

# Three-dimensional, high-porosity conducting skeletal structure from biodegradable microparticles with vapor-phase polymerized conformal surface layer



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## ABSTRACT

Three dimensional (3D) electric conducting porous structures are a promising platform that could be utilized in emerging 3D structural electronics, energy storage systems, and biomedical applications. A poly(3,4-ethylenedioxythiophene)/silica (PEDOT/SiO<sub>2</sub>) composite with foam-like conducting open skeletal structures and pore sizes exceeding 100 μm is presented. A two-step procedure was used to prepare this functional porous structure. First, a conformal coating layer was synthesized via vapor-phase polymerization onto a randomly sized biodegradable microparticle assembly. Vapor-phase polymerization allowed for facile coating of the nanoscale layer in a relatively short processing time (30 min). At this stage, non-invasive chemical modification can be also accomplished on the surface of microparticles that have complex surface morphology. Secondly, biodegradable microparticles were selectively removed to form a high-porosity skeletal conducting structure. The composite demonstrated structural integrity despite an unusually high porosity of greater than 96%, which was confirmed through micro-computed tomography (CT). The results show that this foam-like conducting open skeletal structure of the PEDOT/SiO<sub>2</sub> composite is a good candidate for new applications.

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## 1. Introduction

Conductive three-dimensional (3D) porous materials are becoming more important for their potential use in emerging applications [1–3]. Carbonaceous materials and conducting polymers are primary candidates for electrical conduction in a matrix. Since conducting polymers were first synthesized in the mid-1970s, they have been used in various applications such as lithium-ion batteries [4], photovoltaic devices [5], photocatalysis [6], and electrochromic devices [7] owing to their wide range of electrical conductivity and mechanical flexibility. In biomedical applications, the use of conducting polymers for electrical stimulation (conductivities from

10<sup>-4</sup> to 9 S/cm) can tune cellular activities such as cell migration [8] and cell growth [9,10]; their applications as neural probes [11], prostheses [12], and controlled release systems [13,14] have been also demonstrated. In these applications, increasing the contact surface or interface area is often an effective approach to improving the performance, which is generally achieved through interconnected three-dimensional (3D) porous and hierarchical structures. However, it is challenging to integrate high-porosity 3D structures with large pore sizes in macroscopic dimensions because of the poor mechanical properties of conducting polymers [15]. It is important to retain structural stability because such stability is related with the final performance of the 3D porous structure. For example, a free-standing structure of conducting hollow microparticles with shells composed of polyaniline nanofiber/carbon nanofibers exhibited better performance as capacitors than a structure with a collapsed morphology [16].

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the more

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successful conjugate polymers, exhibiting high stability, low bandgap, high conductivity, and transparency [17,18] at nanoscale thicknesses. In addition, it shows good biocompatibility [19], probably because its structure is similar to that of natural materials such as melanin [20]. Recently Atanasov et al. reported the fabrication of a conformal PEDOT thin film using oxidative molecular layer deposition, which showed high conductivity [21]. However, it required a high deposition temperature ( $\sim 150^\circ\text{C}$ ), which limits its use with polymer substrates that have lower glass transition or melting temperatures.

In this paper, we report the conformal coating of a nanoscale PEDOT layer onto biodegradable and biocompatible poly(D,L-lactide-co-glycolide) (PLGA) microparticles free from surfactants via vapor-phase polymerization (VPP). Further, we fabricated a 3D, high-porosity (over 96%) conductive skeletal structure based on a PEDOT/SiO<sub>2</sub> hybrid as well as PEDOT coated on a colloidal assembly.

## 2. Material and methods

### 2.1. Fabrication of microparticles

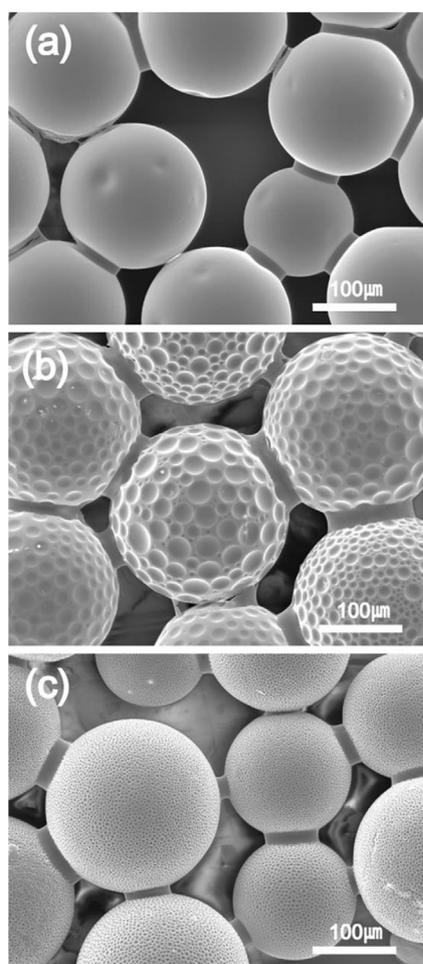
The polymers used to fabricate smooth or golf-ball-shaped microparticles were PLGA [D,L-lactide:glycolide = 65:35,  $\mu_{\text{inh}}$ : 0.55–0.75 dl g<sup>-1</sup> in hexafluoroisopropanol (HFIP), Lactel]. The polymer was dissolved in dichloromethane (DCM, 10 wt %) and

then introduced into a 1 wt % poly(vinyl alcohol) (PVA, 87–89% hydrolyzed, Mw  $\approx$  13,000 to 23,000, Aldrich) aqueous solution to form an oil-in-water emulsion under stirring. DCM in the oil phase was evaporated for 3 h under a hood at room temperature under continuous stirring. Microparticles were washed three times with double-distilled water. To fabricate golf-ball-shaped microparticles, 2-methylpentane (TCI, Japan) was dissolved in the oil phase, where the ratio of polymer to 2-methylpentane was 7:3 [22]. In this work, we used two different golf-ball-shaped microparticles with different sized dimples on the surface to obtain precise information on the coating thickness and non-invasive coating prepared by a tube-type microfluidic device, which is reported in detail in our previous paper [23]. The use of the microfluidic device provided microparticles of uniform size with bigger dimples. The difference between these microparticles and those with small dimples in a fabrication step is that oil-phase droplets exiting from the microfluidic device were placed under constant stirring in a 1 wt% PVA aqueous solution. This led to formation of small dimples on the surface of the microparticles.

