Sequential Infiltration Synthesis of Doped Polymer Films with Tunable Electrical Properties for Efficient Triboelectric Nanogenerator Development

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Triboelectric nanogenerator (TENG) is rising as a promising technology for converting mechanical energy into electricity with merits of high output, simple design, and low cost. Recent research efforts have largely improved its power density and thus enabled a number of applications varying from driving small electronics, to charging batteries, and to activating chemical reactions. A typical TENG design possesses two dissimilar surfaces (mostly polymer) with different electron affinities, electrons transfer across the interface to compensate for the difference of surface potentials. This charge separation is the primary principle of mechanical to electric conversion. A typical TENG design possesses two electrodes attached to the triboelectric active materials, where electrostatic charges are induced. Once the device capacitance changes (e.g., by displacement), current flow occurs between the two conductive electrodes and thus outputs electric power. Therefore, controlling the charge density on the triboelectric surfaces is the most fundamental strategy for improving the performance of TENG. Nowadays, surface modification of triboelectric polymer is the predominant approach to regulate the charge density. For instance, morphologies like nanowire, nanoparticle, or other nanoscale patterns are frequently adopted to raise the surface area of triboelectric materials and thus enable more charge carrying site. In addition, surface functionalization and ionized species can also be introduced to improve the charge density on polymer surfaces. However, operation of TENGs requires intimate contact and sometimes friction between the triboelectric materials, which inevitably induces wearing of surface. In this regard, surface modification/engineering yields little contributions toward the performance gain in long-term operation. Therefore, one essential solution is to extend the property engineering from mere surface to the bulk of material.

Atomic layer deposition (ALD) is a powerful thin film growth technique on the basis of sequential self-limiting surface reactions. When implemented to certain polymer materials, the large permittivity of metalorganic precursors allows deep infiltration of the inorganic compounds during the ALD process, leading to inorganic/organic hybrid materials. This process is known as sequential infiltration synthesis (SIS). It has been successfully used to convert the block co-polymer nanopatterns into more durable inorganic patterns and to improve the polymeric lithography resistance to subsequent etching. Inspired by this development, we expect SIS could effectively tailor the internal composition and electrical properties of polymer films, which may provide an ultimate solution for triboelectric material design in the development of high-performance TENGs. In this Communication, we report an internal AlOx doping of several polymers via SIS, including polydimethylsiloxane (PDMS), polyimide (Kapton), and poly(methyl methacrylate) (PMMA). We showed that SIS can introduce AlOx molecules ≈3 µm deep into these polymers, which effectively tuned the bulk electrical property of the film. TENG devices using the modified polymer films exhibited enhanced power output; and this enhancement remained effective after the surface of polymer film was polished off for more than 2 µm. This polymer doping approach opens a new route to bulk electrical property modification of polymer films, demonstrating a promising strategy for improving the performance of functional polymer based devices, such as TENGs.

AlOx was selected as the inorganic material to dope the polymer film since trimethlyaluminum (TMA, ALD precursor of Al2O3) has desirable permittivity in a number of polymers including polystyrene, polypropylene, polyethylene, poly(vinyl) chloride), and PMMA. A homemade ALD system was applied to sequentially introduce TMA and H2O vapor toward the polymer film at 80 °C with controlled exposure time and cycles. The SIS doping process followed a typical ALD operation procedure except that the supplying time of TMA was extended to 5 s to promote its infiltration into the polymer film (see the Experimental Section for details). The infiltration results were first characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Figure 1a,b shows the cross-sectional images and corresponding elemental mappings of the pristine PDMS film and the same film after 5-cycle sequential TMA/H2O infiltration (marked as AlOx-doped PDMS), respectively. PDMS elements including silicon (Si), oxygen (O), and carbon (C) were all identified uniformly distributed in the pristine film and no aluminum (Al) signal was detected (Figure 1a, ii–v). From

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DOI: 10.1002/adma.201502546
the SIS-treated PDMS film, Al signal was clearly detected and was concentrated within the top ≈3 µm region revealing the effective infiltration depth (Figure 1b, ii). No Al signal could be detected deeper inside the film (Figure S1, Supporting Information). Other than the Si element that was still uniformly distributed in the entire PDMS film (Figure 1b, iii), both O and C elements exhibited a concentrated signal within the top ≈3 µm region that was in good accordance with Al distribution. The concentrated O element could be attributed to H₂O precursor infiltration that reacted with TMA forming Al₂O bonds. The unreacted methyl groups on TMA could be the main source responsible for the concentrated C signal. This elemental distribution analysis evidences the successful deep infiltration of both precursors in the polymer film and no surface coating of Al₂O₃ was identified.

