Three-Dimensional Au-Coated Electrosprayed Nanostructured BODIPY Films on Aluminum Foil as Surface-Enhanced Raman Scattering Platforms and Their Catalytic Applications

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ABSTRACT: The design and development of three-dimensional (3D) nanostructures with high surface-enhanced Raman scattering (SERS) performances have attracted considerable attention in the fields of chemistry, biology, and materials science. Nevertheless, electrospraying of organic small molecules on low-cost flexible substrates has never been studied to realize large-scale SERS-active platforms. Here, we report the facile, efficient, and low-cost fabrication of stable and reproducible Au-coated electrosprayed organic semiconductor films (Au@BDY-4T-BDY) on flexible regular aluminum foil at a large scale (5 cm × 5 cm) for practical SERS and catalytic applications. To this end, a well-designed acceptor−donor−acceptor-type solution-processable molecular semiconductor, BDY-4T-BDY, developed by our group, is used because of its advantageous structural and electrical properties. The morphology of the electrosprayed organic film changes by solution concentration, and two different 3D morphologies with out-of-plane features are obtained. Highly uniform dendritic nanoribbons with sharp needle-like tips and vertically oriented nanoplates (∼50 nm thickness) are achieved when electrospraying solution concentrations of 240 and 253% w/v (mg/mL) are, respectively, used. When these electrosprayed organic films are coated with a nanoscopic thin (30 nm) Au layer, the resulting Au@BDY-4T-BDY platforms demonstrate remarkable SERS enhancement factors up to 1.7 × 106 with excellent Raman signal reproducibility (relative standard deviation ≤ 0.13) for methylene blue over the entire film. Finally, Au@BDY-4T-BDY films showed good catalytic activity for the reduction of 4-nitrophenol to 4-aminophenol with rate constants of 1.3 × 10−2 and 9.2 × 10−3 min−1. Our results suggest that electrospraying of rationally designed organic semiconductor molecules on flexible substrates holds great promise to enable low-cost, solution-processed, SERS-active platforms.

KEYWORDS: Surface-enhanced Raman scattering, organic semiconductor, electrospraying, small molecule, catalysis

INTRODUCTION

Surface-enhanced Raman scattering (SERS) is one of the most powerful analytical tools in chemistry and materials science, and it shows high sensitivity in nondestructive label-free imaging of various chemical species with a rapid response.1 In a typical SERS technique, weak Raman scattering signals (scattering cross section = 10−30 cm2/molecule) are intensified using rationally designed metallic or inorganic semiconductor-based substrates.1,2 The dominant mechanism behind the SERS process is the electromagnetic enhancement, which results from the amplification of electromagnetic fields around the analyte molecules by the excitation of localized surface plasmon resonances of a SERS-active substrate.2 The other common contributor to SERS enhancement is the chemical mechanism, which principally relies on charge transfer processes between analyte molecules and the SERS-active surface.2−5 Since the discovery of the SERS technique in 1970s,6 three-dimensional (3D) coinage metallic (e.g., Au, Ag, Cu) nanostructures have attracted considerable attention as high-performing SERS substrates because the gaps and crevices known as “hot spots” in their morphologies enhance the local electromagnetic field and their large surface area allows improved adsorption of analyte molecules.2,6,7 The current techniques to fabricating 3D hierarchical SERS substrates are based on either top-down or bottom-up nanofabrication methods.6 Although top-down methods such as electron-beam lithography and nanoimprint...
Scheme 1. Schematic for the Fabrication of Au-Coated Electrospayed BDY-4T-BDY Organic Film on Aluminum (Au@BDY-4T-BDY) 

“The first step shows the fabrication of micro-/nanostructured BDY-4T-BDY organic film via electrospaying, and the second step shows the deposition of Au thin film (30 nm) by PVD.

lithography provide accurate control over the design and fabrication, these methods are costly and onerous. In the case of the bottom-up strategy, micro-/nanostructured SERS-active platforms are typically produced from building blocks of noble metallic nanoparticles. Although this strategy seems to be simple and inexpensive, the uncontrolled aggregation in most cases leads to a discrepancy in the resulting SERS signals. To this end, it is still quite desirable to produce high-performance 3D SERS-active platforms at a large scale via low-cost, reproducible, and facile methods.

