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Subhodeep Chatterjee and Zong-Hong Lin conceived and planned the experiments. Subhodeep Chatterjee, Subhajit Saha, Snigdha Roy Barman and Dukhyun Choi carried out the experiments. Subhodeep Chatterjee, Zong-Hong Lin and Sangmin Lee illustrated the sensing mechanism. Imran Khan and Yu-Ping Pao contributed to sample preparation. Subhodeep Chatterjee, Subhajit Saha, Snigdha Roy Barman, Imran Khan, Yu-Ping Pao and Zong-Hong Lin contributed to the interpretation of the results. Zong-Hong Lin took the lead in writing the manuscript. All authors provided critical feedback and helped shape the research, analysis and manuscript.
Enhanced Sensing Performance of Triboelectric Nanosensors by Solid-Liquid Contact Electrification

Graphical Abstract

Solid-liquid triboelectric nanosensors (TENSs) were successfully demonstrated by utilizing TiO\textsubscript{2} nanosheet arrays as the solid triboelectric layer, and various liquids including water, ethanol and acetone were compared to optimize the sensing performance. The ligand-to-metal charge transfer is attributed to the sensing mechanism, which results in lowering the work function of the TiO\textsubscript{2} nanosheet arrays and boosting the output voltage.
Enhanced Sensing Performance of Triboelectric Nanosensors by Solid-Liquid Contact Electrification

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Abstract:
Triboelectric nanogenerators (TENGs) and triboelectric nanosensors (TENSs) are the prime backbones for the realization of environmental mechanical energy harvesting and self-powered sensing applications. However, the low efficiency of concurrent solid-solid contact electrification creates a major bottleneck for the growth of highly promising technologies. To address this problem, herein, we report a strategic protocol to design a TENS by solid-liquid contact electrification for chemical sensing purposes as well as an efficient approach for the chemical enhancement of solid-liquid TENGs. In particular, TiO$_2$ nanosheet arrays and various solvents (including water, ethanol and acetone) are employed as solid triboelectric materials and contact liquids, respectively, for the demonstration of solid-liquid contact electrification for mechanical energy harvesting and catechin detection. As a self-powered sensor, the TiO$_2$ nanosheet array-based TENS provides superior advantages such as long-term stability, frequency-independent output and humidity-insensitive properties compared to previously reported solid-solid TENSs. The chemically enhanced sensing mechanism of the TiO$_2$ nanosheet array-based TENS for catechin detection is further confirmed with the decrease in the work function and can provide a wide linear window (100 nM to 100 µM) and a low detection limit (30 nM). All the results support solid-liquid TENSs pave a new path toward efficient self-powered sensors for environmental and healthcare monitoring.

Keywords: Contact electrification, chemical enhancement, triboelectric nanogenerator, TiO$_2$, self-powered sensor, catechin
1. Introduction

In the context of the increasing demand for energy, harvesting renewable energy has become a prime concern in the field of energy research. Over the past few years, extensive research efforts in this field have yielded nanogenerators as promising candidates for harvesting renewable energy from mechanical vibration [1, 2], wind [3, 4] and heat [5, 6]. In particular, triboelectric nanogenerators (TENGs) have been proven to be cost effective, easily fabricable and robust devices for mechanical energy collection [7, 8]. TENGs can harvest mechanical energy through a periodic contact-separation process where surface charge transfer occurs when two materials with opposite triboelectric polarity come into contact with each other. In response to mechanical vibration, oppositely charged surfaces can create a potential difference that directs the flow of electrons through an external circuit [9, 10].

Later, in 2013, triboelectric nanosensors (TENSs) that further functionalize the surface of TENGs with probe molecules were demonstrated as an emerging analytical tool for the self-powered detection of small molecules and heavy metal ions, such as mercury ions [11], dopamine [12, 13], phenol [14], catechin [15] and thrombin [16]. TENSs provide an efficient alternative approach to replace conventional chemical sensors based on amperometry [17], potentiometry [18] or conductimetry [19], which demand external power during the sensing process. However, improvement in triboelectric performance is one of the major challenges for developing entirely integrable, stand-alone TENSs. For the contact electrification of solid-solid materials, several approaches have been reported to maximize the charge density on triboelectric surfaces either by selecting materials with a large difference in triboelectric polarity [20] or changing the morphology of contact surfaces by growing different nanostructures or depositing nanomaterials to increase the surface-to-volume ratio [8-11]. However, achieving long-range
nanostructural uniformity on flexible and wear-resistant surfaces is highly challenging and therefore creates a serious bottleneck for the realization of solid-solid TENSs.

