

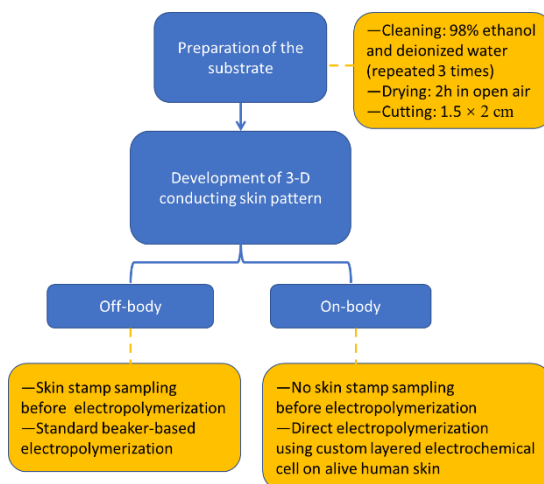
## 3-D and electrically conducting functional skin mapping for biomedical applications

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### EXPERIMENTAL

#### Preparation and characterization of 3-D electrically conducting skin patterns

The general scheme of 3-D electrically conducting skin patterns preparation is shown in **Figure S1**. Commercially available plastic-gold substrate (polyethylene terephthalate covered with gold layer (Eastman)) was cleaned with deionized water and 98% ethanol to remove any impurities (repeated 3 times) after which was dried in open air and cut into 1.5 × 2 cm pieces. Then off-body and on-body skin patterning protocols were performed. For off-body skin patterning, skin prints (sebum on gold) were obtained by simply pressing the clean plastic-gold substrate onto the untreated skin surface (skin containing natural extract, sebum).



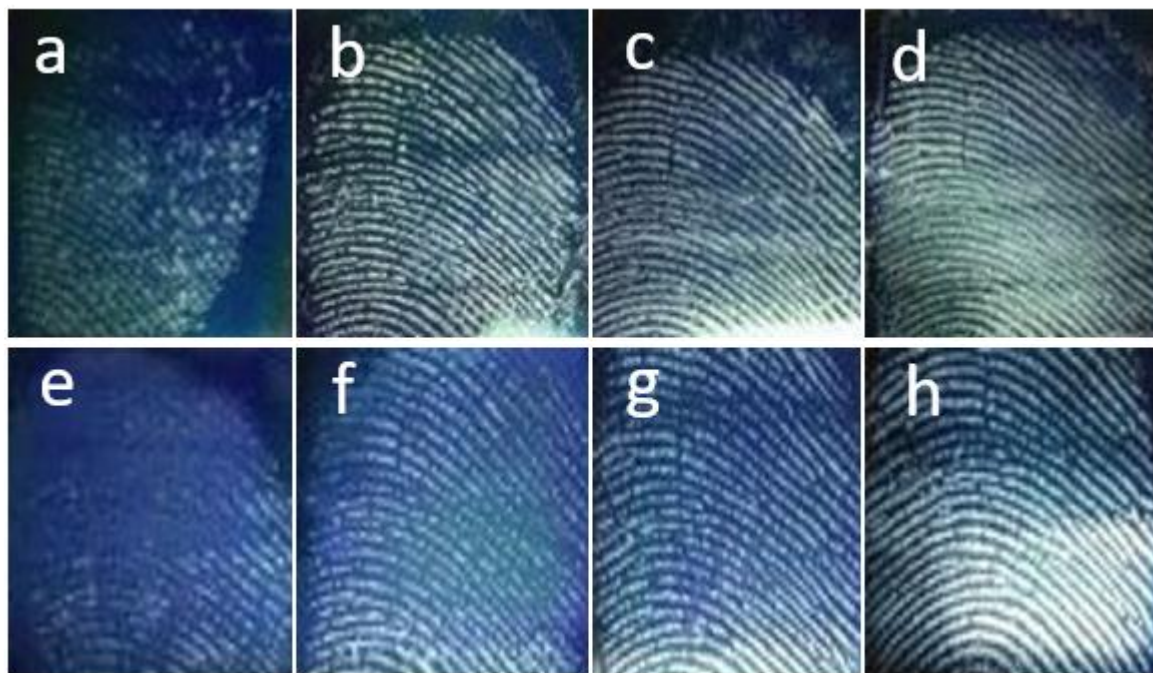
**Figure S1.** Procedure of off-body and on-body 3-D electrically conducting skin pattern development.