Electrospinning and electrospaying are simple, efficient, and inexpensive techniques to fabricating micro-/nanostructures from solution. When a certain electric field is applied to the tip of the syringe containing the electrospaying/electrospinning solution, an electrically charged jet ejects from the Taylor cone formed in the vicinity of the tip and strikes toward the grounded collector. By the effect of high voltage, the solution gets thinned on the aluminum surface, increasing its surface area, which results in solvent evaporation and uniform nano-/microstructure formation on the collector. To this end, electrospinning of micro-/nanofibers has been restricted to high-molecular-weight polymeric solutions because of the required entanglements and overlapping between polymer chains for continuous stretching of electrified jet and uniform fiber formation. However, recent studies indicate that electrospinning of nonpolymeric systems (i.e., small molecules with certain molecular weights or macromolecules) is also possible when sufficient intermolecular interactions exist between molecular backbones. Until now, only a few molecular systems including phospholipids, surfactants, and cyclodextrins have been reported to show successful electrospinning of fibers from solution. On the other hand, electrospaying of small molecules and macromolecules has recently attracted great attention as a promising method of producing micro-/nanostructured materials. Although, during a typical electrospinning process, fabricated micro-/nanofibers are deposited in the plane of the collector, electrospaying offers the great advantage of creating highly textured 3D micro-/nanostructures that extend directly out of plane, which offers the potential for SERS and catalysis applications.

4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY)-based small molecules with their excellent thermal/photochemical stability, good solubility, intense absorption/emission profiles, high photoluminescence quantum yield, and small Stokes shifts are used in a broad range of applications including fluorescent switches, biochemical labeling, chemosensors, and electro-luminescent devices. In our previous study, we designed and synthesized a novel solution-processable molecular semiconductor, BDY-4T-BDY, based on an acceptor–donor–acceptor (A–D–A) molecular π-architecture. The corresponding solution-processed films not only showed good semiconductor performances in n-channel organic field-effect transistors but also exhibited highly crystalline microfibers along the shearing direction thanks to their strong intermolecular forces. This new BODIPY-based semiconductor is envisioned as an attractive molecular building block to fabricating micro-/nanostructured soft materials so that Au layers can be deposited on top via physical vapor deposition (PVD) to create a hybrid structure, which can be used for SERS and catalysis applications. The rationale to use BDY-4T-BDY is as follows: (i) the compound is highly soluble in common organic solvents for use in the electrospaying process, (ii) the compound has directional molecular self-assembly and crystal growth tendency under mechanical stress, which might be also effective under electrical stress to grow directional features via electrospaying; and (iii) the compound is an organic semiconductor, and the electrospaying method may induce out-of-plane morphology growth as a result of its somewhat conductive nature at high voltage (12.5 kV). Furthermore, BDY-4T-BDY’s high chemical and thermal stabilities may contribute to the robustness and stability of the corresponding SERS and catalysis platforms.

Herein, in light of these findings, we present a facile approach to fabricating flexible, stable, and reproducible gold-coated electrospayed BDY-4T-BDY films on flexible regular aluminum foil for practical SERS and catalysis applications (Scheme 1). Electrospaying of BDY-4T-BDY solutions in a CHCl3/dimethylformamide (DMF) (2:1) mixture gave a highly uniform dendritic nanoribbon-based morphology with sharp needle-like tips and vertically oriented nanoplate-based (~50 nm thickness) morphology depending on the solution concentration. These micro-/nanostructured morphologies were combined with a nanoscopic (30 nm) Au layer (Au@BDY-4T-BDY), which resulted in remarkable SERS performances with enhancement factor (EF) up to 1.7 × 10⁶ and
excellent reproducibility (relative standard deviation (RSD) \( \leq 0.13 \)). Additionally, catalytic activities of the current flexible platforms were tested for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), and the rate constants were found to be \((0.9-1.3) \times 10^{-2}\).