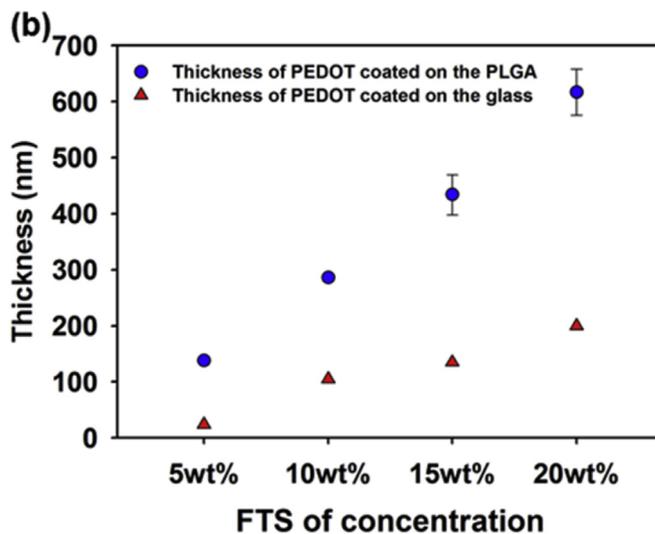
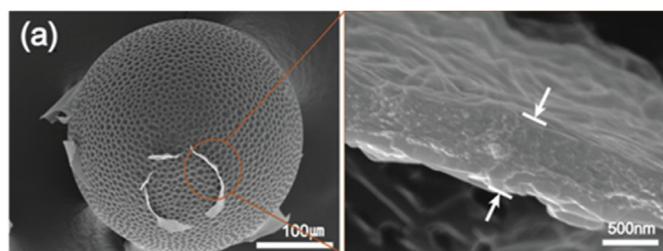
To fabricate the 3D colloidal assembly, washed microparticles were placed in a 1-mL Eppendorf tube and centrifuged at 3000 rpm for 5 min in order to decant excess water. A 3D colloidal assembly with an irregular shape was obtained. A rectangular 3D colloidal assembly structure was obtained by placing colloids in a rectangular mold (Fig. S1), after which it was fully dried.

### 2.2. Vapor-phase polymerization (VPP)

3,4-Ethylenedioxythiophene (EDOT, MDBROS) as the monomer for PEDOT, ferric *p*-toluenesulfonate (FTS, ALDRICH) as an oxidizing agent, and tetraethyl orthosilicate (TEOS, SAMCHUN) as a precursor



**Fig. 1.** SEM images of PEDOT-coated PLGA microparticles with (a) smooth surface, (b) big dimples on the surface, and (c) small dimples on the surface, fabricated using 10 wt % FTS through VPP.



**Fig. 2.** (a) SEM image of PEDOT coated layer on PLGA microparticle with oxidant concentration of 20 wt% and (b) thickness of the coating layer for different FTS concentrations.

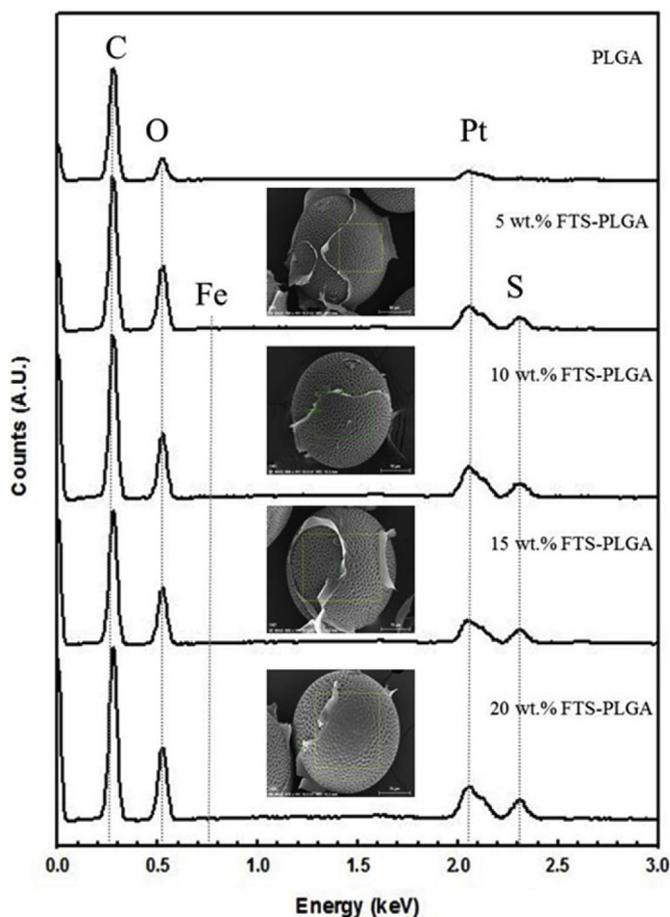


Fig. 3. EDX analysis of PEDOT coated PLGA particle varying FTS concentration.

of the  $\text{SiO}_2$  inorganic network were used without further purification. 1-Butanol (JUNSEI), which is a dilution solvent of the oxidizing agent, was used as received. A glass slide (Paul Marienfeld GmbH & Co. KG) was used as a pedestal for the PLGA particles. FTS was dissolved in 1-butanol at a concentration of 5–20 wt% by stirring the solution for approximately 30 min. The mixed oxidant solution was spin-coated onto the glass slide at 300 rpm for 10 s and then at 500 rpm for 30 s consecutively. After the mixed oxidant solution was dried at 40 °C for 5 min, the FTS-coated PLGA particles were transferred to a VPP chamber. The reaction chamber was purged with nitrogen gas for 60 min prior to VPP. The nitrogen blanket was maintained throughout the polymerization at a flow rate of 600 mL/min and the reaction temperature was maintained at 40 °C. The EDOT or mixture of EDOT and TEOS was placed at the bottom of the VPP reaction chamber, and the coated PLGA particles were exposed to the EDOT or mixed EDOT/TEOS vapor for 30 min. A TEOS concentration of 50% was used in the mixture of EDOT and TEOS. After polymerization, the PLGA particles were immersed in distilled water for 2 h to remove any unreacted oxidant and then dried at room temperature for 5 min at 60 °C. DCM was applied dropwise onto the PEDOT- or PEDOT/ $\text{SiO}_2$ -coated 3D cluster microparticles for 5 min to remove PLGA microparticles selectively, resulting in the 3D conducting skeletal structure.

