Flexible Thermoelectric Double-Layer Inorganic/Organic Composites Synthesized by Additive Manufacturing

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This study shows an approach to combine a high electrical conductivity of one composite layer with a high Seebeck coefficient of another composite layer in a double-layer composite, resulting in high thermoelectric power factor. Flexible double-layer-composites, made from Bi\(_2\)Te\(_3\)-based-alloy/polylactic acid (BTBA/PLA) composites and Ag/PLA composites, are synthesized by solution additive manufacturing. With the increase in Ag volume-ratio from 26.3\% to 41.7\% in Ag/PLA layers, the conductivity of the double-layer composites increases from 12 S cm\(^{-1}\) to 1170 S cm\(^{-1}\), while the Seebeck coefficient remains \(\approx 80 \mu V \cdot K^{-1}\) at 300 K. With further increase in volume ratio of Ag until 45.6\% in Ag/PLA composite layer, the electrical conductivity of the double-layer composites increases to 1710 S cm\(^{-1}\), however, with a slight decrease of the Seebeck coefficient to 64 \(\mu V \cdot K^{-1}\). The electrical conductivity and Seebeck coefficient vary only to a limited extent with the temperature. The high Seebeck coefficient is due to scattering of low energy charge carriers across compositionally graded interfaces. A power factor of 875 \(\mu W \cdot m^{-1} \cdot K^{-2}\) is achieved at 360 K for 41.7 vol.% Ag in the Ag/PLA layers. Solution additive manufacturing can directly print this double-layer composite into intricate geometries, making this process is promising for large-scale fabrication of thermoelectric composites.

1. Introduction

Thermoelectric (TE) devices are based on materials that convert heat (temperature differences) to electrical energy or vice versa.\(^{[1–3]}\) The TE efficiency is related to the dimensionless figure of merit, \(ZT = S^2 \sigma T / \kappa\), where \(S\) is the Seebeck coefficient, \(\sigma\) is the electrical conductivity, \(\kappa\) is the thermal conductivity, and \(T\) is the absolute temperature. For the temperature range near room temperature, Bi-Te-based alloys are among the most important TE materials. However, the use of costly and sometimes toxic elements and the extremely scarce Te, limits their widespread use. To this end, it has better to reduce the usage of Bi-Te-based alloys. Furthermore, the fragility and poor mechanical flexibility of Bi-Te-based alloys limit their use to non-planar heat sources, although most heat sources are non-planar. While there are some studies on inducing mechanical flexibility in fully inorganic TE materials for use at high temperature,\(^{[4–8]}\) organic,\(^{[9–11]}\) or inorganic/organic hybrid materials\(^{[12]}\) are more suited near room temperature. Polymer-based composites with inorganic TE fillers tend to be readily processed and have good mechanical flexibility,\(^{[12–17]}\) however, their \(ZT\) is generally lower than that of fully inorganic TE materials.\(^{[18]}\) Optimizing the materials’ TE efficiency and reducing Bi-Te-based alloys loading in the composites, in combination with ease of processing, is therefore an important challenge in developing inorganic/organic composites and hybrid materials for thermoelectrics.

Additive manufacturing (3D printing), has many advantages, such as rapid fabrication of complex geometric structures, waste minimization, reduced consumption of raw materials and time, freedom of design, and automation.\(^{[19]}\) Traditional additive manufacturing methods include stereolithography apparatus (SLA), fused deposition modeling (FDM), selective laser melting (SLM), and solution printing (SP). Additive manufacturing can be used for fabrication of TE materials and devices with almost any desired geometric structures. For example, He et al.\(^{[20]}\) added Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) in photoresins, and then prepared corresponding bulk materials using a mimicked SLA method, achieving a ZT value of 0.12 at 43 °C. Oztan et al.\(^{[20]}\) synthesized Bi\(_2\)Te\(_3\)/acylonitrile butadiene styrene composites with 80 wt\% Bi\(_2\)Te\(_3\) by FDM, with a ZT value of 0.54 at room temperature. Shi et al.\(^{[22]}\) prepared a porous Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) material by selective laser sintering (SLS), and a ZT value of \(\approx 1.29\) at 54 °C was obtained. Qiu et al.\(^{[23]}\) prepared BiSbTe bulk materials by a SLM combined with thermal explosion technology achieving a ZT of 1.1 at 316 K.