Since the charge density over a solid triboelectric surface is closely related to the surface chemical properties, surface chemical engineering via functionalization has also been reported extensively for attaining enhanced solid-solid contact electrification. However, chemically modified solid-solid contact electrification suffers mostly from low sensitivity and short-term stability for several reasons. First, it has been observed that after contact between two solid materials, the generated triboelectric charges are usually confined within specific regions on the solid surfaces. Therefore, it is very difficult to obtain complete transfer and separation of triboelectric charges after the contact process, which severely affects the electric output and consequent sensitivity of TENS. Moreover, solid-solid contact electrification is highly sensitive to ambient conditions such as surrounding humidity and atmospheric pressure. Additionally, continuous collision and friction between two solid surfaces with wear abrasion results in mechanical degradation with time, which in turn deteriorates the sensing performance of the TENS.

Recent research efforts indicate that the abovementioned problems may be overcome if solid-solid contact electrification is replaced with solid-liquid contact electrification. TENGs based on solid-liquid contact electrification can harvest ambient mechanical [21, 22] and electrostatic energy under various liquid environments [23, 24] and therefore have great potential to be employed as efficient tools for chemical sensing. A zero threshold of shearing force enables liquids to facilitate complete contact with other solid materials, generating better triboelectric outputs. Apart from this, the liquid layer acts as a good lubricant that allows smooth movement of solid and liquid surfaces, thereby improving the durability of the solid-liquid TENG.
Moreover, the output performance of the solid-liquid TENG is not affected by environmental factors [25].

However, the solid surface after contact separation usually contains some residual liquid, which creates a barrier in achieving high electric output. Considerable research efforts have been dedicated to achieving superhydrophobic solid surfaces by developing specific nanostructures that can overcome the surface wetting problem. Second, high triboelectric output is also expected if organic volatile nonpolar solvents are utilized as the contact liquid instead of making the solid surface hydrophobic. However, the implementation of this concept to avoid surface wetting problems remains almost unexplored in the literature.

To bridge this gap, herein, we not only report solid-liquid TENS for the self-powered detection of chemicals for the first time but also apply volatile solvents to overcome the sensor surface wetting problem. The solid-liquid TENS is designed with TiO$_2$ nanosheet arrays as the solid triboelectric material and various solvents (water, ethanol and acetone) as the contact liquid. In particular, TiO$_2$ was employed as a triboelectric layer for our TENS due its nontoxicity, biocompatibility and cost effectiveness. Moreover, Chemical enhancement of solid-liquid contact electrification is also verified by selecting catechin as the targeting molecule. The electron donating catechol group of catechin promotes the transfer of electrons to Ti through the formation of ligand-to-metal charge transfer (LMCT) complex. Therefore, the surface charge density of TiO$_2$ varies as per the concentration of catechin and the TENS can selectively detect the target analyte. In fact, real-time and cost-effective monitoring of catechin concentrations in different food beverages and human plasma is extremely important because of the antioxidative properties of catechin, which can prevent cardiovascular diseases, cancer, diabetes [26-28], etc.

Under optimized conditions, the TiO$_2$ nanosheet array-based TENS designed in this work
exhibits a limit of detection (LOD) as low as 30 nM and a wide sensing range from 100 nM to 100 µM.