**EXPERIMENTAL SECTION**

Fabrication of Au-Coated Electro spun Micro-/Nanostructured BDY-4T-BDY Films. The synthesis, purification, and characterization of BDY-4T-BDY were performed according to our reported procedure28 (Supporting Information). For the fabrication of electrosprayed micro-/nanostructures, BDY-4T-BDY solid (3.6 mg for 240% w/v (mg/mL) solution and 3.8 mg for 253% w/v (mg/mL) solution) was weighed and dissolved in a solvent mixture of CHCl\(_3\) (1 mL) and DMF (0.5 mL). Afterward, the solution was filtered through a poly(tetrafluoroethylene) filter (0.45 \(\mu\)m) and electrosprayed using Inovenso, NE300, consisting of a syringe with a stainless steel needle, an electrically grounded collector, and a high voltage supply. Electrospraying was conducted with a positive voltage of 12.5 kV applied to the stainless steel needle with the solution feed rate of 80 \(\mu\)L/min with a syringe pump. The electrosprayed BDY-4T-BDY micro-/nanostructured films were collected on the collector covered with aluminum foil (5 cm \(\times\) 5 cm) at a constant distance of 10 cm between the needle and the collector. The as-prepared electrosprayed films were coated with a nanoscopic layer of gold (30 nm) via the PVD method (NANOVAK (DSA100; Kru
tact angle measurements were conducted on a drop shape analyzer.

Fabrication and Characterization of Au-Coated Electro spun Micro-/Nanostructured BDY-4T-BDY Films. The ultraviolet–visible (UV–vis) absorption spectra of electrosprayed nano-/microstructured films were obtained using a Shimadzu 2600 UV–vis spectrophotometer and S1. The morphology of the organic films was found to change dramatically with concentration. As shown in Figure S1, higher concentrations (270–300% w/v (mg/mL)) lead to nonuniform aggregate-based morphologies with very limited out-of-plane features. This can be ascribed to the high concentrations of the solutions, which probably facilitate the aggregation of organic small molecules during solvent evaporation. When the solution concentration is controlled at 253% w/v (mg/mL), mostly a vertically oriented nanoplate-based (~50 nm thickness) morphology was obtained for BDY-4T-BDY(2). Finally, when the solution concentration was further lowered to 240% w/v (mg/mL), a highly uniform dendritic nanoribbon-based morphology with sharp needle-like tips was obtained for BDY-4T-BDY(1). When these two morphologies (Figure 1) are compared, the concentration is found to play a critical role and a dilute solution (240% w/v (mg/mL)) is required to avoid aggregation-based particulates and to obtain a uniform dendritic nanoribbon-based morphology. In contrary to typical electrosprayed small-molecule films, which usually have particulate-based morphological features,29,30 BDY-4T-BDY(1) films having dendritic nanoribbon-based structures grown in the out-of-the-collector direction build favorable 3D micro-/nanostructured morphol-
For SERS and catalysis applications. During the electrospaying process, although the flow rate is stable in the vicinity of the needle tip, as the solvent evaporates, it enters a bending instability phase with further stretching of the solution jet under electrostatic forces. When the conductivity of the electrospaying solution increases, 3D structures extending perpendicular to the collector surface can be formed. In our work, the formation of rather unusual 3D micro-/nanostructured morphologies might be attributed to somewhat conductive nature of the BDY-4T-BDY semiconductor solution at high voltage (12.5 kV). Next, micro-/nanostructured BDY-4T-BDY films (5 cm x 5 cm) were coated with a nanoscopic Au layer (30 nm) via the PVD method, which shows that the 3D micro-/nanostructured organic morphology is preserved after the PVD process and Au atoms are deposited on this micro-/nanostructured hydrophobic surface as close-packed nanoparticles (~15–20 nm in size) (Figure S2).