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Although the above-mentioned additive-manufacturing approaches can be used for preparation of TE materials, there are still some issues that need to be solved. For instance, the selection of the photoresins for the SLA process is limited; the FDM process requires a temperature above 200 °C for melting the polymer or inorganic-polymer composite filaments; the photoresins or polymers in the filaments for the SLA and FDM process need to be removed as much as possible, since they are insulators; and for SLM, the printed materials are prone to oxidation and phase impurities, which need to be conducted under a protective atmosphere.[23] Recently, we prepared tungsten carbide (WC)/polylactic-acid (PLA) composites using a solution printing (SP) process.[24] The SP process can directly print solutions which contain polymer matrices and inorganic fillers into almost any desired, even intricate, geometries at room temperature.

In order to improve the thermoelectric properties of materials, carrier transport in inorganic/organic composites needs to be investigated and ideally tailored. An approach to achieve this can be double- or multiple-layer composites, where several layers contribute to conduction and thermoelectric conversion. Here, we report synthesis by SP additive manufacturing of mechanically flexible double-layer inorganic/organic composites, with layers composed of Bi$_2$Te$_3$-based alloy/polylactic-acid (BTBA/PLA) composites and Ag/PLA composites. Their thermoelectric properties have been investigated from 300 to 360 K, leading to a proposed mechanism for the carrier transport in these double-layer inorganic/organic composites.

2. Results and Discussion

Figure 1a is a schematic of the additive manufacturing process of the BTBA/PLA–Ag/PLA double-layer composites. Videos S1 and S2 and Figure S1a–d, Supporting Information show the additive manufacturing process of the BTBA/PLA–Ag/PLA double-layer composites. Table 1 shows the samples designations and parameters of BTBA/PLA–Ag/PLA double-layer composites, BTBA/PLA single layer composites, and Ag/PLA single layer composites. Figure S2, Supporting Information shows photos of the SCA1, SCA2, SCA3, SCA4, SCA5, samples as well as the back sides (BTBA/PLA layer composites) and front sides (Ag/PLA layer composites) of the DC1, DC2, DC3, DC4, and DC5, respectively. The BTBA/PLA layer composites and Ag/PLA layer composites have different color.

Figure 2a–c show the temperature dependence of electrical conductivity, Seebeck coefficient, and power factor ($S^2$σ) of the double-layer composites with varying Ag content (DC1, DC2, DC3, DC4, and DC5). The temperature dependence of electrical conductivity, Seebeck coefficient, and power factor of SCBT, SCA1, SCA2, SCA3, SCA4, and SCA5 are shown in Figure 2d–f for comparison. At 300 K, with the increase in volume ratio of Ag from 26.3% for DC1 to 45.6% for DC5, the electrical conductivity of the double-layer composites sharply increases from 12.3 to 1710.2 S cm$^{-1}$. This value is much higher than that of SCBT ($=0.53$ S cm$^{-1}$ at 300 K, Figure 2d), which is attributed to the higher electrical conductivity of Ag ($6.7 \times 10^5$ S cm$^{-1}$), however it is lower than that of Ag/PLA single layer composites, which are measured to be $=454, 1672, 2230, 2979,$ and $4765$ S cm$^{-1}$ for SCA1, SCA2, SCA3, SCA4, and SCA5, respectively, at 300 K (Figure 2d).

Despite the increase in volume ratio of Ag from 26.3% for DC1 to 41.7% for DC4, the Seebeck coefficient of the double-layer composites remain almost constant, with Seebeck coefficient $=80$ µV K$^{-1}$ at 300 K. Further increase in volume ratio of Ag until 45.6% for DC5, reduces the Seebeck coefficient of the double-layer composites to 64 µV K$^{-1}$ at 300 K. The Seebeck coefficient of the double-layer composites is much higher than that of the values for Ag/PLA single layer composites ($=1.0$ µV K$^{-1}$ for SCA1, SCA2, SCA3, SCA4, and SCA5 at 300 K, as shown in Figure 2e), however it is much lower than that of SCBT ($=187$ µV K$^{-1}$ at 300 K, as shown in Figure 2e), which is not surprising given the relatively low Seebeck coefficient of pure Ag ($=1.5$ µV K$^{-1}$ at room temperature$^{[26]}$).
Table 1. The composites and the sample designation of BTBA/PLA–Ag/PLA double-layer composites, BTBA/PLA single layer composites, and Ag/PLA single layer composites.