### 2.3. Characterization

The morphologies of the microparticles and 3D assemblies were observed using a scanning electron microscope (SEM, MIRA LMH, TESCAN) equipped with an energy-dispersive X-ray (EDX) analysis detector (Bruker AXS XFlash detector 5010). The thickness of the conformal coating layer was measured ten times from a detached region using the SEM images. Micro-CT (SkyScan 1272, Bruker AXS), which is non-destructive tool for visualizing the interior of an object, was used to image and characterize the pores in the 3D skeletal structure. We performed 3D model reconstruction and analyses by using software supplied by the micro-CT manufacturer

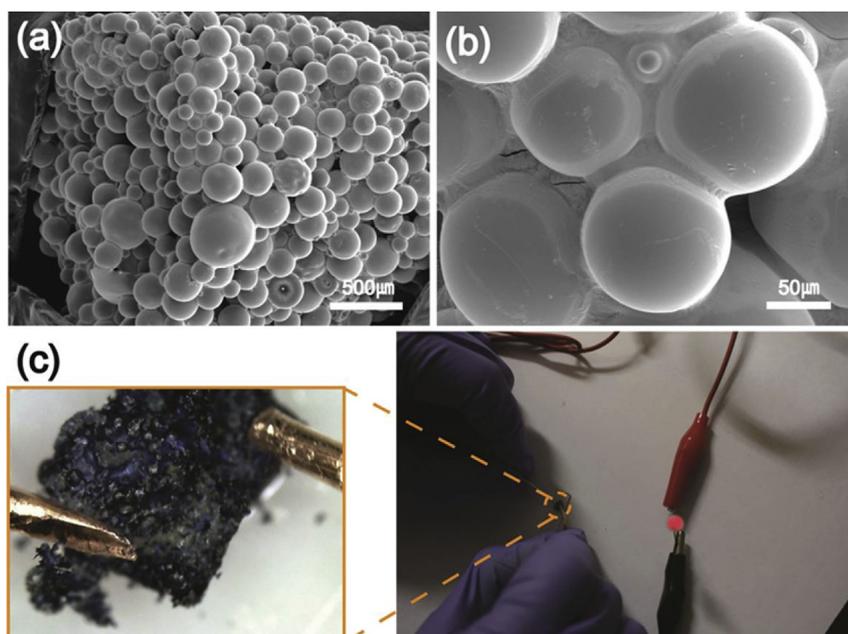
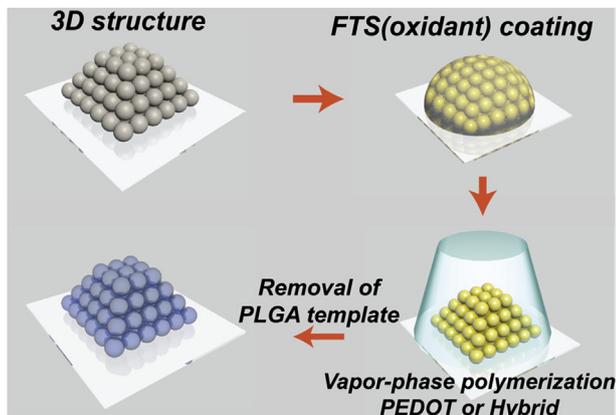


Fig. 4. (a) SEM image of the 3D-structured PEDOT-coated PLGA microparticle assembly fabricated using 20 wt% FTS through VPP, (b) magnified view of (a), and (c) A photograph of the electric conduction of 3D-structured PEDOT-coated PLGA microparticle assembly.



**Fig. 5.** Schematic of the fabrication process for PEDOT/silica hybrid-coated 3D structure.

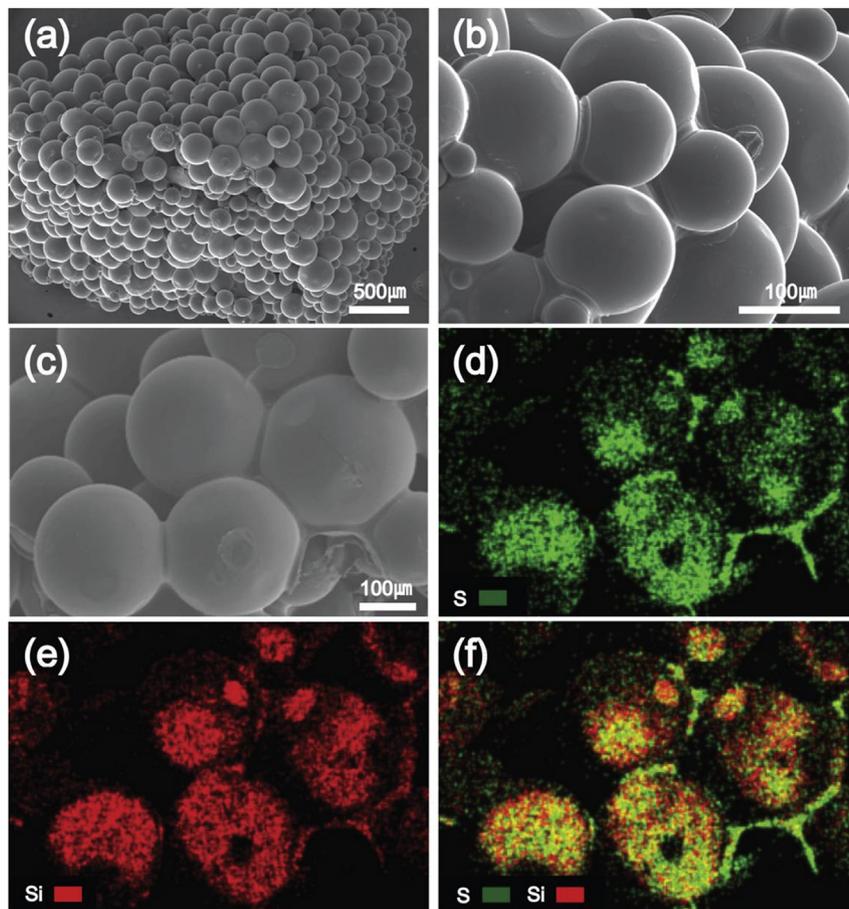
(NRecon, SkyScan). The X-ray source was operated at a voltage of 50 kV and a current of 200  $\mu$ A.