The elemental feature and bonding state of Al₂Oₓ-doped PDMS film were further studied by X-ray photoelectron spectroscopy (XPS). Figure 1c shows the XPS spectra of both pristine PDMS and Al₂Oₓ-doped PDMS samples. The characteristic peaks of PDMS including Si 2p, Si 2s, C 1s, O 1s, and O KLL peaks were identified from both films. From the Al₂Oₓ-doped PDMS sample, a small signal of Al 2p also appeared in the low binding energy region, suggesting the existence of Al element. To reveal the chemical environment of Al inside the polymer, Al 2p spectrum was individually scanned and compared with Al 2p peak of standard ALD-grown Al₂O₃ on silicon substrate (Figure 1d). The shift of peak position from 75.6 to 74.7 eV evidenced the presence of unstable defective oxides such as Al₂O and AlO.⁴¹ The nonstoichiometric aluminum oxide may introduce extra charge carrier sites, which could raise the total charge capacitance of Al₂Oₓ-doped PDMS film and therefore enhance the output of TENGs. To evaluate this hypothesis, the dielectric constant was measured from both PDMS films. As shown in Figure 1e, Al₂Oₓ doping raised the dielectric constant from ≈2.4 of the pristine PDMS to ≈2.7 within the testing frequency range. Higher dielectric constant suggests that the Al₂Oₓ-doped PDMS film could handle more induced electrostatic charges resulted from the triboelectric effect.

The deep infiltration of Al is attributed to the good solubility of TMA precursor in the polymer material. With the similar chemical property, diethylzinc (DEZ) also exhibited excellent infiltration capability into PDMS to dope PDMS with ZnOₓ. EDS elemental mapping of the PDMS film after 5-cycle SIS of DEZ and H₂O clearly identified Zn elements within the top.
Because inorganic precursors typically exhibit very limited solubility in organic polymer materials, they are not desirable for SIS polymer doping. As a demonstration, titanium tetrachloride (TiCl₄) and vanadium oxytrichloride (VOCl₃) were applied to infiltrate PDMS. EDS elemental mapping of the PDMS film after 5-cycle SIS of TiCl₄ and VOCl₃ revealed nearly none Ti and V signal from the entire cross-section region (Figures S4 and S5, Supporting Information). However, it should be noted that TiOₓ, VOₓ, and other metal oxides doping in polymers are expected to be effective if metal organic ALD precursors like titanium isopropoxide (TTIP) and vanadium oxytriisopropoxide (VTIP) were used. The broad selection of metal organic ALD precursors evidences the excellent flexibility of the SIS technique in triboelectric polymer doping.

Typically, materials with distinct electron affinities (i.e., maximum difference in the tendency to gain or repulse electrons from each other) are desired to maximize the charge generation upon contact for high-performance TENG design. Same materials or materials with close electron affinities are not able to produce appreciable electric output. The SIS doping technique allows us to arbitrarily tune the bulk electron affinities of polymer materials and thus largely broadens the material choices.

Figure 2. Design and performance of AlOₓ-doped PDMS TENG. a) Schematic of charge redistribution between pristine PDMS and AlOₓ-doped PDMS films upon contact as a consequence of triboelectrification. b) The open-circuit voltage (V_{oc}), c) short-circuit current density (J_{sc}), and d) charge transfer amount under short-circuit condition (ΔQ_{sc}) of TENGs composed of PDMS with and without AlOₓ doping. The inset in (c) is the enlarged current output (dashed square box in (c)) created by one pressing and releasing cycle.
for the untreated PDMS pair. Although theoretically, the PDMS pair was not supposed to exhibit any electric output, the small signal might be caused by the slight variation of PDMS films in terms of size, thickness, and surface roughness. The electrical property engineered by SIS doping was found very durable. A TENG device was repeatedly tested for 60 days and no deterioration of output voltage could be identified (Figure S7, Supporting Information).