| Samples                              | Compositions | Sample designation |
|--------------------------------------|--------------|--------------------|
| BTBA/PLA–Ag/PLA double-layer composites |              | DC1                |
|                                      | 1            | 2.0:0.5 39.6%      |
|                                      | 1            | 2.0:0.5 39.6%      |
|                                      | 1            | 2.0:0.5 39.6%      |
|                                      | 1            | 2.0:0.5 39.6%      |
|                                      | 1            | 2.0:0.5 39.6%      |
| BTBA/PLA single layer composites     |              | SCBT               |
|                                      | 1            | 2.0:0.5 39.6%      |
| Ag/PLA single layer composites       |              | SCA1               |
|                                      | 1            | 1.5:0.5 26.3%      |
|                                      | 1            | 2.0:0.5 32.3%      |
|                                      | 1            | 2.5:0.5 37.3%      |
|                                      | 1            | 3.0:0.5 41.7%      |
|                                      | 1            | 3.5:0.5 45.6%      |
| SCA2                                |              | SCA2               |
| SCA3                                |              | SCA3               |
| SCA4                                |              | SCA4               |
| SCA5                                |              | SCA5               |

Figure 2. a) Electrical conductivity, b) Seebeck coefficient, and c) power factor of DC1, DC2, DC3, DC4, and DC5. d) Electrical conductivity, e) Seebeck coefficient, and f) power factor of the SCBT, SCA1, SCA2, SCA3, SCA4, and SCA5 (Error margins: see Experimental Section).
With the increase in volume ratio of Ag from 26.3% for DC1 to 41.7% for DC4, the power factor of the double-layer composites is drastically increased from 8.2 to 774 µW m⁻¹ K⁻² at 300 K, which is attributed to the significant enhancement in electrical conductivity. Further increase in volume ratio of Ag is found to reduce the power factor of the double-layer composites, attaining a value of 702 µW m⁻¹ K⁻² at 300 K in DC5, which is attributed to the slight decrease in Seebeck coefficient.

The power factors of the double-layer composites are found not to vary much with temperature, as their electrical conductivity and Seebeck coefficient are found to remain almost unchanged with temperature. The highest power factor is calculated to be 875 µW m⁻¹ K⁻² at 360 K for the double-layer composites (DC4) with 41.7 vol. % of Ag in Ag/PLA composite layer, which is much higher than that of Ag/PLA single layer composites (≈0.05, 0.08, 0.14, 0.31, and 0.27 µW m⁻¹ K⁻² for SCA1, SCA2, SCA3, SCA4, and SCA5, respectively, at 300 K, as shown in Figure 2f) and SCBT (1.86 µW m⁻¹ K⁻² at 300 K, as shown in Figure 2f), prepared using the same procedure. This indicates that the fabrication of double-layer inorganic/polymer composites is an effective way to enhance the TE performance of inorganic/polymer composites. Our highest reported value of the power factor is higher than typical reported values for inorganic/polymer composites, such as, a Ni nanowire/poly(vinylidene fluoride) (PVDF) composites (220 µW m⁻¹ K⁻² at 380 K for the composites with 80 wt% Ni nanowires),[6] SWCNTs/PEDOT:PSS (105 µW m⁻¹ K⁻² with 60 wt% SWCNTs at room temperature),[7] a SiC/PEDOT:PSS (128.3 µW m⁻¹ K⁻² with 3 wt% SiC at room temperature),[8] a Bi₀.₅Sb₁.₅Te₃ nanosheet/PEDOT:PSS composite (32.26 µW m⁻¹ K⁻² with 8 wt% Bi₀.₅Sb₁.₅Te₃ nanosheets at room temperature),[9] a Bi₀.₅Sb₁.₅Te₃ nanosheet/PEDOT:PSS composite (58.9 µW mK² with 10 wt% Bi₀.₅Sb₁.₅Te₃ nanosheets at 380 K),[10] and a Co nanowires/PVDF composite (523 µW m⁻¹ K⁻² with 80 wt% Co nanowires at 320 K).[11] Therefore, the present study shows a promising approach to improve TE performance in inorganic/organic composites. The compositions, morphologies, and transport mechanisms of double-layer composites have been investigated in order to understand the underlying mechanism, leading to their higher power factor than that of the single layer composites.