The stamps of the skin on gold substrates were then transferred to typical beaker-based electrochemical cell. The skin stamp on gold acted as working electrodes while platinum mesh (2 × 7 cm) served as counter electrode and an Ag/AgCl (KCl saturated) served as a reference electrode. The electropolymerization solution contained 0.03 mol dm<sup>-3</sup> 3,4-ethylenedioxythiophene (EDOT) and 0.1 mol dm<sup>-3</sup> polystyrene sulfonate (PSS) (both obtained from Sigma Aldrich). The electropolymerization was performed galvanostatically by applying a current density of 0.2 mA cm<sup>-2</sup> (in three electrode cell) to the plastic-gold substrate for the duration of 450s (for data presentation not full time range was shown). After electropolymerization the working electrode was washed with deionized water and left to dry in the open air. For off-body skin patterning, the skin print was collected just before the actual electropolymerization. The custom layered electrochemical cell (developed here for the very first time) consisting of gold substrate (working electrode), platinum mesh (counter electrode) and Ag/AgCl (KCl saturated) (reference electrode) was applied. To avoid short-circuiting and to allow electropolymerization solution retention around electrochemical cell, electrodes were separated with the layers of paper substrate (cellulose filter paper, grade 390, Sartorius, Singapore). The electrochemical cell was then placed on an untreated, alive human subject skin where clean gold surface was in direct contact with the alive skin. The reference electrode was used to press the electrochemical cell onto the skin. Detailed scheme presenting the custom layered electrochemical cell is shown in the main article, **Figure 3** (main article). The electropolymerization solution containing 0.03 mol dm<sup>-3</sup> 3,4-ethylenedioxythiophene (EDOT) and 0.1 mol dm<sup>-3</sup> polystyrene sulfonate (PSS) was spiked onto the electrochemical cell and in the area of the cell-skin direct contact. The volume

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**Figure S2** High-resolution camera pictures of off-body 3-D electrically conducting skin patters developed on Au-PET (upper row) and Pt-PET substrates (lower row) after various pressure applied between sampling substrate and the skin during the skin stamp pattern sampling, namely: 218 N cm<sup>-2</sup> (a and e), 436 N cm<sup>-2</sup> (b and f), 871 N cm<sup>-2</sup> (c and g) and 1316 N cm<sup>-2</sup> (d and h).

(3 ml) was sufficient to soak the paper substrate with electropolymerization solution as well as sufficient time was given (30 s) for the solution to reach gold | alive skin interface. The electropolymerization was performed galvanostatically by applying a current density of 0.2 mA cm<sup>-2</sup> (in three electrode cell) to the plastic-gold substrate for the duration of 450s. After electropolymerization the working electrode was washed with deionised water and left to dry in the open air. All the solutions were aqueous, prepared using deionized water. A CHI 700E series electrochemical Analyzer (Shanghai Chenshan, China) was used to electropolymerize 3-D electrically conducting skin patterns. All measurements were performed at room temperature, 22-23 °C.

The electrochemical behaviour of the different electrodes was assessed by cyclic voltammetry (CV). The measurements were performed in three electrode cell, where the 3-D electrically conducting skin pattern acted as working electrode, platinum mesh (2 × 7 cm) served as counter electrode and an Ag/AgCl (KCl saturated) served as a reference electrode. The measurements were performed in 0.1 mol dm<sup>-3</sup> KCl solution. The potential was cycled between -0.6 and 0.7 V with a scan rate of 0.1 V s<sup>-1</sup> (five cycles in total were performed, only the fifth cycle was used for graph preparation). Along with substrate surface area, CVs were used to calculate of area-based specific capacitance.

The surface morphology of the obtained 3-D electrically conducting skin patterns were investigated using high-resolution camera (Nikon D90) and a field emission scanning electron microscope (FE-SEM) (JSM-7600F, USA), while topography was studied by an atomic force microscope (AFM) (XE-Series, Park, Korea).

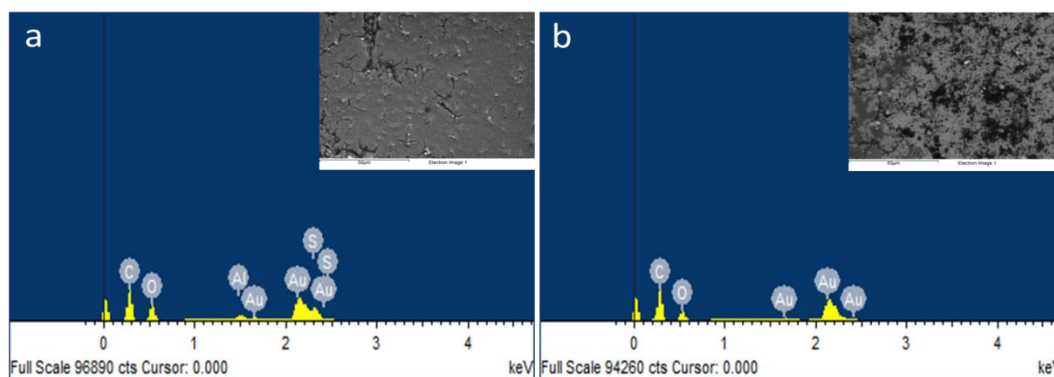
An energy dispersive X-ray spectroscopy (EDAX) was used to confirm the presence or absence of the conducting polymer in the developed 3-D electrically conducting skin patterns by investigating elemental composition of sebum and conducting polymer modified regions of 3-D skin patterns.