An individual peak profile of the $j\text{--}t$ curve further reveals the influence of AlO$_x$ doping to the electron affinity of PDMS films. During the measurement, the positive and negative electrodes of the current meter were connected to pristine PDMS and AlO$_x$-doped PDMS films, respectively. Therefore, positive signal represents current flow from the pristine PDMS to AlO$_x$-doped PDMS, and vice versa. As shown in the inset of Figure 2c, a positive current pulse was generated first when both surfaces were brought into contact, suggesting electrons were moved from AlO$_x$-doped PDMS electrode to pristine PDMS electrode. This evidenced the AlO$_x$ doping enabled strong tendency of giving away electrons to the untreated PDMS. When the two surfaces were detached, the local charge equilibrium was broken again and electrons flew back generating a negative current pulse. The AlO$_x$-doped PDMS and pristine PDMS films were also assembled with traditional positive (PMMA) and negative (polytetrafluoroethylene, PTFE) triboelectric materials. Due to the reduced electron affinity, enhanced output was obtained from the pair of PTFE-AlO$_x$-doped PDMS, while PMMA-AlO$_x$-doped PDMS exhibited reduced output (Figure S8, Supporting Information). These results further evidenced this SIS polymer doping strategy can be effectively and generally applied to polymer-based TENG devices.

To further investigate the SIS doping effect, multiple PDMS films were subjected to SIS doping with different cycles and then assembled into TENG devices with identical configuration as described previously (Figure S6, Supporting Information). The open circuit voltage was tested under identical conditions as the measure of their electrical property variation. The peak $V_{oc}$ was plotted as a function of the SIS cycle and shown in Figure 3a. It was found that only two cycles of SIS were able to boost the average value of $V_{oc}$ from 0.3 to 1.9 V, suggesting the high effectiveness of this polymer modification approach. The $V_{oc}$ further increased following the SIS cycles and saturated at $\approx$2.4 V after ten cycles of infiltration. The $V_{oc}$ variation is believed to be closely related to the unique reaction process of SIS AlO$_x$ in polymer materials. During the first approximately ten cycles of infiltration synthesis, TMA diffused into PDMS and accumulated inside the polymer film, resulting in the rapid increase of $V_{oc}$. Further deposition might saturate the surface layer and prevent further infiltration inside. Thus the growth mode switched back to regular ALD deposition of continuous AlO$_x$ film on the surface.[24] Because additional cycles of infiltration contributed no internal doping, the electric property and corresponding triboelectric voltage output would not exhibit any further change. This investigation reveals the up limit of the SIS doping strategy.

Compared to conventional surface modification/functionalization, a unique merit of SIS doping is the property engineering in bulk volume, which is substantially important for TENG application because of the inevitable wearing issue during operation. To illustrate this merit, we polished the AlO$_x$-doped PDMS film to different level and measured the performance of corresponding TENG devices. As shown in Figure 3b, the polymer film was still capable of delivering $\approx$95% of the highest $V_{oc}$ after the top $\approx$2 μm was polished away from the polymer surface. This favorable outcome can be intuitively expected since the detectable penetration depth of AlO$_x$ was $\approx$3 μm and considerable amount of AlO$_x$ still existed in the PDMS film with a tailored electric property after the removal of top $\approx$2 μm. After removing $\approx$3 μm PDMS from the surface, the voltage output started to reduce dramatically and eventually reached the minimal $V_{oc}$ at $\approx$0.3 V when more than $\approx$5 μm polymer was removed. The minimal voltage output was at the same level as that generated by a pair of untreated PDMS surfaces (Figure 2b) because of the complete removal of AlO$_x$ dopants in the polymer. The insets of Figure 3b compare the
EDS mappings of PDMS film before and after removing the top ≈5 µm material, confirming the absence of Al element.

This SIS doping strategy is versatile in engineering the property of a broad range of polymer materials because of the appreciable permittivity of the metalorganic precursor within most polymer chains. As a demonstration, two more polymers, Kapton and PMMA, were selected for SIS AlOₓ doping. EDS analysis confirmed successful infiltration of Al-containing materials.