Figure 3 shows SEM images of front and back surfaces and fracture surfaces of the composites. As the volume ratio of Ag increases from 26.3% for DC1 to 45.6% for DC5, the content of Ag on the front surface (Ag/PLA composite layer side) of the double-layer composites are increased, leading to a rougher front surface (Ag/PLA composite layer side) of the double-layer composites (Figure 3a,e,i). Layered structure of BTBA is visible in the back surface (BTBA/PLA composite layer side) images of the composites (Figure 3c,g,k, which are the high-magnification SEM images of the areas marked by pink squares in the Figure 3b,f,j, respectively), and the fracture surfaces images (the inset in Figure 3d,l) of the composites, which is the typical morphology of BTBAs.[29] The front sides (Ag/PLA composite layer side, Figure 3a,e,i) are visibly denser than that of back sides (BTBA/PLA composite layer side) in the double-layer composites (Figure 3b,f,j), which is attributed to the smaller particle size of Ag than BTBA particles. Figure 3d,h,l show the SEM image of fracture surfaces of DC1, DC3, and DC5, with thickness ≈226, 266, and 270 µm, respectively. The boundary (the black dot line in Figure 3d) of Ag/PLA composite layer and BTBA/PLA composite layer is observed from the fracture surface SEM image in the double-layer composites. Figure 4a shows SEM image of two BTBA/PLA–Ag/PLA double-layers attached together as shown in the inset of Figure 4a. Figure 4b...
shows EDS mapping of the cross-sectional area of the attached double-layers. The EDS mapping in Figure 4c–f show the elemental distribution of Bi, Sb, Te, and Ag on the cross-sectional area shown in Figure 4a. BTBA and Ag particles are homogeneously dispersed in the corresponding composite layers of BTBA/PLA and Ag/PLA. The interface of BTBA/PLA composite layer and Ag/PLA composite layer is not sharp, as indicated by the SEM images in Figure 4g–l. Figure 4g shows a magnified SEM image of the selected small area in Figure 4a. Figure 4h shows EDS mapping of the corresponding area. EDS mappings in Figure 4i–l shows the elemental distribution of Bi, Sb, Te, and Ag.

The SEM image analyses and EDS maps indicate that there are three different regions in BTBA/PLA–Ag/PLA double-layer composites: 1) BTBA/PLA composite region; 2) Ag/PLA composite region; and 3) the interfacial region between the two composite layers (Figures 5 and 6, and Figures S3–S5, Supporting Information). The composition of BTBA/PLA and Ag/PLA composite regions contain BTBA and PLA and Ag and PLA, respectively, as verified by the XRD analyses (Figure 7) of back and front sides of DC5. All the peak positions in the DC5 of the back side (BTBA/PLA composite layer, BTBA/PLA composite region) and front side (Ag/PLA composite layer, Ag/PLA composite region) agree with the pure BTBA (Bi$_{0.4}$Sb$_{1.6}$Te$_3$, PDF#72-1836) and Ag (PDF#65-2871). The boundary regions of BTBA/PLA–Ag/PLA composite contain BTBA, Ag, and PLA. The concentration of BTBA is found to decrease from BTBA/PLA to Ag/PLA region, while the concentration of Ag increases (as schematically demonstrated in Figure 6), that is, the interfacial region of the double-layer is compositionally graded.

For thermoelectric measurements, the temperature gradient across the double-layer composites is produced following the scheme as shown in Figure 6. When one end of the double-layer composite is kept in contact with heat source, but from BTBA/PLA PLA layer side, as shown in Figure 6; the holes from the heat source region can diffuse to the electrode through two different routes. One is the direct route a → h, through the BTBA/PLA layer, and the other is through the alternate route a → b → c → d → e → f → g → h, as illustrated in Figure 6. Since the electrical conductivity of BTBA/PLA layer is low,
the direct route is not favorable for charge transport. In contrast, the electrical conductivity of Ag/PLA layer is higher than BTBA/PLA layer. Thus, the charge carriers are likely to follow the second route. Therefore, the double-layer composites have much higher electrical conductivity than that of single layer BTBA/PLA composites.