### Optimization of off-body 3-D electrically conducting skin patterns development

The optimization of the 3-D electrically conducting skin patterns development was performed for off-body variation of 3-D skin patterns development. The optimization process included finding the most suitable working electrode and electropolymerization conditions; skin pattern stamp sampling and sebum removal for universal skin stamp pattern sampling. The evaluation of the modification during the optimization process were evaluated using high-resolution camera (Nikon D90) and a field emission scanning electron microscope (FE-SEM) (JSM-7600F, USA).

#### *Electropolymerization conditions and choice of working electrode*

Various off-body 3-D electrically conducting skin pattern arrangements including support and the electroactive layer were investigated, namely: plastic-gold (PET-Au), plastic-platinum (PET-Pt), paper-gold (paper-Au), and paper-platinum (paper-Pt). For that, polyethylene terephthalate (PET) or paper (cellulose filter paper, grade 390, Sartorius, Singapore) were used. PET substrates were cleaned with deionized water and 98% ethanol for three times before drying in open air and cut into 1.5 × 2 cm pieces while paper substrates were



**Figure S3** EDAX elementary analysis of a conducting polymer (a) and sebum (b) modified regions of off-body 3-D electrically conducting skin patterns. Considering the procedure of off-body 3-D electrically conducting skin pattern development described in previous section, concentrations of EDOT studied were 0.1, 0.2, 0.3, 0.4 and 0.5% (by volume), while electropolymerization durations studied were 150, 300, 450, 500 and 750 s.

untreated before cutting into  $1.5 \times 2$  cm pieces. Subsequently, gold or platinum were sputtered on PET or paper using a sputter coater (JFC-1600, JEOL, Japan) with 20 mA current for 200 s that resulted in approx. 65 nm film thicknesses. The concentration of EDOT in the electropolymerization solution and duration of electropolymerization were investigated as factors influencing the quality of developed off-body 3-D electrically conducting skin.

#### *Skin pattern stamp sampling*

For off-body 3-D electrically conducting skin patterning various conditions of pressure between skin and the substrate during skin pattern stamp collection were investigated, namely: 218, 436, 871 and  $1316 \text{ N cm}^{-2}$ . The pressure of the skin-substrate contact was calculated from the mass obtained during the pressing the skin against the substrate that was placed onto the electronic balance (Mettler Toledo, Singapore). For each pressure, two different substrates were used, gold covered plastic and platinum covered plastic.

#### *Sebum removal for universal skin stamp pattern sampling*

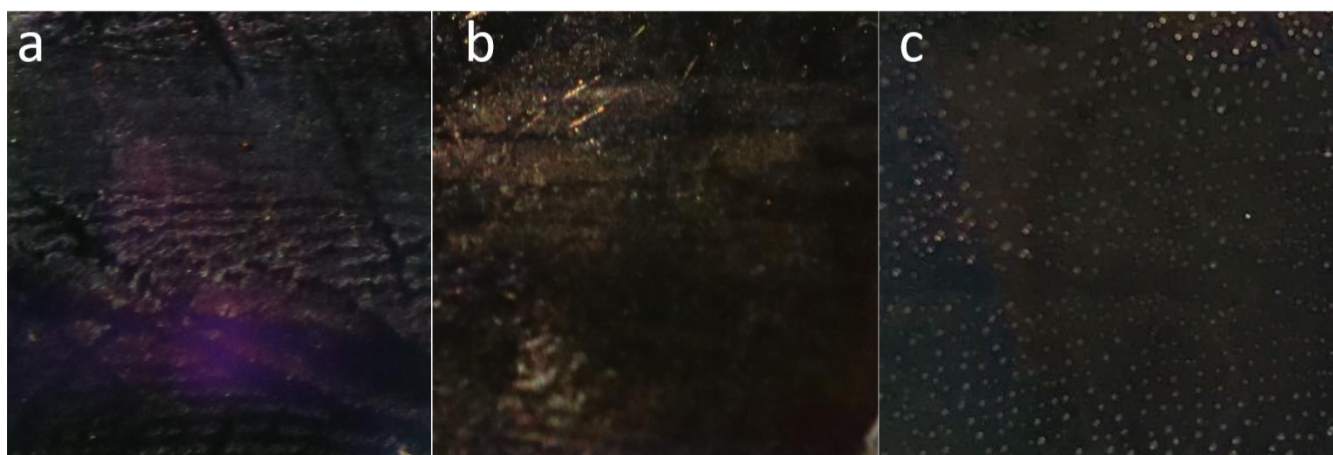
Skin pattern stamps were taken from untreated human subject skin. However, possible removal of the sebum by 98% of ethanol or skin washing with household detergent with subsequent application of oil were studied as a method to universalize the collection of the skin pattern stamp from rather unpredicted conditions of human skin and variations of person to person sebum composition.

