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Green Synthesised Silver Nanocomposite for Thermoregulating E-Textiles †

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Abstract: Personal thermal management devices provide a behaviourally aligned route to address dependence on energy-intensive heating and cooling systems. E-textiles form an ideal foundation for these devices. In this study, a Joule heating e-textile has been developed using green synthesised silver nanoparticles and polypyrrole, which can easily be dip-coated onto an environmentally benign linen fabric. A Plackett–Burman design was used to optimise the nanoparticle synthesis. Characterisation and electrothermal analysis were carried out to confirm the successful synthesis of silver nanoparticles (40–80 nm, polydispersity index (pdi): 0.25) and an electrical resistance of 28.5 Ω. Joule heating of 66 °C at 6 V applied DC voltage was attained.

Keywords: e-textiles; electronic textile; silver nanoparticles; green synthesis; polypyrrole; personal thermal management (PTM); Joule heating; design of experiment (DOE); Plackett–Burman method; linen

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1. Introduction

Personal thermal management (PTM) devices are part of an emerging field of technology aimed at addressing the environmental impact of heating and cooling systems, which account for 16% of global energy consumption [1] and 40% of energy-related carbon dioxide emissions [2], whilst also improving the wearer's thermal comfort. E-textiles form an optimal foundation for PTM devices due to their concurrence with thermal comfort adaptation behaviours. Current thermoregulating textile technologies, such as phase change materials [3], provide enhanced thermal comfort, but their functionality is often restricted to when there is an elevation of body temperature. These passive technologies do not allow the user control over their thermal environment. Active thermal comfort strategies aim to overcome the limitations of passive PTM through the use of encapsulated thermistors [4–7], conductive polymers [8–10] and nanomaterials [11–14]. Most current nanomaterial PTM textile research focuses on carbonaceous compounds, which are expensive and lack the conductivity of metallic compounds. Despite the rapid increase in PTM research, to date, there has been no published research demonstrating Joule heating e-textiles based on nanofunctionalised linen fabrics using silver nanoparticle–polypyrrole composites.

Silver nanoparticles (AgNPs) are highly electrically conductive and industrially scalable [15,16]. Polypyrrole is a conjugated polymer that has been selected to enhance the electrical conductivity as well as the adhesion of silver nanoparticles to linen textiles through hydrogen bonding [17]. A linen textile was selected due to its renewability, biodegradability and low energy requirements compared with petrochemical-based textiles, as well as low water consumption compared with cotton [18,19]. Herein, this research demonstrates the development of a green synthesised AgNP–polypyrrole nanocomposite applied to linen

through a dip-coating method. Green synthesised nanoparticles commonly suffer from a lack of homogeneity and reliable production. Therefore, a Plackett–Burman design of experiment (DOE) was utilised to identify the optimum parameters for the green synthesis of AgNPs using lime peel extract. The Plackett–Burman method is economical for detecting the main effects, but two-factor interaction is confounded; therefore, it does not distinguish the effect of interactions between variables from the main effects.

2. Materials and Methods

2.1. Materials

Silver nitrate solid ($AgNO_3$) (99% titration, CAS number 7761-88-8), ferric chloride ($FeCl_3$) (CAS number 7705-08-0), pyrrole (>98% assay, CAS number 109-97-7) and sodium carbonate powder (Na_2CO_3) (99.5% assay) were purchased from Sigma-Aldrich. Distilled (DS) water and methanol were used from laboratory stock. All chemicals were received as purchased and used without further purification. Limes were purchased from a local supermarket and washed in tap water prior to use. Valencia natural even-weave linen (approx. 240 gsm) was purchased from Whaleys Bradford.

2.2. Green Synthesis of Silver Nanoparticles

Silver nanoparticles were synthesised according to a modified literature method based on the work of Pugazhenthiran et al. (2021) [20] and Dutta et al. (2020) [21]. Fresh lime peels were cut into small pieces and added to DS water (1:10 w/v) in a borosilicate flask and boiled for 20 min. The extract was then filtered using Fisherbrand filter paper (Grade 601, QL 100, 110 mm diameter). In a typical experiment, silver nitrate solution was added to a conical flask. Lime peel extract (LPE) was added to the solution dropwise using a burette. Once all LPE was added, the pH of the solution was measured and Na_2CO_3 was added to adjust the pH. Parameters were set as per the requirements for the Plackett–Burman protocol. The solution was then centrifuged for 5 min at 3000 RPM to remove any biomass, and the precipitate was discarded. The supernatant was centrifuged (1 h, 6000 RPM, DS water), and the precipitate was rinsed and centrifuged again (20 min, 6000 RPM, methanol). The precipitate was then removed and dried in oven before weighing on an analytical balance.

2.3. Plackett–Burman Optimisation of Synthesis

Minitab software [22] was used to create and analyse a 5 factor, 2 level design with 20 runs and 1 centre point was used.