The high Seebeck coefficient of the double-layer nanocomposites is attributed to the scattering of low energy charge carriers along the route $a \rightarrow b \rightarrow c \rightarrow d \rightarrow e \rightarrow f \rightarrow g \rightarrow h$. In conventional measurement, the heat source is kept in contact with one cross-sectional end of the sample, and thus no temperature gradient is produced along cross plane direction of the sample, which yields no diffusion of charge carriers along $a \rightarrow b$ and $g \rightarrow h$ directions. In this case, the Seebeck coefficient of the composites will be determined by the Equation (1):

$$S = \frac{\sigma_{Ag}S_{Ag} + \sigma_{BTBA}S_{BTBA}}{\sigma_{Ag} + \sigma_{BTBA}}$$

where $\sigma_{Ag}$ and $\sigma_{BTBA}$ represent the electrical conductivity of Ag/PLA and BTBA/PLA composite layer, respectively, and $S_{Ag}$ and $S_{BTBA}$ represent the Seebeck coefficient of Ag/PLA and BTBA/PLA composite layer, respectively. From the expression (1) it is clear that for $\sigma_{Ag} \gg \sigma_{BTBA}$, the resultant Seebeck coefficient $S= S_{Ag}$, that is, the Seebeck coefficient will be dominated by the Ag/PLA composite layer. Ag, due to its metallic properties, has a very low Seebeck coefficient. Consequently, the addition of Ag in the Ag/PLA layer causes the low Seebeck coefficient of double-layer composites in a conventional measurement configuration (Figure 2e).

In the present measurement configuration, as shown in Figure 6, the charge carriers will follow the alternate charge transport route, where the charge carriers pass through the interfacial barrier along $b \rightarrow c$ and $f \rightarrow g$ directions. Thus, the low energy charge carriers are scattered at the interface, leading to a higher Seebeck coefficient. The Seebeck coefficient of non-degenerate semiconductors is related to scattering factors of charge carriers following the Equation (2):[32]

$$S = \frac{k_B}{\epsilon} \left[ (2.5 + r) + \ln \left( \frac{2(2\pi m^\ast k_B T)^{1/2}}{\hbar n} \right) \right]$$

Figure 5. a) SEM fracture surface image of DC5, b) EDS layered image for the corresponding area in panel (a).

Figure 6. Schematic illustration of transport mechanism of the charge carriers in the double-layer inorganic-polymer composites.

Figure 7. XRD patterns of the front side (Ag/PLA layer composites) and back side (BTBA/PLA layer composites) of the DC5.
where $k_B$, $h$, $r$, and $m^*$ are the Boltzmann constant, Planck constant, scattering parameter, and effective mass of the carrier, respectively. The scattering of charge carriers at the interfacial region along $b \rightarrow c$ and $f \rightarrow g$ directions increase the scattering parameter, resulting in enhancement of Seebeck coefficient based on Equation (2). The work function of the Ag particles is $\approx 4.3$ eV.[31] The BTBA particles have a higher work function (e.g., $\Phi_{BTBA} = 5.3$ eV).[32] The band gap between the BTBA and metallic Ag particles forms a Schottky barrier, and the nanometer-sized energy barriers are formed at the Ag/BTBA interface. Therefore, the BTBA/PLA–Ag/PLA composite boundary region (e.g., from $b \rightarrow c$ in Figure 6), and Ag/PLA–BTBA/PLA composite boundary region (e.g., from $f \rightarrow g$ in Figure 6), may prevent low energy holes for transmission, as a results only the holes with high-energy can pass through the interfaces (Figure 5).[35,36] The combined effect of the above-mentioned three factors lead to the double-layer composites not only maintain a high electrical conductivity, but also yield a high Seebeck coefficient for the DC1, DC2, DC3, and DC4; however, due to the relatively low Seebeck coefficient of Ag, further increasing the volume ratio of Ag until 45.6% for DC5, the Seebeck coefficient decreased from $\approx 80$ to 64 $\mu$V K$^{-1}$ at 300 K, although the electrical conductivity sharply increased.