## RESULTS AND DISCUSSION

Typically 0.1% (by volume) EDOT concentration is used during electropolymerization of PEDOT.<sup>51</sup> In our study however, owing to the application of relatively high surface of the working electrode  $1.5 \times 2$  cm the best conditions of electropolymerization were found to be when 0.3% (by volume) of EDOT in electropolymerization solution was used. Additionally, when current density of  $0.2 \text{ mA cm}^{-2}$  was applied to the working electrode the optimal duration of the electropolymerization was found to be 450 s (results not shown here). Further experiments (main article) were performed with determined optimized conditions for EDOT concentration in the electropolymerized solution and the duration of the electropolymerization.

When investigating various arrangements of the working electrodes, namely: PET-Au, PET-Pt, paper-Au and paper-Pt it was found that owing to high porosity of paper, it is not suitable to be the effective enough support for metal layer and subsequent skin pattern stamp sampling and development of clear 3-D electrically conducting skin pattern (results not shown here). On the other hand, PET was successfully applied as support for both gold and platinum layers. **Figure S2** presents a series of 3-D electrically conducting skin patterns developed on PET-Au (upper row) and PET-Pt substrates (lower row). Both, PET-Au and PET-Pt substrate were further investigated towards optimal conditions for skin pattern stamp sampling. **Figure S2** presents high-resolution camera pictures of off-body 3-D electrically conducting skin patterns developed on PET-Au and PET-Pt substrates after various pressure applied between sampling substrate and the skin during the skin stamp pattern sampling. In both cases, higher the pressure applied between the sampling surface and the skin higher the contrast between sebum and conducting polymer modified regions. Thus, the pressure of  $1316 \text{ N cm}^{-2}$  was found the most suitable for sampling the skin pattern on PET-Au and PET-Pt substrates and was applied during sampling of the skin patterns (main article).

Further on, to confirm the presence and absence of conducting polymer in the sebum and conducting polymer modified surfaces on developed off-body 3-D electrically conducting skin patterns based on PET-Au substrate, EDAX analysis was performed (**Figure S3**). PEDOT(PSS) contain relatively high concentration of sulphur, thus the signal from sulphur was indication of presence or absence of conducting polymer in the investigated regions of the 3-D electrically conducting skin patterns. Signal from sulphur was registered only in the regions where conducting polymer was electrosynthesized, while space where sebum was stamped onto the PET-Au surface were left without electropolymerised PEDOT(PSS). This confirms 3-D nature and successful selective modification of the surface corresponding to the topography of the skin that was confirmed also by AFM of the off-body 3-D electrically conducting skin patterns described in the main article.



**Figure S4** High-resolution camera pictures of sebum removal by 98% ethanol (a) and common detergent (b) and subsequent application of masking substance for universal skin stamp pattern sampling, common cooking oil (c).

Since sebum is not standardized complex bio substance, which differs from person to person.<sup>S2</sup> using PET-Au substrate, sebum removal and subsequent application of masking substance (common cooking oil) for universal skin stamp pattern sampling were investigated. High-resolution camera pictures of sebum removal by 98% ethanol and common detergent followed by application of masking substance (common cooking oil) for universal skin stamp pattern sampling is shown in **Figure S4**. The application of 98% of ethanol does not remove the sebum from human skin, leaving distorted sebum lines. On the other hand, application of the detergent removes sebum from the human skin. Subsequent application of oil on the skin for the recovery of sebum-like lines was unsuccessful as deposited oil created droplets in form of discontinued sebum lines. In this respect, although removal of sebum was performed successfully by application of detergent, the attempt to apply oil as standardized sebum-like substance for skin pattern sampling was found unsuccessful. Further optimization of sebum-like substance is needed, however, for the need of this communication untreated human sebum was applied to sample the stamp of skin pattern (applied in the main article).

## REFERENCES

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