θ–2θ XRD scans were performed to reveal out-of-plane crystallinity of electrosprayed organic films, and the corresponding XRD spectra are shown in Figure 2. It is clearly observed that both films are crystalline, showing almost the same crystalline phases. The major diffraction peaks were observed at 2θ = 16.98–17.02°, indicating that electrosprayed BODIPY films employ a major crystalline phase with an interlayer d-spacing of 5.2 Å along the substrate normal. The presence of high-angle diffractions as the major peaks in electrosprayed films is consistent with those of solution-sheared films of BDY-4T-BDY. Note that this value is remarkably smaller than the computed long-axis molecular length (~2.4 nm), and it is highly consistent with the computed length along the short molecular axis (~7 Å). Thus, molecular packing of BDY-4T-BDY molecules in the film phase most likely features either a highly tilted molecular orientation (θ > 75° from the substrate normal) on the substrate or molecular short-axis alignment along the substrate normal. Either way, this type of molecular orientation may induce strong π···π* and C–H···π* interactions in the out-of-plane direction, producing well-defined vertically oriented micro-/nanostructures. Indeed, the π···π stacking interactions were evident in the XRD spectra of BDY-4T-BDY(1), showing a broadened peak centered at 2θ ~ 24° (π···π stacking ~ 3.7 Å), which is typical for films of crystalline small molecular semiconductors. In addition, a secondary crystalline phase was evident for BDY-4T-BDY(2) films with the primary diffraction peak at 2θ = 4.70° (d-spacing = 1.8–1.9 nm) along with higher-order diffractions at higher angles (14.18, 25.66, 44.98, and 65.18°). This crystalline phase might refer to a typical edge-on molecular long-axis orientation on the substrate based on the computed molecular lengths (~2.4 nm), and it might be associated with the formation of a vertically oriented nanoplate-based (~50 nm thickness) morphology on the surface.

The UV–vis absorption spectra of electrosprayed films before and after gold deposition were recorded in the reflective mode, and the corresponding spectra are shown in Figure 3.
film consists of pure BDY-4T-BDY molecules (Figure S3). In addition, FTIR spectra of BDY-4T-BDY molecules and their resultant electrosprayed films also reveal no chemical change after electrospraying (Figure S4). We also performed the contact angle measurements to determine the wettability of electrosprayed films. As shown in Figure S4, the water contact angle of the electrosprayed organic films was found to be $\sim 129^\circ - 132^\circ$, which indicates highly hydrophobic surface characteristics. When this film is compared with the drop-casted organic film on glass (contact angle $\sim 88^\circ$), very high contact angles of the electrosprayed films on aluminum should originate from the presence of fluorine substituents on an organic $\pi$-framework and micro-/nanostructured morphology. It is noteworthy that after nanoscopic gold (30 nm) deposition the films remain hydrophobic ($\sim 127^\circ - 131^\circ$), which is consistent with the earlier studies on micro-/nanostructured metal surfaces.37,38

Figure 4. Representative SERS spectra of MB on Au@BDY-4T-BDY(1) and Au@BDY-4T-BDY(2). The Raman peaks at 1620 cm$^{-1}$ used for EF calculations are indicated on the spectra.

Figure 5. (a) Reproducibility of SERS spectra of MB collected on 30 randomly selected spots on Au@BDY-4T-BDY(1) film and the intensity histogram of some prominent peaks at (b) 449, (c) 1437, and (d) 1620 cm$^{-1}$. The dashed red lines indicate the average intensity of each peak.
Figure 6. UV–vis absorption spectra of 4-NP as a function of time, indicating the catalytic activity of pristine and Au-coated electrosprayed semiconductor films: (a) BDY-4T-BDY(1), (b) Au@BDY-4T-BDY(1), and (c) Au@BDY-4T-BDY(2), (d) percent conversion of 4-NP to 4-AP as a function of time, (e) kinetics of the 4-NP reduction process assisted by gold-coated electrosprayed platforms.