2.4. In Situ Polymerisation of AgNP Pyrrole on Linen

A linen fabric (even-weave natural, 2.5 cm^2, approx. 0.17 g) was soaked in AgNP solution; then, 0.1 M pyrrole monomer solution was added. The polymerisation initiator ($AgNO_3$ 0.1 M or $FeCl_3$ 0.22 M) was next added to the solution and covered to protect it from light. The polymerisation reaction was carried out for up to 96 h.

2.5. Characterisation

AgNP formation was confirmed via UV–Vis spectroscopy (UV/Vis/NIR Spectrophotometer, Jasco V-700 series). AgNP size and polydispersity were analysed using dynamic light scattering (DLS) (Malvern Zetasizer Nano ZS). Elemental analysis was conducted using an energy dispersive X-ray fluorescence spectrometer (EDX-XRF) (Shimadzu EDX-7000 XRF). Resistance was measured using an LCR bridge (Rohde and Schwarz HM8118). Joule heating performance was tested using an FLIR thermal camera whilst the linen fabric was connected to a DC voltage supply via crocodile clips.

3. Results and Discussion

3.1. Silver Nanoparticle Morphological Analyses

AgNP synthesis was confirmed through spectral UV–Vis analysis by exhibiting the characteristic surface plasmon absorption maxima between 391 nm and 453 nm [23]. AgNPs undergo surface plasmon resonance, causing an absorption of light at higher wavelengths than non-plasmonic particles of the same size [24]. A secondary peak, or very broad peak, can be seen where AgNPs have agglomerated. As expected, many of the parameters did not form AgNPs, with broad peaks indicating agglomeration and peaks with absorption maxima at long wavelengths indicating oxidation of the silver.

The results from the 21 DOE runs were analysed through Minitab, and the response optimiser function was employed to produce a solution for optimal AgNP synthesis using LPE. AgNPs were synthesised using the Minitab solution parameters (pH $\pm$ 0.7). The resultant silver nanoparticles produced a UV–Vis peak at 420 nm with a diameter of 117 nm and a polydispersity index of 0.243 (Figure 1). The absorption maxima peak and polydispersity index were close to the predicted solution, and subsequent experiments were repeatable. However, the particle size (diameter/nm) obtained from the zeta sizer was larger than predicted. This could be due to the effect of pH on the size and addition of sodium carbonate not providing the required degree of precision, or the agglomeration of the particles during analysis. A repeat experiment would benefit from using a wider range of Na_2CO_3 solutions with different molarities to finetune the pH adjustment. The pH of the reaction directly impacts on the size and stability of AgNPs, with higher acidity syntheses tending to produce more agglomerated AgNPs [25]. The polydispersity index of 0.243 indicates a monodisperse collection of AgNPs [25].

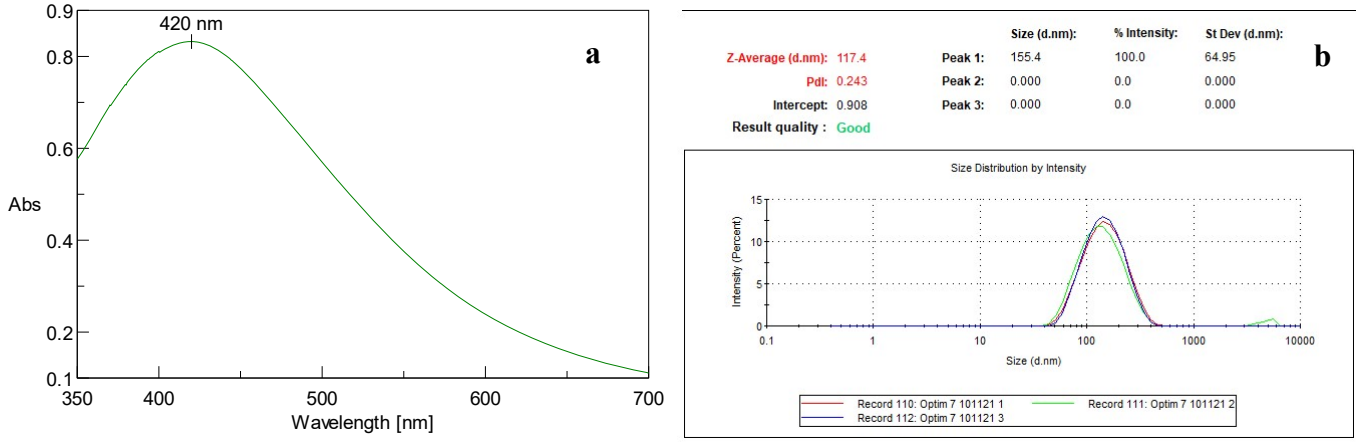

Figure 1. (**a**) UV–Vis spectra for optimised nanoparticles, (**b**) DLS analysis for optimised silver nanoparticles.