The combined effect of BTBA with high Seebeck coefficient and Ag with high electrical conductivity exhibits outstanding contributions for improving the TE performance of the double-layer composites. This new transport mechanism of holes in double-layer inorganic-polymer composites offers a new strategy to enhance the TE performance of composites, and solution additive manufacturing can directly print the solutions which contain polymer matrixes and inorganic fillers into almost any designed intricate geometries of thermoelectric composites.[37] Therefore, this strategy for enhancing the TE properties and process for fabrication of inorganic/organic composites can be used for other inorganic-polymer composite systems.

3. Conclusions

Flexible double-layer inorganic/organic composites, containing layers of BTBA/PLA composites and Ag/PLA composites, have been fabricated by solution additive manufacturing. A highest power factor of 875 $\mu$W m$^{-1}$K$^{-2}$ was achieved at 360 K for the double-layer inorganic/organic composites with 41.7 vol. % of Ag in the Ag/PLA layer composites. The high TE performance is due to combined interfacial effects and carrier transport in the double-layer inorganic/organic composites. This transport mechanism in the double-layer inorganic/organic composites offers a strategy to enhance the thermoelectric performance of composites, and solution additive manufacturing can be used for a wide range of inorganic/organic composite systems.

4. Experimental Section

Materials: BTBA (Bi$_2$Sb$_3$Te$_3$, 200 mesh) was obtained from Shanghai Liuzu New Material Science and Technology, Inc.). Ag (200 mesh) and chloroform were purchased from Sinopharm Chemical Reagent Co., Ltd. PLA (1.75 mm 3D filament) was obtained from Shenyang Gein Technology Co., Ltd. All the materials have been used in their as-received state without further treatment or purification.

Preparation of BTBA/PLA Single Layer Composites: The preparation of BTBA/PLA single layer composites was as follows: PLA (0.5 g) was dissolved in chloroform (5 mL) to form Solution I, and then BTBA (2.0 g) was added and stirred for 2 h to produce Solution II. Solution II was inhaled in the syringes (10 mL) and then printed using a 3D solution printer (Shenzhen Polymer Science and Technology LTD. Model: PLM-I) with nozzle diameter of 0.5 mm and print speed of 300 mm min$^{-1}$ on the glass substrate to form the BTBA/PLA single layer composites.

Preparation of BTBA/PLA–Ag/PLA Double-Layer Composites: The preparation of BTBA/PLA–Ag/PLA double-layer composites is as follows: PLA (0.5 g) was dissolved in chloroform (5 mL) to form Solution I. An appropriate amount of Ag (1.5, 2.0, 2.5, 3.0, or 3.5 g) was added to Solution I and stirred for 2 h to produce Solution II. Solution II was inhaled in the syringes (10 mL) and then printed using a 3D solution printer (Shenzhen Polymer Science and Technology LTD. Model: PLM-I) with nozzle diameter of 0.5 mm and print speed of 300 mm min$^{-1}$ on the as-prepared BTBA/PLA single layer composites. After drying at room temperature for 12 h, the chloroform was evaporated from the mixed solution, forming the BTBA/PLA–Ag/PLA double-layer composites. The process for preparation of Ag/PLA single layer composites was similar to that of BTBA/PLA–Ag/PLA double-layer composites, which is directly printed from Solution II on the glass substrate.

Characterization: The compositions and morphologies of the samples were characterized by X-ray diffraction (XRD) (Bruker D8 Advance, Germany) and scanning electron microscopy (SEM LEO 1550 Gemini equipped with Oxford AZtec system of energy dispersive X-ray spectrometer (EDS)). The SEM sample was prepared by conventional mechanical polish. In-plane Seebeck coefficients and electrical conductivities of the bottom surface (BTBA/PLA layer) for BTBA/PLA–Ag/PLA double-layer composites were measured simultaneously in an MRS-3L thin-film thermoelectric test system in a low-vacuum atmosphere ($\leq 500$ Pa) from 300 K to 360 K with instrument test errors of 6% and 5% for Seebeck coefficient and electrical conductivity, respectively (Wuhan Giant Instrument Technology Co., Ltd., China). Three measurements of the Seebeck coefficients and electrical conductivities were performed for each sample, and the average values are reported.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
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