2. Experimental Section

2.1 Growth of TiO$_2$ nanosheet arrays on Ti wire and catechin modification

TiO$_2$ nanosheet arrays were grown over Ti wire via a two-step hydrothermal synthesis reported previously [29, 30]. The detailed process is schematically represented in Scheme 1. In the first step, Ti wire was cleaned ultrasonically in acetone, ethanol and water sequentially for 10 minutes and then placed in a Teflon-lined stainless-steel autoclave filled with NaOH solution (0.2 M). Then, the sealed autoclave was heated in an oven at 140°C for more than 24 hours, which led to the reaction between Ti and the alkali solution, resulting in densely grown Na$_2$Ti$_2$O$_4$(OH)$_2$ nanosheet arrays on the surface of the Ti wire (Figure S1). After cooling and rinsing in water, the Ti wire was immersed in HCl solution (1 M) for 10 minutes to substitute Na$^+$ with H$^+$ via an ion-exchange process, which led to the formation of H$_2$Ti$_2$O$_4$(OH)$_2$ nanosheet arrays. Then, the samples were rinsed in water again and dried at ambient temperature overnight. Finally, the Ti wire was calcined in an oven at 500°C for 3 hours to obtain TiO$_2$ nanosheet arrays on its surface.

For surface modification with catechin, the separate Ti wires with TiO$_2$ nanosheet arrays were directly immersed in different concentrations of catechin solution (1 nM, 10 nM, 100 nM, 1 µM, 10 µM, 100 µM, 1 mM and 10 mM) and allowed to react for 1 hour. After the reaction, the catechin-modified samples were dried at ambient temperature prior to the material characterizations and electrical measurements.
2.2 Material characterizations and electrical measurements

For comprehensive study of the morphology, structure, and chemical composition of the samples, the grown TiO$_2$ nanosheet arrays and catechin-modified TiO$_2$ nanosheet arrays were extensively characterized through various advanced techniques. The phase purity and crystallinity of the grown samples were analyzed by using a powder X-ray diffractometer (XRD, Rigaku TTRAX III). The surface morphology of the as-prepared TiO$_2$ nanosheet arrays was characterized by using field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) and cold-field emission scanning electron microscopy (SEM, Hitachi SU8010). Compositional analysis was carried out by X-ray photoelectron spectroscopy (ESCALAB 250 XI, Thermo Scientific). The X-ray photoelectron spectrometer was equipped with an Al K$\alpha$ X-ray source and hemispherical analyzer. All binding energies have been corrected for sample charging effect with reference to the C1s line at 284.6 eV, and the high-resolution core-level spectra were deconvoluted by using CASA XPS software. The work function of the synthesized samples was measured by ultraviolet photoelectron spectroscopy (UPS) using a He I ($h\nu=21.2$ eV) UV source under ultrahigh vacuum conditions. Moreover, the dimension and natural crystallinity of the grown samples were investigated by high-resolution transmission electron microscopy (HRTEM, JEOL-JEM-F200). Amplitude modulated Kelvin probe force microscopy (AM-KPFM) was employed to monitor the surface potential distribution of the catechin-modified TiO$_2$ nanosheet arrays. Furthermore, a low-noise voltage preamplifier (Stanford Research Systems Model SR560) was used to measure the output performance of the developed solid-liquid TENS.

2.3 Measurement setup of the solid-liquid TENS
The solid-liquid TENS was operated under a single-electrode configuration where the Ti wire and the ground acted as the electrodes. The as-synthesized TiO$_2$ nanosheet arrays and catechin-modified TiO$_2$ nanosheet arrays grown on the Ti surface act as the solid-friction layer, and solvents (water, ethanol and acetone) loaded on a glass container play the role of contact liquids. The active sensing area of the TENS device was calculated as 1.911 cm$^2$ (wire diameter = 2 mm, length = 3 cm). The container was then placed on a swing oscillator such that the solid layer could make periodic contact with the solvents to generate triboelectric charges and consequent stable electric output. A bridge rectifier circuit was connected between the TENS and SR-560 electrometers to regulate the voltage cycles only.