### 3. Results and discussion

#### 3.1. Microparticles with PEDOT conformal layer

A microparticle can be considered a simple 3D structure for

PEDOT conformal coating. However, there have been only a few successful synthetic routes [24] reported for PEDOT-coated colloids after the first successful coating of micrometer-sized polystyrene latex with a PEDOT shell [18]. We first fabricated biodegradable PLGA microparticles with smooth or dimpled surfaces, previously developed by our group, using an oil-in-water (O/W) emulsion solvent evaporation method [22,23]. The particle diameters were 100–500  $\mu$ m, with an average diameter of 205  $\mu$ m (Fig. S2). EDOT was vapor polymerized onto microparticles spread on a glass plate by using a home-made apparatus and 10 wt % FTS in 1-butanol as an oxidant at 40  $^{\circ}$ C, which is much lower than the glass transition temperature of PLGA. The remaining FTS was removed by washing with double-distilled water after polymerization for 30 min. As shown in the scanning electron microscopy (SEM) images in Fig. 1, PEDOT was successfully deposited onto the surfaces of the microparticles. It is noteworthy that a nanoscale conformal coating of PEDOT was successfully achieved, even for the particles with complex surface morphologies. This indicates that the coating of PEDOT was non-invasive (i.e., no change in the surface morphology), which could not be easily accomplished by using coating solutions [25,26]. With conventional chemical modification, which is generally accomplished with solvents, it is difficult to maintain the structural appearance of microparticles owing to solvent attack on the bottom layer during the coating process. It is noteworthy that our synthetic route to provide a non-invasive functional coating on microparticles with complex surface textures enables both physical and chemical modification to



**Fig. 6.** (a, b) SEM image of the 3D-structured hybrid-coated PLGA microparticle assemblies fabricated using 20 wt% FTS through VPP. (c) SEM image, and (d) EDX elemental mapping image of sulfur (green) and (e) silicon (red). (f) Merged image of (d) and (e). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

conventional smooth, round microparticles, which have been separately used to modify the properties of microparticles for specific application.

To control the PEDOT conformal layer thickness on the microparticles, the initial concentration of FTS in the 1-butanol for vapor polymerization initiation was altered. The surface layer was detached using adhesive tape to investigate the thickness of the coating layer, as shown in Fig. 2. Fig. 3 shows the EDX analysis results of the surface of the PEDOT-coated microparticles. The sulfur peak represents the sulfur moiety in PEDOT. The relative atomic percentages of sulfur were 1.28, 1.47, 1.60, and 1.72% with increasing FTS concentration from 5 to 20 wt%. As confirmed from the increase of the sulfur peak in the EDX results (Fig. 3), the thickness of the PEDOT shell increased from 143 to 610 nm as the FTS concentration increased from 5 to 20 wt %, respectively, indicating control of the conformal coating thickness of PEDOT. The increase in the PEDOT conformal coating thickness on the PLGA microparticles provided a more bluish color to the microparticles. This corresponds well to the thickness variation at a 2D plane surface with the change in FTS concentration. The thicknesses of PEDOT on a microparticle and a planar surface were compared and both were found to increase with increasing initial oxidant concentration. However, thicker films were obtained for the microparticles (Fig. 2b).

### 3.2. PEDOT conformal coating onto microparticle assemblies

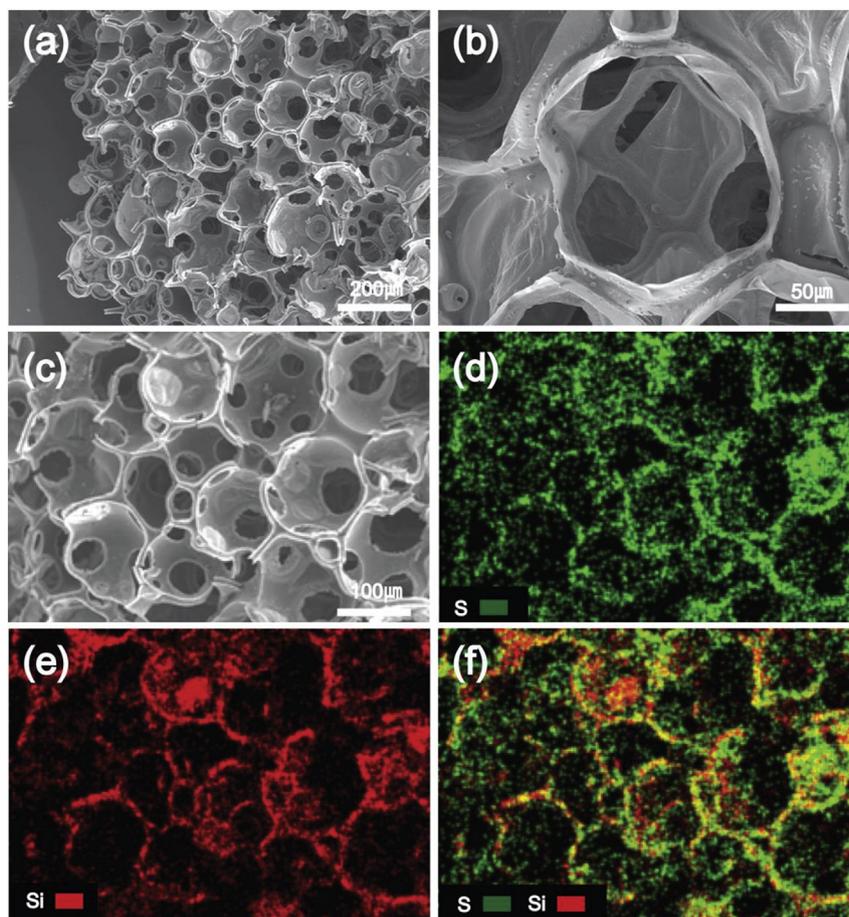
Because of the widespread availability of microparticles and