SERS and Catalytic Activity of Electrosprayed Nano-/Microstructured Films. The 3D micro-/nanostructured surface morphology of the current Au-coated electrosprayed organic films over large areas (5 cm × 5 cm), when compared with smooth two-dimensional morphologies typically used in optoelectronics, provide unique advantages, such as increased surface area, formation of hot spots, and capture of target molecules. Therefore, we envision that the current micro-/nanostructured organic films combining with a nanoscopic layer of gold (30 nm) would be a promising candidate for practical SERS and catalytic applications. For SERS experiments, 5 μL of the aqueous solution of MB (1 × 10^{-5} M), which is used as the reporter molecule, was deposited on pristine BDY-4T-BDY film and Au@BDY-4T-BDY film. Coin-shaped Raman samples with sizes of 2 ± 0.5 mm were obtained on the film surface. First, we tested the SERS performance of pristine organic films (Figure S6), which, as expected, did not yield any Raman signal. This result is attributed to the absence of plasmonic metal to create electromagnetic enhancement and unfavorable energy levels to lead to the chemical enhancement mechanism. However, after gold deposition, well-defined and precise SERS signals were collected with acceptable signal-to-noise ratios for both morphologies (Au@BDY-4T-BDY(1) and Au@BDY-4T-BDY(2)) (Figure 4). The most prominent peaks in the spectra are consistent with our earlier reports and can be summarized as follows: 1620 cm^{-1} (ν(C–C) ring stretches), 1395/1437 cm^{-1} (ν(C–N) symmetric and asymmetric stretches), and 449 cm^{-1} (δ(C–N–C) skeletal deformation mode). Additionally, to quantify and compare SERS performances of Au-coated electrosprayed organic films, we calculated the EF using the most prominent peak at 1620 cm^{-1} via the given formula

\[
\text{EF} = \frac{N_{\text{reference}} \times I_{\text{Au@BDY-4T-BDY(α)}}}{N_{\text{Au@BDY-4T-BDY(α)}} \times I_{\text{reference}}}
\]

where \(I_{\text{reference}}\) and \(I_{\text{Au@BDY-4T-BDY(α)}}\) are the Raman intensities of MB on silicon wafer and the adsorbed MB on Au@BDY-4T-BDY(1), respectively, and \(N_{\text{reference}}\) and \(N_{\text{Au@BDY-4T-BDY(α)}}\) are the number of MB molecules for the reference sample and Au@BDY-4T-BDY(n), respectively. Accordingly, the EFs are calculated to be 1.7 × 10^{6} for Au@BDY-4T-BDY(1) and 3.6 × 10^{6} for Au@BDY-4T-BDY(2). For both cases, these enhancements in SERS signals are attributed to the electromagnetic enhancement mechanism. Electromagnetic contributions to the SERS signals in these systems mainly stem from highly rough micro-/nanostructured surfaces of the current platforms, which employ closely spaced Au nanoparticles as well (Figure S2). This unique 3D morphology decorated with nanostructured gold particles can generate hot spots with an extremely high electric field enhancement as a result of tip-focusing, cavity resonances, and antenna effects. As shown in Figure 4, the higher SERS peak intensity and EF obtained for Au@BDY-4T-BDY(1), as compared to those for Au@BDY-4T-BDY(2), might be attributed to the higher density of micro-/nanostructures and the presence of nanoribbon-like morphology with sharp needle-like tips, which is more favorable to create hot spots than nanoplates.