2.4 Catechin detection from commercially available green tea

Method of standard addition was adopted to detect the unknown catechin concentration in commercially available green tea specimen. Prior to detection, the green tea sample has been diluted in 5 ml of D.I. water. Then the diluted samples were spiked with different standard concentration of catechin (0, 20 µM, 40 µM, 60 µM & 80 µM) and the remaining volume was filled up by adding D.I. water in order to keep the volume constant for each standard added concentration. Later catechin spiked solutions were reacted with TiO$_2$ nanosheet arrays for 1 hour to enable the selective binding between Ti and catechol group. Output voltage responses were recorded for the TiO$_2$ nanosheet arrays modified with those catechin spiked solutions and the corresponding calibration curve was obtained. The concentration of the diluted sample can be determined from the slope ($m$) and $y$-intercept of the calibration curve ($c$) using the equation: $x = \frac{c}{m}$. Otherwise it is also allowable to determine the unknown concentration of the diluted sample directly from the absolute value of $x$-intercept of the calibration curve.
3. Results and discussion

3.1 Structural and compositional analysis

Grown TiO$_2$ nanosheet arrays exhibit strong crystallinity and high phase purity, which is evidenced from the XRD pattern of the synthesized samples, as shown in Figure 1a. The inset of Figure 1a shows a digital photograph of the TiO$_2$ nanosheet arrays grown over a single Ti wire. Strong XRD peaks corresponding to the (011), (123), (220), and (224) lattice planes can be readily attributed to the formation of anatase TiO$_2$ (JCPDS Card No. 65-2900) [15]. The formation of a thin sheet-like geometry of TiO$_2$ on Ti wire is confirmed from the FESEM and TEM images, as shown in Figure 1b and 1c, respectively. The FESEM image clearly indicates the long-range uniformity of vertically grown TiO$_2$ nanosheets over the Ti surface. The thickness of each sheet is found to be approximately 2-5 nm. These nanosheets also exhibit well-resolved lattice fringes with an interplanar spacing of 0.31 nm, corresponding to the (011) lattice plane of anatase TiO$_2$ (inset of Figure 1c). It is also interesting to note that even after surface modification by catechin, the TiO$_2$ nanosheet arrays retain their structural integrity (FESEM image, Figure S2).

XPS survey scan and EDS analysis reveal the presence of all constituent elements on the sample surface (Figure S3). The surface chemical composition of the TiO$_2$ nanosheet arrays before and after catechin modification was thoroughly analyzed by high-resolution XPS. Ti 2p core level spectra of both the TiO$_2$ nanosheet arrays and catechin-modified TiO$_2$ nanosheet arrays contain two peaks corresponding to the $2p_{1/2}$ and $2p_{3/2}$ spin orbit split components of Ti$^{4+}$ ions (Figure 1d). It is also interesting to note that after catechin modification, the Ti 2p core level spectra shift to the lower binding energy side, which is a direct consequence of the electron density enrichment around the Ti atoms due to the formation of Ti-O-C bonds on the surface of
Catechin-induced Ti-O-C bond formation can also be traced from the analysis of high-resolution O 1s core level spectra of the TiO$_2$ nanosheet arrays and catechin-modified TiO$_2$ nanosheet arrays shown in Figure S4 and Figure 1e, respectively. The high-resolution core level spectra of O 1s show a clear contribution from the lattice oxygen and surface adsorbed hydroxyl groups present in the TiO$_2$ nanosheet arrays. However, surface modification with catechin reveals a significant contribution from Ti-O-C bonds (531.7 eV) and C-O-C or C-OH bonds (533.2 eV) due to the attachment of catechin molecules on the surface of the TiO$_2$ nanosheet arrays [32]. The same trait is again reflected from the high-resolution core level spectra of C 1s (Figure 1f), which boast the contributions of C-C or C=C (284.7 eV), C-O (286.3 eV) and C=O (288.6 eV) bonds appearing from the surface catechin molecules [33, 34]. The obtained results conclusively verify the post-functionalization attachment of catechin to the TiO$_2$ nanosheet arrays.