their assemblies, the addition of a conformable conducting layer on their surface increases the materials available when fabricating microparticles that exhibit electric conductance. However, it is challenging to apply a PEDOT conformal coating to complex 3D biodegradable structures such as microparticle assemblies, in which mechanical stability is required.

To investigate the possibility of applying a PEDOT conformal coating onto complex 3D structures, a colloidal assembly based on smooth, round PLGA microparticles with sizes ranging from 100 to 500  $\mu\text{m}$  was fabricated. Particles with somewhat random sizes were assembled to increase contact among the microparticles. Poly-dispersed microparticles were centrifuged to form a 3D structure. PEDOT was coated onto the microparticles using VPP by following the aforementioned procedure used for coating dispersed microparticles, and the presence of a smooth PEDOT conformal coating on the microparticle surfaces was confirmed through SEM images (Fig. 4a and b). To ensure sufficient conductivity of the 3D colloidal cluster with PEDOT conformal coating, a continuous electrical connection should exist throughout the structure. Electric conduction was confirmed through LED lighting, with the thin PEDOT layer providing a conduction route on the surface of the 3D structure (Fig. 4c).

### 3.3. Fabrication of conducting 3D skeletal structure

A highly porous 3D structure composed of an electrically conductive frame could be attractive in applications such as



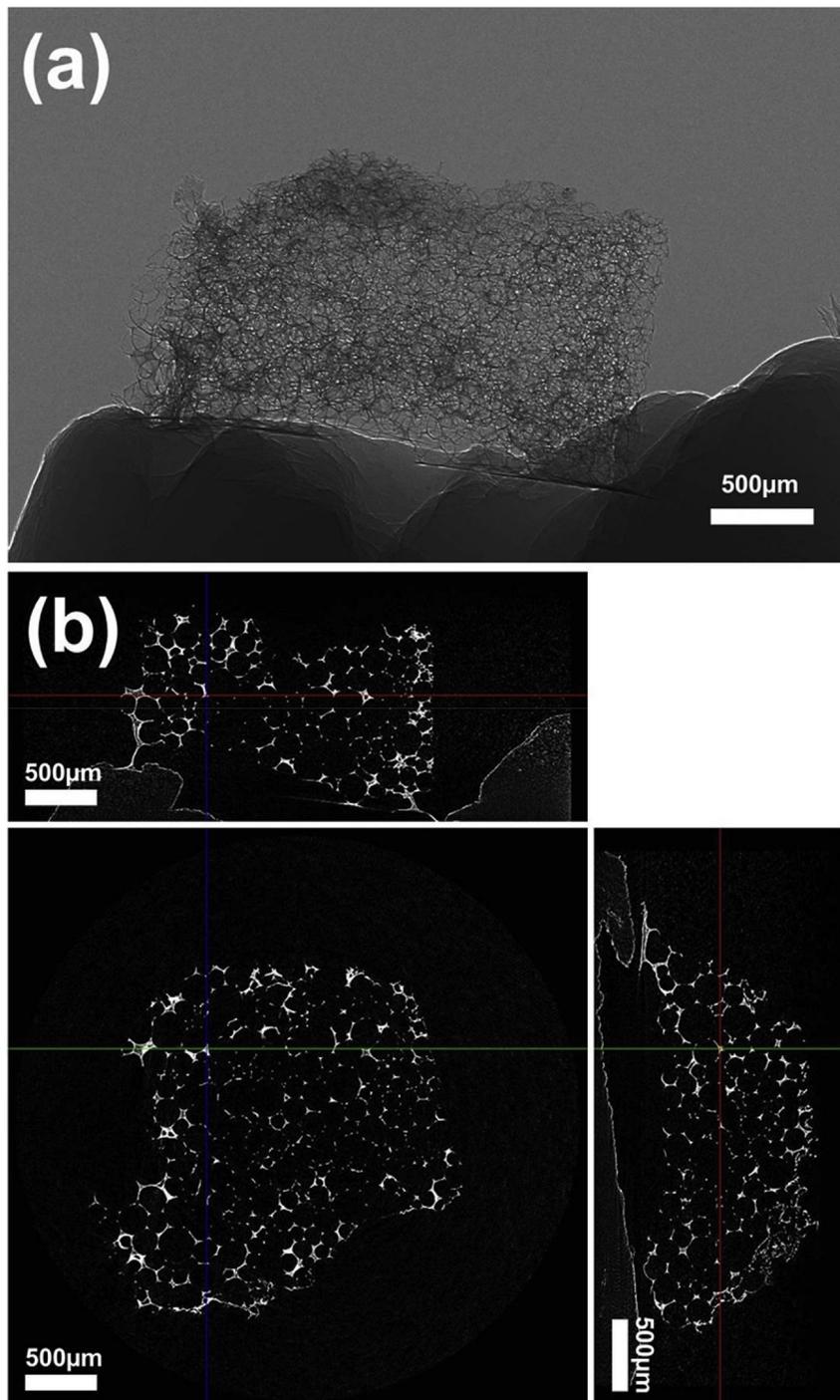
**Fig. 7.** (a, b) SEM image of the 3D-structured PEDOT/SiO<sub>2</sub> hybrid skeletal structure using 20 wt% FTS through VPP after the selective extraction of the PLGA. (c) SEM image, (d) EDX elemental mapping image of sulfur (green) and (e) silicon (red). (f) Merged image of (d) and (e). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sensors, scaffolds, and electrodes. For example, 3D structures with mechanical stability exhibiting electric conductance throughout the matrix can be potential platforms for neural tissue engineering. Large pore sizes corresponding to the size of living cells are required in tissue engineering. It can be anticipated that a stable structure of a conducting material with large pore sizes can be advantageous in templates for biomedical applications. Microparticles can be made to possess a porous structure [27] but there are limitations to obtaining a high-porosity 3D structure by itself.