The poor reproducibility of SERS signals has been one of the main obstacles that should be addressed to realize an ideal SERS substrate. To investigate the reproducibility of the current Au-coated electrosprayed organic films, we collected SERS spectra from 30 randomly selected spots on the surface prepared under identical conditions. The collected spectra for 30 randomly selected spots and the corresponding intensity distributions for the most prominent peaks at 449, 1437, and 1620 cm^{-1} are summarized in Figure 5. To quantify and clarify the reproducibility, the RSD values are calculated to be 0.13, 0.10, and 0.11 for the peaks at 449, 1437, and 1620 cm^{-1}, respectively. Our results clearly indicate excellent SERS
reproducibility of the current Au@BDY-4T-BDY platforms over large areas (Figure S7, 5 cm × 5 cm).

In addition to SERS applications, we have also evaluated the catalytic activity of Au-coated organic films for the reduction of 4-NP to 4-AP. Although this catalytic conversion is thermodynamically possible in the presence of aqueous NaBH₄, the kinetic barrier, due to the large potential difference between the borohydride donor (BH₄⁻) and acceptor (4-NP) molecules, limits the degree of this reaction.41,42 However, in the presence of metal nanoparticles, electron relay from donor to acceptor molecules is easily actualized. The catalytic reduction of 4-NP can be effectively monitored via UV−vis absorption spectra (Figure 6). First, we employed the pristine BH₄⁻ reduction of 4-NP can be easily actualized. The catalytic conversion (Figure S8). For the case of Au@BDY-4T-BDY(1) films, almost complete conversion was achieved within 180 min. However, Au@BDY-4T-BDY(2) film led to a relatively lower catalytic activity with a significant retention time of ≈20 min. Considering pseudo-first-order reaction kinetics as shown in Figure 6e, the rate constants are found to be 1.3 × 10⁻² and 9.2 × 10⁻³ min⁻¹ for Au@BDY-4T-BDY(1) and Au@BDY-4T-BDY(2), respectively. When compared to that of Au@BDY-4T-BDY(2), the slightly higher catalytic activity of Au@BDY-4T-BDY(1) films with negligible retention time can be attributed to its favorably higher density surface morphology with high-aspect-ratio dendritic nanoribbons. Note that the rate constant for Au@BDY-4T-BDY(2) is calculated after the retention time of ≈20 min. These rate constants are comparable to those of some recently reported Au-based catalysts in the literature (Table S1); however, large-scale and facile fabrication of the current Au@BDY-4T-BDY substrates may open new avenues for the development of recoverable, low-cost, and large-scale solid-state catalysis platforms.43−45

**CONCLUSIONS**

In summary, we have reported a simple and versatile approach to fabricating large-scale, flexible, and reproducible SERS-active substrates based on 3D micro-/-nanostructured Au-coated electrosprayed semiconductor films (Au@BDY-4T-BDY). Our fabrication method involves electrospraying and PVD, which not only provide a number of hot spots but also yield a large surface area for the adsorption of analyte molecules. Owing to the favorable organic morphologies achieved via simple electrospraying, remarkable SERS performances were achieved in terms of enhancement and reproducibility. Also, the Au-coated electrosprayed micro-/-nanostructured films showed good catalytic activity in the reduction of 4-NP to 4-AP. Taken together, our findings clearly show that electrosprayed molecular semiconductor thin films, when coated with a nanoscopic noble metallic layer, hold great promise for the fabrication of 3D SERS platforms. The bottom-up synthesis of out-of-plane grown semiconductor micro-/-nanostructures via the electrospraying technique is ideal for the production of low-cost, flexible, and reliable large-scale SERS-active platforms and catalysts. Moreover, by changing the structures of the semiconductor molecules used, the SERS and catalytic performances of the resulting platforms can be varied to realize further applications.

**ASSOCIATED CONTENT**

© Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b03042.

Synthetic procedures and characterizations of BDY-4T-BDY: Scheme S1, Figures S1−S8, and Table S1 (PDF)

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**NOTES**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was partially supported by Gazi University (Grant No: 05/2015-19) and the Scientific and Technological Research Council of Turkey (TUBITAK) grant number 114M226. G.D. and H.U. acknowledge support from the Turkish Academy of Sciences, Distinguished Young Scientist Award (TUBA-GEBIP).

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