### 3.2 Working principle of the solid-liquid TENS

Figure 2 illustrates the working principle of the solid-liquid TENS, which is mainly based on two sequential phenomena of contact electrification and electrostatic induction. Contact electrification generates static surface charges, and electrostatic induction drives the electrons under the potential difference created by the applied mechanical force. In the actual experiment, the TiO$_2$ nanosheet arrays and contact liquid are subjected to controlled mechanical force through a swing oscillator to make periodic contact-separation movements for the generation of serial triboelectric outputs. When TiO$_2$ nanosheet arrays are immersed in the liquid, owing to their different tendencies to gain or lose electrons as per the position in the triboelectric series [15], electrons are injected from the TiO$_2$ nanosheet arrays to the contact liquid. Hence, the TiO$_2$
surface becomes positively charged, and the surface of the contact liquid becomes negatively charged, as shown in Figure 2a. As the produced triboelectric charges from either side are entirely balanced by each other upon full contact, no electrons flow through the external circuit.

In the next step, as the TiO$_2$ surface is gradually withdrawn from the contact liquid, the state of equilibrium is broken as the TiO$_2$ surface still retains its positive charges (Figure 2b). In this situation, to maintain the electrical neutrality, electrons will flow from the ground through the external circuit to the Ti electrode. The observed output current is proportional to the potential difference between the TiO$_2$ surface and the ground. This process continues until an equilibrium state is reached, and the TiO$_2$ surface becomes entirely separated from the liquid (Figure 2c). As soon as the TiO$_2$ surface initiates contact with the liquid again, it generates an opposite potential difference that results in electrons flowing from the Ti electrode to the ground to achieve electrical neutrality (Figure 2d). As a result, a current in the reverse direction is obtained in the external circuit. The process continues until the TiO$_2$ surface makes full contact with the liquid, and the potential difference becomes zero. Thus, a series of periodic contact-separation processes between the contact liquid and TiO$_2$ nanosheet arrays generates continuous varying output voltage curves.

3.3 Stability test and sensing performance of the solid-liquid TENS

To observe the durability and stability of the solid-liquid TENS, the contact-separation operation was performed for a prolonged time (3 hours). The first and last 100 voltage cycles within this 3-hour operation window are shown in Figure 3a. The results indicate that the solid-liquid TENS is highly stable, as there are no fluctuations in the electric output in the last 100 voltage cycles compared to the first 100 cycles. It is further confirmed that even after a prolonged operation
time, the TiO$_2$ nanosheet arrays retain their structural integrity (FESEM image, Figure S5). These results ensure the advantages of solid-liquid contact electrification with respect to solid-solid contact electrification in terms of long-term stability and durability [15]. Actually, the lubricating property of liquid allows the smooth movement of the solid surface in the contact solvent, which in turn boosts the stability of the device. We also investigated the output voltage of the TENS as a function of the contact-separation frequency from 0.17 Hz to 0.5 Hz, as shown in Figure 3b. The frequency-independent output response clearly indicates that rapid variation in the triboelectric charges at the solid-liquid interface hardly affects the performance of the solid-liquid TENS even at a higher contact frequency as acetone evaporates very quickly from the TiO$_2$ nanosheet arrays. It is also interesting to note that the performance of the solid-liquid TENS remains unaffected by external environmental factors such as humidity (Figure 3c). The obtained results strongly suggest that in terms of durability and environmental stability, solid-liquid triboelectric systems exhibit performance superior to that of solid-solid triboelectric systems reported previously [35-37].

The sensing performance of the TiO$_2$ nanosheet array-based TENS was investigated, as well as the verification of the chemically enhanced triboelectric output. All the measurements were carried out at an operation frequency of 0.17 Hz. It is interesting to note that the output voltage increases gradually from 0.75 V to 1.2 V with increasing catechin concentration ranging from 1 nM to 10 mM (Figure 4a). This enhanced output could due to that the generated triboelectric output voltage is greatly influenced by the triboelectric charge transfer process, which is proportional to the surface potential difference of the two triboelectric materials. Catechin-functionalized TiO$_2$ nanosheet arrays also exhibit long operational stability, which is reflected by the stable output voltage cycles under the contact-separation process carried out for 3 hours.
(Figure S6). Even after 3 hours of operation, the output voltage cycles hardly exhibit any deviation compared to the initial voltage cycles. Hence, it is conclusively verified that catechin functionalization over TiO$_2$ surface is stable enough and does not undergo any desorption under prolonged time of operation. The obtained results clearly indicate the robustness and mechanical stability of the solid-liquid TENS for practical applications.