3.2. Thermoelectric Performance of Polypyrrole Silver Nanoparticle Linen

The electrical resistance of the developed polypyrrole–AgNP linen (PAL) reached a very low value of 28.5 Ω (at 1 mm thickness, this is equivalent to 285 Ω/sq.) using optimised AgNPs with 0.1 M pyrrole and 0.1 M $AgNO_3$ (PAL-$AgNO_3$-0). This is comparable to the values reported in state-of-the-art thermoregulatory nanomaterial-based e-textiles which range from 0.16 Ω/sq [12] to 1.16 $\times$ 10^4 Ω/sq [26]. Joule heating analysis revealed that PAL-$AgNO_3$-0 reached a temperature of 66 °C with 6 V applied DC voltage (Figure 2). The electrical resistance of PAL using the optimised AgNPs with 0.1 M pyrrole and 0.22 M $FeCl_3$ (PAL-$FeCl_3$-0) was 395.36 Ω, and the Joule heating performance was 28.7 °C with 6 V applied DC voltage. Polypyrrole-coated linen fabrics without AgNPs exhibited an electrical resistance of 421 Ω and reached a temperature of 24.5 °C at 6 V DC input.

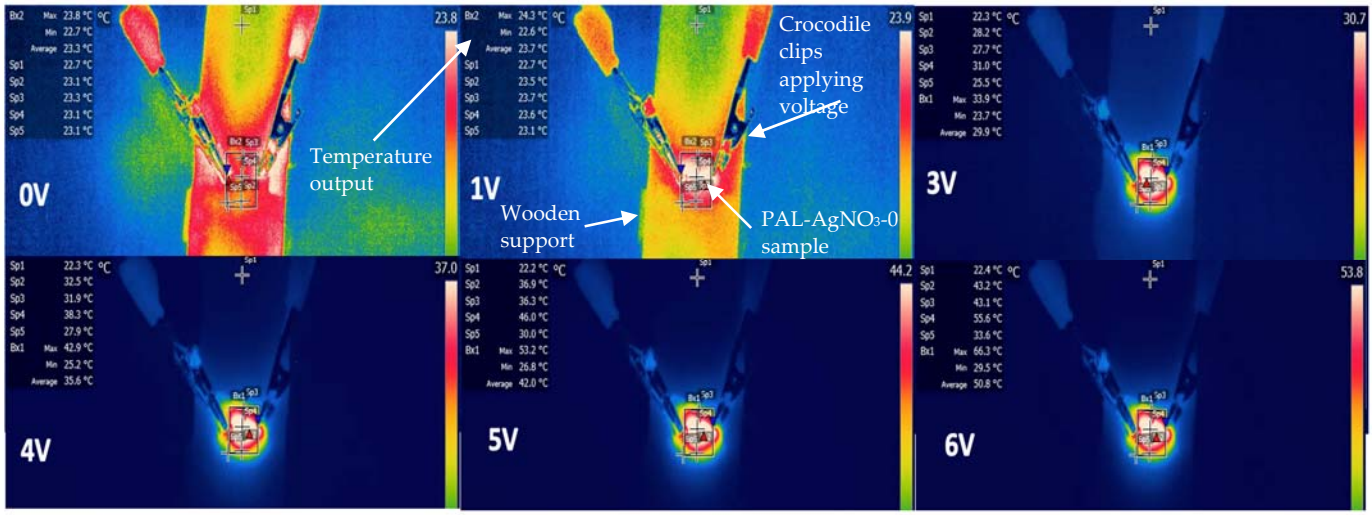

Figure 2. Thermal camera images for polypyrrole–silver nanoparticle linen at various applied voltages.

3.3. EDX-XRF Analysis

Elemental analysis for PAL-$AgNO_3$-0 revealed that the inorganic compounds present on the surface of the fabrics were traces of calcium (0.004%) and copper (0.001%), and no silver was detected. However, the electrothermal performance of PAL-$AgNO_3$-0 significantly exceeded that of polypyrrole-only linen. PAL-$FeCl_3$-0 exhibited the presence of 0.9% silver in the EDX spectra and several trace elements. Further research is under way to explore this finding.

4. Conclusions

In this study, AgNPs have been successfully synthesised using lime peel extract as the reducing agent, providing a simple and low-cost route. The synthesis has been optimised using a Plackett–Burman experimental design to identify key parameters enabling the synthesis to be tuned to reliably obtain the desired size of AgNPs. A nanocomposite was subsequently developed using the green synthesised AgNPs and polypyrrole polymerised in situ on linen fabrics to obtain a linen-based e-textile that demonstrates a low electrical resistance of 28.5 Ω and a Joule heating performance of 66 °C at 6 V applied DC voltage. Further optimisation studies are under way; future work will analyse the results of this study and investigate the temperature-dependent electrical resistance, mechanical properties, and morphology of the developed e-textiles.

Author Contributions: A.N. conceived the idea, conducted the experiments, and wrote the paper. S.R. and N.S.M. reviewed and edited the manuscript. S.R. and N.S.M. supervised and administered the project. All authors have read and agreed to the published version of the manuscript.

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