We selectively removed PLGA microparticles through solvent

extraction from PLGA microparticle assemblies with PEDOT conformal coating on the surface to obtain 3D structure with high-porosity and large pore sizes (diameter exceeding 100  $\mu\text{m}$ ). Unfortunately, this resulted in the collapse of the 3D structures (Fig. S3). The PEDOT nanoscale conformable coating layer and the thicker layer at the necking region between the removed microparticles presented insufficient mechanical stability to support the 3D skeletal structure.

We recently reported a hybrid conducting system comprising a flat, thin layer on a 2D surface that can function as a transparent



**Fig. 8.** Representative micro-CT images of (a) the 3D-structured hybrid-coated PLGA after the selective extraction of the PLGA and (b) the exploitation of the xyz-separable characteristics of the 3D structure.

conducting electrode [28]. We investigated whether this composite system could be applied to a 3D structure. We polymerized EDOT and TEOS simultaneously onto golf-ball-shaped microparticles using VPP. The surfaces showed a morphology (Fig. S4) similar to that shown in the SEM images in Fig. 1, in which only PEDOT was used for conformal coating on the microparticles. Successful synthesis of the PEDOT/SiO<sub>2</sub> hybrid coating layer on the surfaces of the microparticles was confirmed by energy-dispersive X-ray spectroscopy (EDX) mapping, which showed a distribution of PEDOT (sulfur) and SiO<sub>2</sub> (silicon) throughout the surface. Furthermore, a non-invasive coating was also obtained for the hybrid coating.

We applied this hybrid conformal coating onto the 3D structure formed from the assembly of polydispersed PLGA microparticles. A representative scheme for the preparation of the conducting skeletal structure is demonstrated in Fig. 5. The EDX elemental

mapping of this structure also showed a distribution of silicon and sulfur throughout the surface of the microparticles in 3D structure, indicating the uniform coating of the hybrid layer as from the isolated microparticles (Fig. 6 and Fig. S5). Here, we used a reaction temperature of 40 °C, which is suitable for soft materials. The glass transition temperature ( $T_g$ ) of PLGA is approximately 55 °C, and polymerization should occur at a temperature below  $T_g$  to maintain the structural integrity of the microparticles. In the hybrid composition of PEDOT and silica, PEDOT provides the electric conduction, and thus the amount of silica should be optimized to reduce resistance but still provide adequate mechanical properties.

PLGA microparticles were removed by dissolving microparticles using DCM, forming a 3D skeletal structure with structural integrity (Fig. 7 and Fig. S6). Electric conduction was observed for this structure as well. Unlike the PEDOT 3D skeletal structure, structural

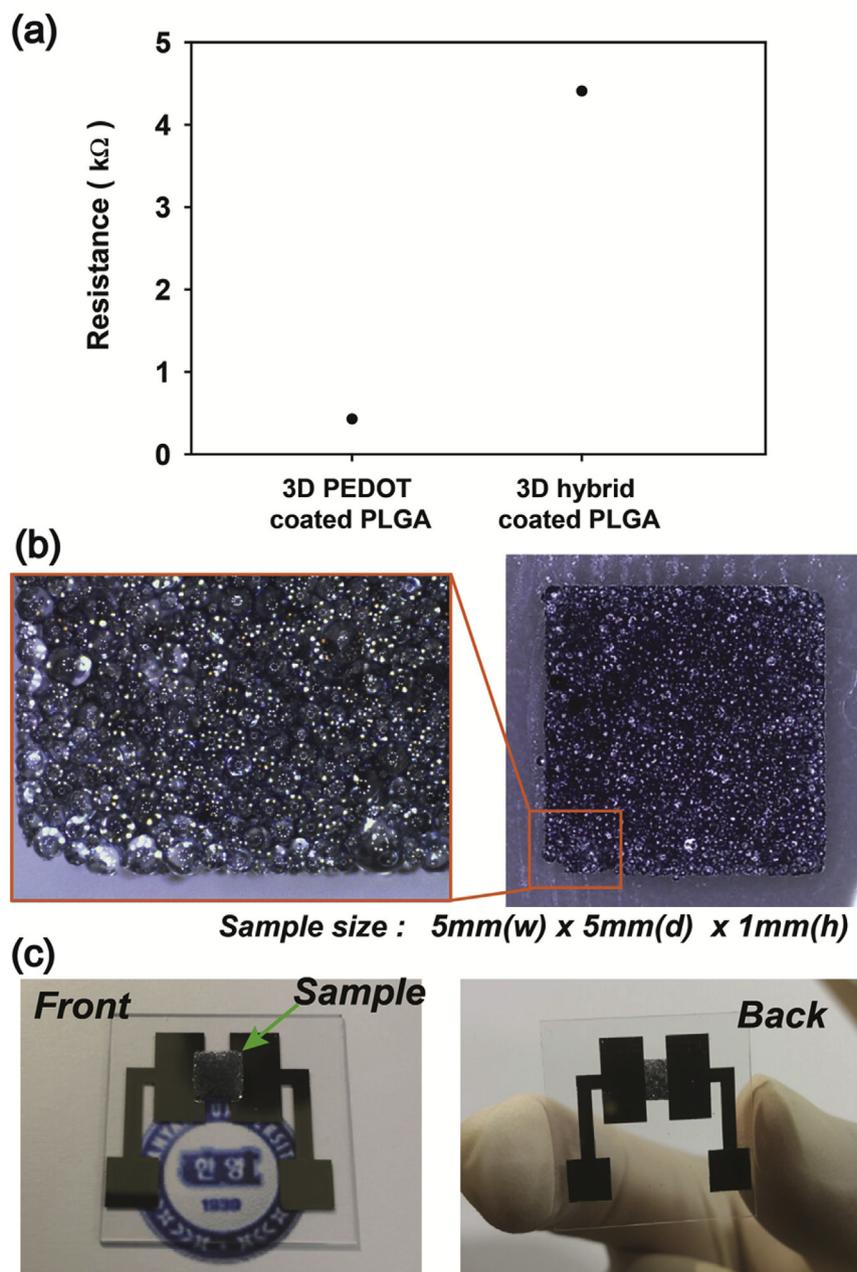


Fig. 9. (a) Resistance of the PEDOT- or hybrid-coated 3D structure, (b) Optical microscope images, and (c) photographs of the sample used for resistance measurement.

integrity was secured with the use of the PEDOT/SiO<sub>2</sub> composite surface layer after removal of the microparticle template. Therefore, one approach to obtaining a conducting 3D structure with structural integrity is to use a hybrid material with a simple synthesis technique. Silica is approved by the Food and Drug Administration (FDA) for oral consumption and is widely studied for use in biomedical applications such as tissue engineering and controlled drug release. Silica gel possesses low cellular toxicity as compared to other inorganic oxide nanoparticles [29]. Thus, the 3D structure coated with PEDOT and silica has potential for use in biomedical applications in which electric conductivity is required.

#### 3.4. Electric conductivity of 3D skeletal structure with high porosity

The porous character of the 3D skeletal structure formed from the PEDOT/silica composite was observed using micro-CT (Fig. 8). A porous structure was observed throughout the matrix. Also the pore-size distribution of the 3D porous structure was obtained by the measurement (Fig. S7). The measured specific surface area, object volume, and total volume of 3D skeletal structure were  $1.21 \times 10^8 \mu\text{m}^2$ ,  $2.99 \times 10^8 \mu\text{m}^3$ , and  $8.14 \times 10^9 \mu\text{m}^3$ , respectively. Interestingly, the measured porosity was greater than 96% (Porosity of 96.3 and 97.7% were obtained for two different 3D skeletal structure samples). As far as we know, this value is uncommon even for a high porous structure with smaller than several microns. However, the present 3D structure shows not only electric conductivity but also high porosity, with pore sizes greater than 100  $\mu\text{m}$ .

Because the PLGA colloidal assemblies with PEDOT and PEDOT/SiO<sub>2</sub> conformal surface layers are anisotropic mixtures of continuous electric conducting and insulating regions, the electric conductivities were compared for the two different 3D-structured assemblies with the same dimensions (5 mm  $\times$  5 mm  $\times$  1 mm). PLGA microparticles were not removed in this case so as to perform the comparison under stable structural integrity. Each 3D structure was placed on a test vehicle that was prepared by inkjet printing with Ag nano-ink for the measurement of the electrical conductivity. As expected, the PEDOT-coated 3D structure showed higher electric conductivity as compared to the composite structure with the same dimensions (Fig. 9). This suggests that there is a trade-off between electric conductivity and mechanical stability that should be optimized according to the specific application.

#### 4. Conclusions

We report the fabrication of a 3D conductive porous structure from a conformal layer formed by vapor-phase polymerization on microparticle assemblies. A conformal layer of a transparent conducting polymer, PEDOT, was deposited with and without silica onto the 3D structure of a biodegradable polymer consisting of microparticles and their assembly. The PEDOT and SiO<sub>2</sub> composite shell could be noninvasively coated onto microparticles while retaining their complex surface morphology, resulting in modulation of both the chemical and physical properties of the microparticles. The structural integrity was maintained with removal of the template structure of the biodegradable polymers when SiO<sub>2</sub> and PEDOT were jointly vapor-phase polymerized onto the 3D structure. The fabrication provided a high-porosity 3D conductive skeletal structure that shows potential for biodegradable and green electronics applications.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2016.09.008>.

#### References

- [1] M. Chen, L. Zhang, S. Duan, S. Jing, H. Jiang, C. Li, Highly stretchable conductors integrated with a conductive carbon nanotube/graphene network and 3D porous poly(dimethylsiloxane), *Adv. Funct. Mater.* 24 (2014) 7548–7556.
- [2] X. Xia, D. Chao, Z. Fan, C. Guan, X. Cao, H. Zhang, H.J. Fan, A new type of porous graphite foams and their integrated composites with oxide/polymer core/shell nanowires for supercapacitors: structural design, fabrication, and full supercapacitor demonstrations, *Nano Lett.* 14 (2014) 1651–1658.
- [3] J. Pal, S. Sharma, S. Sanwaria, R. Kulshreshtha, B. Nandan, R.K. Srivastava, Conductive 3D porous mesh of poly( $\epsilon$ -caprolactone) made via emulsion electrospinning, *Polymer* 55 (2014) 3970–3979.
- [4] P. Sengodu, A.D. Deshmukh, Conducting polymers and their inorganic composites for advanced Li-ion batteries: a review, *RSC Adv.* 5 (2015) 42109–42130.
- [5] K.S. Lee, J.H. Yun, Y.H. Han, J.H. Yim, N.G. Park, K.Y. Cho, J.H. Park, Enhanced light harvesting in dye-sensitized solar cells with highly reflective TCO- and Pt-less counter electrodes, *J. Mater. Chem.* 21 (2011) 15193–15196.
- [6] S. Ghosh, N.A. Kouamé, L. Ramos, S. Remita, A. Dazzi, A. Deniset-Besseau, P. Beaunier, F. Goubard, P.H. Aubert, H. Remita, Conducting polymer nanostructures for photocatalysis under visible light, *Nat. Mater.* 14 (2015) 505–511.
- [7] A.M. Österholm, D.E. Shen, A.L. Dyer, J.R. Reynolds, Optimization of PEDOT films in ionic liquid supercapacitors: demonstration as a power source for polymer electrochromic devices, *ACS Appl. Mater. Interfaces* 5 (2013) 13432–13440.
- [8] A. Gumus, J.P. Califano, A.M.D. Wan, J. Huynh, C.A. Reinhart-King, G.G. Malliaras, Control of cell migration using a conducting polymer device, *Soft Mat.* 6 (2010) 5138–5142.
- [9] A.F. Quigley, J.M. Razal, B.C. Thompson, S.E. Moulton, M. Kita, E.L. Kennedy, G.M. Clark, G.G. Wallace, R.M.I. Kapsa, A conducting-polymer platform with biodegradable fibers for stimulation and guidance of axonal growth, *Adv. Mater.* 21 (2009) 4393–4397.
- [10] J.E. Collazos-Castro, J.L. Polo, G.R. Hernández-Labrado, V. Padial-Cañete, C. García-Rama, Bioelectrochemical control of neural cell development on conducting polymers, *Biomaterials* 31 (2010) 9244–9255.
- [11] K.A. Ludwig, N.B. Langhals, M.D. Joseph, S.M. Richardson-Burns, J.L. Hendricks, D.R. Kipke, Poly(3,4-ethylenedioxythiophene) (PEDOT) polymer coatings facilitate smaller neural recording electrodes, *J. Neural Eng.* 8 (2011) 014001.
- [12] P. Fattahi, G. Yang, G. Kim, M.R. Abidian, A review of organic and inorganic biomaterials for neural interfaces, *Adv. Mater.* 26 (2014) 1846–1885.
- [13] D. Svirskis, J. Travas-Sejdic, A. Rodgers, S. Garg, Electrochemically controlled drug delivery based on intrinsically conducting polymers, *J. Control. Release* 146 (2010) 6–15.
- [14] Y. Li, R.J. Ewen, S.A. Campbell, J.R. Smith, Electrochemically controlled release of anti schistosomiasis agents from polypyrrole, *J. Mater. Chem.* 22 (2012) 2687–2694.
- [15] Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei, H.M. Cheng, Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition, *Nat. Mater.* 10 (2011) 424–428.
- [16] C. Yang, P. Liu, P. Du, X. Wang, Stabilization of carbon nanotubes-based hollow cages for energy storage: from collapsed morphology to free-standing structure, *Electrochim. Acta* 105 (2013) 53–61.
- [17] M.G. Han, S.P. Armes, Synthesis of poly(3,4-ethylenedioxythiophene)/silica colloidal nanocomposites, *Langmuir* 19 (2003) 4523–4526.
- [18] M.A. Khan, S.P. Armes, Synthesis and characterization of micrometer-sized poly(3,4-ethylenedioxythiophene)-coated polystyrene latexes, *Langmuir* 15 (1999) 3469–3475.
- [19] S.C. Luo, E.M. Ali, N.C. Tansil, H.H. Yu, S. Gao, E.A.B. Kantchev, J.Y. Ying, Poly(3,4-ethylenedioxythiophene) (PEDOT) nanobiointerfaces: thin, ultra-smooth, and functionalized PEDOT films with in vitro and in vivo biocompatibility, *Langmuir* 24 (2008) 8071–8077.
- [20] D.C. Martin, Polymers manipulate cells, *Nat. Mater.* 6 (2007) 626–627.
- [21] S.E. Atanasov, M.D. Losego, B. Gong, E. Sachet, J.-P. Maria, P.S. Williams, G.N. Parsons, Highly conductive and conformal poly(3,4-ethylenedioxythiophene) (PEDOT) thin films via oxidative molecular layer deposition, *Chem. Mater.* 26 (2014) 3471–3478.
- [22] M.R. Kim, S. Lee, J.K. Park, K.Y. Cho, Golf ball-shaped PLGA microparticles with internal pores fabricated by simple O/W emulsion, *Chem. Commun.* 46 (2010) 7433–7435.
- [23] K.-H. Hwangbo, M.R. Kim, C.-S. Lee, K.Y. Cho, Facile fabrication of uniform golf-

- ball-shaped microparticles from various polymers, *Soft Mat.* 7 (2011) 10874–10878.
- [24] M.G. Han, S.H. Foulger, Crystalline colloidal arrays composed of poly(3,4-ethylenedioxythiophene)-coated polystyrene particles with a stop band in the visible regime, *Adv. Mater.* 16 (2004) 231–234.
- [25] W.E. Tenhaeff, K.K. Gleason, Initiated and oxidative chemical vapor deposition of polymeric thin films: iCVD and oCVD, *Adv. Funct. Mater.* 18 (2008) 979–992.
- [26] M.E. Alf, A. Asatekin, M.C. Barr, S.H. Baxamusa, H. Chelawat, G. Ozaydin-Ince, C.D. Petruczuk, R. Sreenivasan, W.E. Tenhaeff, N.J. Trujillo, S. Vaddiraju, J. Xu, K.K. Gleason, Chemical vapor deposition of conformal, functional, and responsive polymer films, *Adv. Mater.* 22 (2010) 1993–2027.
- [27] Y. Gao, Y. Bai, D. Zhao, M.-W. Chang, Z. Ahmad, J.-S. Li, Tuning microparticle porosity during single needle electrospraying synthesis via a non-solvent-based physicochemical approach, *Polymers* 7 (2015) 2701–2710.
- [28] J.H. Yim, Mechanically robust poly(3,4-ethylenedioxythiophene)–SiO<sub>2</sub> hybrid conductive film prepared by simultaneous vapor phase polymerization, *Compos. Sci. Technol.* 86 (2013) 45–51.
- [29] D. Napierska, L.C.J. Thomassen, D. Lison, J.A. Martens, P.H. Hoet, The nanosilica hazard: another variable entity, *Part. Fibre Toxicol.* 7 (2010) 39.