The sensing performance of the TiO$_2$ nanosheet array-based TENS was further confirmed with other contact liquids such as ethanol and water. Similar to acetone, the output voltage is enhanced for both ethanol and water upon functionalization with different concentrations of catechin ranging from 1 nM to 10 mM (Figure S7). The triboelectric output is enhanced from 0.7 V to 1.1 V and 0.4 V to 0.55 V for ethanol and water, respectively. The output voltage ratio curves of the solid-liquid TENS obtained from chemically enhanced contact electrification for different contact liquids are shown in Figure 4b. Compared to water and ethanol, the voltage response trend of the solid-liquid TENS corresponding to acetone shows better chemically enhanced triboelectric performance. For acetone, the highest voltage enhancement factor (approximately 1.6) is obtained upon modification of the TiO$_2$ surface with 10 mM catechin (Figure 4c). The two crucial parameters of TENS of long-range linearity and low limit of detection (LOD) are greatly satisfied when acetone is used as the contact liquid. The LOD value is quantified as the minimum catechin concentration for which an average detectable enhancement in the electrical signal is obtained by visual estimation from the voltage ratio curve (Figure 4b). The voltage ratio curve with acetone demonstrates long-range linearity from 100 nM to 100 µM with an LOD of 30 nM, which is much better than the catechin detection performance shown by solid-solid contact electrification reported previously [15]. Such type of sensing trend where linearity is achieved far after LOD value is widely reported in the literature [38-40].
Selection of volatile organic solvent such as acetone as contact liquid and high selectivity of catechin towards TiO$_2$ nanosheet arrays are the key factors that facilitate the high sensitivity and corresponding low detection limit.

The highest voltage enhancement coming from acetone can be explained in terms of the volatile nature of acetone, which induces quick evaporation from the solid triboelectric surface without affecting the practical friction area of the solid material. On the other hand, among the contact liquids used, water is the most nonvolatile and polar solvent [41]. Upon separation, the evaporation rate of the water residuals on the TiO$_2$ surface is very slow compared to those of acetone and ethanol, which leads to a small triboelectric output voltage. Since the TiO$_2$ surface is not hydrophobic, utilization of comparatively nonpolar liquid as contact solvent exhibits superior voltage response behavior.

### 3.4 Mechanism of enhanced voltage response with catechin functionalization

Catechin-functionalized TiO$_2$ nanosheet arrays exhibit enhanced voltage response behavior as a consequence of greater electron transfer among the triboelectric solid surface and contact liquid. Catechol, the electron donating enediol ligand of catechin, has a strong binding affinity toward the surface Ti atoms of TiO$_2$ by forming a ligand-to-metal charge transfer complex [42-44], as shown in Scheme 1. To probe the interfacial charge transfer phenomena, the surface potential of the solid surface was measured with the help of Kelvin probe force microscopy (KPFM). The surface potential distribution images obtained by KPFM clearly show that surface potential increases consistently with increasing catechin concentration (Figure 5a). The corresponding Gaussian distributions of surface potentials are provided in the Supplementary Material (Figure S8). While the pristine TiO$_2$ surface exhibits a surface potential of 281 mV, surface
functionalization with 1 mM catechin results in an almost twofold increase in the surface potential (548 mV). Since the TiO$_2$ surface becomes more positive with catechin functionalization, the potential difference between the electrode and contact liquid increases significantly.

This enhanced potential difference triggers proficient electron transfer across the solid-liquid interface, leading to enhanced voltage response behavior. In terms of surface potential, it can also be concluded that as a result of chemical modification, the catechin-modified TiO$_2$ sample is placed on the more positive side in the triboelectric series with respect to the TiO$_2$ only sample. A higher surface potential further indicates a change in the work function upon catechin functionalization, which was probed by ultraviolet photoelectron spectroscopy (UPS), as shown in Figure 5b. The work function ($\phi$) of the TiO$_2$ nanosheet arrays before and after catechin modification was calculated from the Fermi level and secondary electron cut-off energy by employing the equation $\phi = 21.22 - (E_{\text{Fermi}} - E_{\text{Cut-off}})$ [45]. The calculated work functions for the TiO$_2$ nanosheet arrays and catechin-modified TiO$_2$ nanosheet arrays are 6.54 eV and 5.52 eV, respectively (Figure 5c). From Figure 5c, it is clear that the decrease in work function after catechin modification facilitates enhanced electron transfer by overcoming the surface potential barrier. Moreover, the high-resolution valence band spectra (Figure S9) strongly indicate that catechin modification leads to an increase in the density of states near the Fermi level, which is a consequence of electron transfer between the catechol group and Ti atoms. These increased densities of states near the Fermi level further promote efficient electron transfer from the solid surface to the contact liquid. In addition, previous reports indicate that chemical modification induced change in hydrophobicity of solid triboelectric surface also plays a crucial role in changing the output of TENG devices [13, 46]. However, in the present study it is observed that
even after chemical modification with catechin, the TiO$_2$ nanosheet surface retains its hydrophilic nature (Figure S10). Therefore, it is conclusively verified that catechin modification induced change in work function is the main dominating factor that facilitates the increase in output voltage of the TENS.

### 3.5 Detection of catechin in real samples

The highly selective binding between TiO$_2$ and the catechol group of catechin has also shown the possibility of deploying our TENS for real-time on-field detection of catechin. To evaluate the practical sensing performance of our TENS, the developed nanosensor was deployed for the detection of catechin from commercially available green tea. The unknown catechin concentration in green tea was determined by the method of standard addition, as this method reduces any interference appearing from other matrix components [47]. The voltage response curves of the TiO$_2$ nanosheet array-based TENS corresponding to different added catechin concentrations are shown in Figure 6a. The output voltage response increases gradually with increasing concentrations of catechin and reaches a maximum of 1.2 V for 80 µM catechin. The output voltage ratio is plotted as a function of the added catechin concentration to obtain the ratiometric calibration curve, as shown in Figure 6b. The output voltage response exhibits long-range linearity with different concentrations of catechin, which indicates that any unknown concentration can be obtained from the slope and $y$ intercept of the calibration curve [48]. The actual average concentration of catechin in undiluted green tea is found to be 87.65 mg/100 ml, which appears in close proximity to the concentration range of epigallocatechin in commonly available green tea around Taiwan and China [49]. The obtained results strongly establish the practical applicability and reliability of solid-liquid TENS for real-time sensing applications.
4. Conclusions:
In summary, the first solid-liquid TENS based on a chemically enhanced mechanism is proposed and demonstrated. The strong binding affinity of catechin toward TiO$_2$ nanosheet arrays reduces the work function and therefore largely increases the transferred charges during contact electrification and consequent electric output. Volatile solvents such as ethanol and acetone as contact liquids eliminate the need for hydrophobic solid surfaces in solid-liquid TENS. The solid-liquid TENS also shows superior performance such as long-term stability, independent operation frequency and humidity resistance characteristics compared to solid-solid TENS. The developed TiO$_2$ nanosheet array-based TENS provides self-powered detection of catechin with a linear range from 100 nM to 100 µM and a lower detection limit of 30 nM. The detection of catechin from commercial green tea also allows the developed TENS to be used in real-time in-field sensing applications. The obtained results strongly highlight the merit of chemical modification strategies in solid-liquid contact electrification as well as promote the bright prospects of TiO$_2$ nanosheet array-based TENS for the development of self-powered portable nanosensors.

Appendix A. Supplementary data
The supplementary data for this article can be found online.

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Figures:

Scheme 1. Schematic representation of the synthetic procedure for TiO$_2$ nanosheet arrays on Ti wire and consequent surface modification with catechin. Ti wire is hydrothermally reacted with NaOH$_{\text{(aq)}}$ for the growth of Na$_2$Ti$_2$O$_4$(OH)$_2$ nanosheet arrays. Then, an ion exchange reaction in HCl$_{\text{(aq)}}$ is performed to replace the Na$^+$ in Na$_2$Ti$_2$O$_4$(OH)$_2$ nanosheet arrays with H$^+$. Finally, the H$_2$Ti$_2$O$_4$(OH)$_2$ nanosheet arrays are cleaned and annealed at 500 °C to form TiO$_2$ nanosheet arrays. The TiO$_2$ nanosheet arrays are immersed in catechin solution, and the ligand-to-metal charge transfer of hydroxyl groups to Ti atoms results in a spontaneous binding affinity between the catechin and TiO$_2$ nanosheet arrays.
Figure 1. (a) XRD pattern of TiO$_2$ nanosheet arrays on Ti wire. The inset shows a digital photograph of the grown TiO$_2$ nanosheet arrays on the Ti wire. (b, c) FESEM and TEM images of synthesized TiO$_2$ nanosheet arrays showing uniform nanostructures and crystallinity. (d-f) High-resolution XPS scans of Ti 2p, O 1s and C 1s demonstrating the binding of catechin on the surface of the TiO$_2$ nanosheet arrays.
Figure 2. Illustration of the working mechanism of TiO$_2$-based solid-liquid TENS. (a) When the TiO$_2$ surface is immersed in contact liquid, the TiO$_2$ surface and contact liquid attain positive and negative charges because of contact electrification. (b, c) Once the separation proceeds, the generated potential induces electron flow from the ground to the Ti wire until equilibrium is reached. The induced negative charges on Ti electrode are shown in blue color. (d) As the TiO$_2$ surface starts to contact the liquid again, the decrease in the potential difference results in electron flow from the Ti wire to the ground and a return to the original status (a).
Figure 3. Demonstration of the durability and stability exhibited by the TiO\textsubscript{2}-based solid-liquid TENS. (a) Selected the first (i) and last (ii) 100 electric outputs among the 3 hours of the contact-separation process representing the time-independent performance of the device. (b) Output voltage cycles of the solid-liquid TENS under different operating frequencies. (c) Representation of the output stability of the solid-liquid TENS under varying humidity conditions.
Figure 4. (a) Representation of enhanced output voltage obtained from TiO$_2$ nanosheet arrays modified with different catechin concentrations of 0 nM (i), 1 nM (ii), 10 nM (iii), 100 nM (iv), 1 µM (v), 10 µM (vi), 100 µM (vii), 1 mM (viii) and 10 mM (ix). Acetone is selected as the contact liquid of the TENS. (b, c) Comparison of the output voltage ratio profile and voltage enhancement factor for different contact liquids of such as water, ethanol and acetone, where $V_c$ indicates the voltage shift due to catechin modification and $V_0$ is the original output voltage.
Figure 5. (a) KPFM images of modified TiO$_2$ nanosheet arrays demonstrating a gradual increase in the surface potential with higher concentrations of catechin. (b) UPS spectra of the TiO$_2$ nanosheet arrays and catechin-modified TiO$_2$ nanosheet arrays indicating the positions of the secondary electron cut-off energy ($E_{\text{cut-off}}$) and Fermi level ($E_F$). (c) Graphical representation of the change in the work function ($\phi$) as a consequence of surface modification with catechin. A reduction in the work function indicates that less energy is required for the electrons to cross the surface potential barrier.
Figure 6. (a) Output voltage of the developed solid-liquid TENS when sensing commercial green tea solution (i) and spiked with different standard catechin concentrations of 20 µM (ii), 40 µM (iii), 60 µM (iv) and 80 µM (v). (b) Calibration curve obtained from the standard addition method for the determination of unknown catechin concentration.
**Highlights**

- The first solid-liquid triboelectric nanosensor (TENS) was developed and shows sensing performance and long-term stability superior to those of solid-solid TENS.
- The ligand-to-metal charge transfer mechanism decreases the work function of TiO$_2$ nanosheet arrays and provides an excellent lower detection limit of 30 nM.
- Volatile solvents function as alternative liquids to water and overcome the requirement of hydrophobic surfaces in solid-liquid TENS.
- This chemical enhancement phenomenon also indicates an efficient approach to boost the electric output of solid-liquid triboelectric nanogenerators.
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: