Biodegradable and conductive chitosan – graphene quantum dot nanocomposite microneedles for monitored delivery of both small and large molecular weight therapeutics

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Supplemental experimental details

Depth of microneedle penetration into skin

Microneedle arrays were inserted into full-thickness chicken skin by hand and were kept for 1 h, after which the skin was prepared for cross-sectioning by treating with ethanol for 10 min to displace water and then embedding in Labonord Q-Path paraffin embedding medium (melting temperature is 57 °C). The samples were then cross-sectioned using a microtome (Brunel bench microtome) and the cross sectioned samples were transferred to microscopy glass slides and re-heated to 57 °C to remove the embedding medium from the samples. Optical microscopy was through an optical microscope (Swift M10L, Swift Optical Instruments).

Supplemental figures

**Figure S1** Data for photoluminescence (PL) quantum yield measurements.
Figure S2 PL spectra showing the selectivity of GQD emission to the excitation wavelength.

Figure S3 Optical microscopy images of chitosan - 1 wt.% fluorescein sodium coated graphene quantum dot (GQD-FL) nanocomposite microneedle arrays that were inserted into full thickness chicken skin: (A) pristine chicken skin, (B) after the insertion of a chitosan - 1 wt.% GQD microneedle array.
Figure S4 Digital image of fluorescein sodium labelled bovine serum albumin (BSA) (~0.08 µg ml⁻¹, similar to curve 2 after 24 h in Figure 7B), showing the characteristic colour of BSA-FL and confirming the medium solutions presented in Figure 8 (after 24 h) mainly contain the BSA coated FL.

Figure S5 Optical microscopy image of microneedle arrays before and after submersion in foetal bovine serum (FBS) and subsequent air drying. By comparing the 0 h and 6 h images, the size of the microneedles remains similar after immersion showing no stability problems for the microneedles in FBS.