⁻¹) and Sb₂Te₃ (2.5 W m⁻¹ K⁻¹) would result in a faster wave velocity and larger oscillations. The velocity of the waves in our system was assessed using the duration in which the output voltage exists. We have previously shown that the duration of the voltage signal corresponds to the reaction wave propagation time which enables us to calculate the linear propagation velocity of the thermopower waves.¹⁰ A high thermal conductivity of the ZnO thermoelectric material provides an

Fig. 2 a) Photo of the 1. Al₂O₃ substrate, 2. ZnO deposited on Al₂O₃ substrate, 3. fuel/ZnO/Al₂O₃ sample and 4. Sample after thermopower wave propagation. b) Oscillatory thermopower voltage signal obtained using the fuel/ZnO/Al₂O₃ device. c) Reaction propagation velocities for the fuel/ZnO/Al₂O₃ thermopower systems.

extra path for heat conduction (i.e. the surface of the ZnO film) in addition to the path provided by the thermally conductive Al₂O₃ substrate. As a result, we initially expect the rate of heat conduction for ZnO-based devices to be approximately 15 times faster than Bi₂Te₃-based thermopower devices. Propagation velocities for the ZnO based devices were measured to range between 12–35 m s⁻¹ (Figure 2c) which was generally 15–25 times higher than the velocities for Sb₂Te₃ (1.2 m s⁻¹) and Bi₂Te₃ (0.4 m s⁻¹) based devices demonstrated in our previous work.¹⁰ This difference nicely corresponds to the variation in the thermal conductivities of these materials and is in excellent agreement with theoretical expectations.

We have previously shown that in a thin film thermopower system configuration, incorporating nitrocellulose as the fuel, the reaction temperature remains under 300 °C.¹⁰ As a result, we needed to estimate the Seebeck coefficient and resistance of the ZnO films within this range.

Kim *et al.* have shown that the Seebeck coefficient of ZnO increases with temperature. In their work, it has been demonstrated that the Seebeck coefficient of ZnO is approximately -300 μV K⁻¹ at 85 °C.^{11a} In our measurements the Seebeck coefficient of the ZnO films was measured to be approximately -360 μV K⁻¹ (see ESI†, S4). At 300 °C the Seebeck coefficient is expected to be approximately -500 μV K⁻¹ based on linear extrapolation.^{11a}

It has been reported that ZnO exhibits a negative temperature coefficient of resistance at temperatures up to 350 °C.¹⁵ We measured ZnO film resistance at temperatures up to 300 °C as shown in Figure 3a, which is in close agreement with the value of the temperature coefficient of resistance suggested in the work of Caillaud *et al.* (approximately -3.5 × 10⁻³ °C⁻¹).^{15a} At 300 °C the resistance was reduced to approximately 250 Ω. This is not an ideal internal impedance for a power source, however it resulted in the maximum current of the order of 2 mA in our system in a short circuit load condition.

Figure 3b illustrates the Raman spectra (indicated as '1') of the as-grown ZnO structure. The peaks observed at around 436 and 576 cm⁻¹ correspond to the E₂ (high) and the

Fig. 3 **a)** Change of resistance of ZnO film with temperature. **b)** Raman spectra of 1. ZnO film, 2. Nitrocellulose coated ZnO film (■ peak denotes strong NO₂ bonds, ♦ denotes strong C–H bonds), 3. After the reaction (■ peak denotes carbon). **c)** SEM micrograph of ZnO film, **d)** XRD pattern of 1. Al₂O₃ substrate, 2. ZnO before thermopower wave propagation, 3. after adding nitrocellulose and 4. after thermopower wave propagation.

dominant A₁ (LO) modes, respectively. The E₂ (high) is a characteristic mode of the ZnO hexagonal wurtzite type lattice.¹⁶ The Raman peaks after the deposition of nitrocellulose (spectrum ‘2’ in Figure 3b) shows the presence of strong C–H and NO₂ bonds.¹⁷ After the thermopower wave propagation the C–H and NO₂ bonds disappear, while carbon peaks appear on the Raman spectra (spectrum ‘3’ in Figure 3b). The exothermic reaction causes the C–H bonds to decompose, while carbon is left behind as the residual product (see ESI†, S5).

The SEM image (Figure 3c) shows that the ZnO film is composed of crystals of varying sizes (250 nm to 1 μm). The roughness of the ZnO films was determined to be approximately 250 nm using atomic force microscopy (AFM). (see ESI†, S6). The X-ray diffraction (XRD) pattern Figure 3d reveals that the ZnO films are highly crystalline with a strong *c*-directional (002) preferred orientation. Addition of nitrocellulose results in an acute reduction in intensity of the 25.3° 2θ Al₂O₃ substrate peak. This is because the 25.3° 2θ Al₂O₃ substrate peak lies in the same region as the principal XRD reflections for nitrocellulose (ICDD No. 03-0114). A general decrease in diffraction intensity due to the nitrocellulose coating inhibiting X-ray penetration is observed.^{10b} The XRD pattern following thermopower wave propagation shows strong ZnO peaks (Figure 3d) verifying that ZnO remained largely intact at the end of the process.

We have demonstrated that ZnO is excellent for application as a core material for thermopower waves’ based energy sources as it exhibits a high Seebeck coefficient (–360 μV K^{–1}), electrical conductivity (250 Ω resistance at 300 °C), and thermal conductivity (15 W m^{–1} K^{–1}).^{11a} The aforementioned properties of ZnO resulted in a highly oscillatory voltage output of the order of 500 mV and peak current of the order of 2 mA.

We have experimentally investigated the coupling of an exothermic reaction from a solid fuel (combination of nitrocellulose and sodium azide) to ZnO layers in order to generate output power at high rates (up to 0.5 kW kg^{–1}). Additionally, the amplitude of the maximum output voltage was at least 300% higher than previously reported thermopower wave systems based on MWNTs, Bi₂Te₃ and Sb₂Te₃.^{9,10} The efficiency

of the ZnO based devices is still under 0.2%. However, these sources are capable of delivering large energy pulses (up to 0.5 kW/kg) in very short durations (typically in 1.5 to 80 ms). Certainly further work is required in order to improve the efficiency. However, by demonstrating the generation of high amplitude alternating voltages (up to 500 mV), our work shows a significant improvement in the performance of thermopower wave systems, which will potentially allow their application as a new class of micro-power sources.

†Electronic supplementary information (ESI) available: Experimental details and additional supporting results. See DOI:

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