Figure 4. Design and performance of a–d) AlOₓ-doped Kapton and e–h) AlOₓ-doped PMMA TENGs. a) Schematically illustration of AlOₓ-doped Kapton TENGs with a configuration of pristine Kapton/ITO/PET as the bottom electrode and AlOₓ-doped Kapton/ITO/PET as the top electrode. b) \(V_{oc}\), c) \(J_{sc}\), and d) \(\Delta Q_{sc}\) characterizations of TENGs made from Kapton with and without AlOₓ doping. e) Schematic of AlOₓ-doped PMMA TENGs with a configuration of ITO/PET as the bottom electrode and AlOₓ-doped PMMA/ITO/PET as the top electrode. f) \(V_{oc}\), g) \(J_{sc}\), and h) \(\Delta Q_{sc}\) characterizations of TENGs assembled from PMMA with and without AlOₓ doping.
molecules. For both materials, the depth of infiltration is ≈3 µm for five cycles of SIS, which is similar to PDMS (Figures S9 and S10, Supporting Information). Based on the polymer’s intrinsic electron affinity, the output of voltage could be tuned toward different directions. Similar to PDMS, Kapton has strong capability of acquiring electrons and always presents a negatively charged surface when contacts most other materials. By SIS doping of AlOₓ, the electron affinity of Kapton could be significantly reduced, same as PDMS. When AlOₓ-doped Kapton was brought together with a pristine Kapton film for triboelectric charge generation, drastic electron transfer was enabled from AlOₓ-doped Kapton to untreated Kapton leaving positive charges on the AlOₓ-doped Kapton surface and the other one charged negatively (Figure 4a). Based on the same operating mechanism described for the PDMS case, triboelectric outputs were substantially increased by SIS doping. As shown in Figure 4b–d, the AlOₓ-doped Kapton TENG device yielded average peak values of 5.1 V for Vosc, 5.6 µA cm⁻² for Jsc, and 47 µC m⁻² for ΔQsc, which were approximately one order of magnitude higher than those generated by the untreated Kapton pairs.

Different from PDMS and Kapton, PMMA is a polymer with a strong tendency to give away electrons when contacts other materials. This is the same capability offered by AlOₓ doping. Therefore, higher positive charge density can be expected by introducing AlOₓ doping into PMMA. Such enhancement is highly desirable for raising the performance of TENGs built with dissimilar materials since it increases the top limit of induced free charges that in turn raises the maximum triboelectric output. To demonstrate this effect, a TENG device was assembled using AlOₓ-doped PMMA and ITO as two contacting surfaces (schematically shown in Figure 4e). In this design, electrons are always injected from PMMA to ITO surface during the contact and results in the accumulation of positive electrostatic charge on the PMMA surface. Figure 4f–h compares the triboelectric outputs of PMMA-based TENGs with and without AlOₓ doping. The measurements clearly showed that upon AlOₓ doping, the Vosc was improved from 0.9 to 3.1 V, Jsc was raised from 1.0 µA cm⁻² to 5.5 µA cm⁻², and ΔQsc was increased from 12 µC m⁻² to 54 µC m⁻². Such a significant enhancement is the consequence of increased positive charge density on the PMMA surface due to AlOₓ infiltration.

In summary, the SIS technique was successfully applied to infiltrate AlOₓ molecules into polymer films and tune their electrical properties. TMA precursor was found to be able to travel into various polymer materials (e.g., PDMS, Kapton, and PMMA) with a diffusion depth of ≈3 µm under mild deposition conditions and form AlOₓ species inside the polymer film. Due to the AlOₓ molecules’ strong tendency of repulsing electron, the electron attaining capability of AlOₓ-doped polymer with strong electron affinity was significantly reduced compared to its original state. This effect allows the creation of high-performance TENG devices with the same polymer materials. If the host polymer has the same trend of repulsing electron as the AlOₓ dopant, such as PMMA, the capacitance of induced charge can be raised and significant performance gain of TENG devices can be expected. Furthermore, different from surface modification/functionualization that was commonly implemented in TENG performance tuning, the SIS doping changes the polymer’s bulk property. Therefore, the resulted enhancement would not be diminished even after the polymer surface was worn during long-term operation. Therefore, the SIS doping strategy holds a great promise in tuning the performance of polymer-based electronic or dielectric devices, such as TENGs for effective mechanical energy harvesting.

**Experimental Section**

*Fabrication of Polymer Films: PDMS films were made from a mixture of liquid PDMS elastomer and cross-linker with a ratio of 10:1, which was uniformly casted on a flat silicon substrate. After degasing in vacuum for 20 min and curing at 80 °C for 2 h, a PDMS film was received. PMMA films were fabricated by spin-coating the liquid precursor onto ITO/PET substrate at 2000 rpm for 120 s and annealing at 70 °C for 30 min. The liquid precursor was made by dissolving PMMA powder (molecular weight: ≈50 000) into chlorobenzene solvent with a concentration of 4 wt%. Commercial Kapton and PTFE tape was directly attached to ITO/PET substrate for TENG assembly. For the wear test of AlOₓ-doped PDMS, the polymer film was polished using the tripod method[40] with a speed of 30 rpm. The finest sandpaper (100 nm) was used to achieve maximal flatness of the polished surface.*

*Doping Polymer via SIS: A home-made ALD system was used to infiltrate AlOₓ into the polymer films. The target polymer film was loaded on a quartz boat and placed at the position 5 cm away from the precursor inlet nozzle. N₂ gas with a flow rate of 40 sccm was introduced into the chamber as the carrier gas, which yielded a base pressure of 650 mTorr. The chamber temperature was maintained at 80 °C during the entire infiltration process. TMA and H₂O vapors were pulsed into the deposition chamber separately with a pulsing time of 5 and 1 s, respectively, and separated by 60 s N₂ purging. Therefore, one SIS cycle involves 1 s of H₂O pulse + 60 s of N₂ purging + 5 s of TMA pulse + 60 s of N₂ purging. After the infiltration, the chamber was cooled down naturally under N₂ flow. The DEZ, TiCl₄, and VOCl₃ infiltration experiments were conducted following the same procedure of AlOₓ penetration except replacing TMA with DEZ, TiCl₄, and VOCl₃.*

*Assembly and Measurements of TENGs: For PDMS- and Kapton-based TENGs, AlOₓ-doped polymer films with a size of 1 cm × 1 cm were attached to the center of an ITO/PET substrate (2 cm × 5 cm), which was considered as the top electrode. Bottom electrode was composed of stainless steel (1 mm in thickness) and connected to the external circuit through copper tapes. For PMMA-based TENGs, a blank ITO/PET and an ITO/PET attached with a AlOₓ-doped PMMA film (1 cm × 1 cm) were used as the bottom and top electrodes, respectively. For PDMS/PTFE and PDMS/PMMA TENGs, PDMS with or without AlOₓ doping (1 cm × 1 cm) was attached on ITO/PET substrate as the top electrode. PTFE and PMMA film (1 cm × 1 cm) attached on ITO/PET substrate were used as the bottom electrode. During the performance measurement, the top electrode was pressed to the bottom electrode by a computer-controlled shaker with a frequency of 10 Hz and the bottom electrode was anchored on the table surface. The voltage outputs were recorded using an Agilent DSO1012A oscilloscope. The current outputs and charge transfer amount of TENGs were measured using an Autolab PGSTAT302N station.*

*Morphology and Elemental Characterizations: SEM measurements and EDS mappings were performed on Zeiss Leo 1530 field-emission microscope. XPS was conducted on a Thermo Scientific K-alpha XPS instrument. The survey range was from 0 to 1000 eV. The Al 2p spectra were measured for characterizing the chemical structures of AlOₓ in the*
PDMS film. Dielectric constant measurements were conducted on the Agilent E4980A Precision LCR Meter.

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

Acknowledgements
The authors thank Professor Paul Voyles and Ms. Pei Zhang for helping with the polishing process and access to the tripod polishing machine. This work was primarily supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under Award No. DE-SC0008711.

Received: May 28, 2015
Revised: June 17, 2015
Published online: