

# Light Controllable Surface Coating for Effective Photothermal Killing of Bacteria

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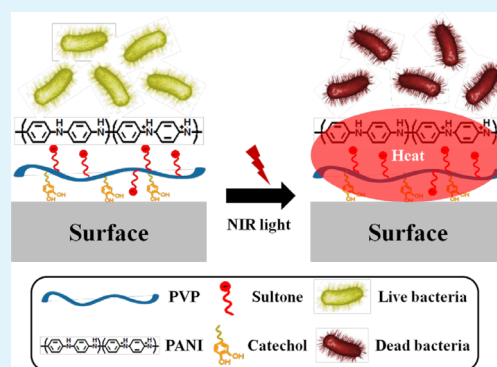
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## S Supporting Information

**ABSTRACT:** Although the electronic properties of conducting films have been widely explored in optoelectronic fields, the optical absorption abilities of surface-coated films for photothermal conversion have been relatively less explored in the production of antibacterial coatings. Here, we present catechol-conjugated poly(vinylpyrrolidone) sulfobetaine (PVPS) and polyaniline (PANI) tightly linked by ionic interaction (PVPS:PANI) as a novel photothermal antibacterial agent for surface coating, which can absorb broadband near-infrared (NIR) light. Taking advantage of the NIR light absorption, this coating film can release eminent photothermal heat for the rapid killing of surface bacteria. The NIR light triggers a sharp rise in photothermal heat, providing the rapid and effective killing of 99.9% of the Gram-positive and -negative bacteria tested within 3 min of NIR light exposure when used at the concentration of 1 mg/mL. Although considerable progress has been made in the design of antibacterial coatings, the user control of NIR-irradiated rapid photothermal destruction of surface bacteria holds increasing attention beyond the traditional boundaries of typical antibacterial surfaces.

**KEYWORDS:** photothermal, NIR, polyaniline, antibacterial coating, catechol



## 1. INTRODUCTION

The growing resistance of microbial strains is a dynamic process that has become a global issue due to the failure of typical antibiotics. One strategy to combat this is to rapidly eradicate the microbes before a change of phenotype occurs.<sup>1</sup> Therefore, in past decades, nanoparticles and nanostructure-based alternative antimicrobial treatments have achieved increasing attention, along with the traditional antibiotic treatments. These antibacterial materials are mostly based on metallic (gold AuNP, silver AgNP, iron Fe<sub>2</sub>O<sub>3</sub>) and semiconductor nanoparticles (graphene oxide), while some come from composited sources like poly aniline, quaternary amine, and similar kinds of cytotoxic chemical agents.<sup>2,3</sup> Their activities against wide ranges of bacterial species make us hopeful about the present and future applications of such antibacterial agents.<sup>1</sup> Although significant progress has been made in this exciting area, continual challenges still remain for the effective and rapid killing of bacterial strains.

In material formulation, polyvinylpyrrolidone (PVP) is considered as a water-soluble natural polymer, which is widely used in pharmaceutical formulations as a stabilizer and protector, enhancing the shelf life of therapeutic agents.<sup>4</sup> To make sticky agents, the catechol moiety is typically utilized in conjunction with different polymeric composites as an adhesive

polymeric coating.<sup>5</sup> In polymeric composites, the sulfoalkylating agents introduced, such as sulfones, are considered important heterocyclic compounds, which carry alkyl chains with negatively (–ve) charged sulfonic acid functionalities that have been emphasized for allowing an increase of the solubility of composite materials.<sup>6</sup> To make conductive materials, polycationic (+ve) polymers like polyaniline (PANI) offer a unique combination of electrical and optical properties similar to metals or semiconductors.<sup>7</sup> Therefore, the inclusion of conducting elements like polyaniline in structural composites enables the transport of electrical signals. Moreover, by using the cationic polarity of PANI and broad length optical absorption, the electrostatic interaction between PANI and its counterionic complex can be explored for the construction of new applicable materials. Besides, a recent study found that PANI possesses excellent antibacterial activity against Gram-positive and Gram-negative strains under both dark and visible light conditions.<sup>8</sup> This promising antibacterial effect demonstrates that PANI may be a new source for the development of highly efficient functional antibacterial materials.

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The current available methods for complete eradication of pathogenic bacteria are slow and destroy the bacteria either physically or chemically.<sup>3</sup> Chemically, pathogenic cells undergo lysis due to interference with the normal metabolic process, are destroyed through physical killing, or are inhibited from attachment/growth on susceptible surfaces.<sup>1</sup> These conventionally available antibacterial systems work at a predetermined rate irrespective of user demands. These demands spark the urgent need for the development of rapid killing methods.

Recently, near-infrared (NIR) light irradiated photothermal treatment appeared as an interesting promising tool to fight against pathogenic cells.<sup>9,10</sup> For hyper-thermal killing (thermolysis), the eradication agents are designed to absorb light at the wavelengths of 650–900 nm (NIR region), which is responsible for the generation of elevated temperatures sufficient to cause irreversible cell damage, through methods such as the disruption of metabolic signals, denaturation of proteins/enzymes, micro thrombosis, and endothelial swelling.<sup>11–13</sup> As a result of NIR light sensitivity, different kinds of photothermal killing agents have gained much interest along with the mainstream killing systems. Therefore, a number of inorganic nanostructure (mostly gold-based) have been accepted as potential photothermal agents, while their biodegradability was not clearly defined. In this aspect, degradable polymeric nanoparticles like polyaniline (PANI) have concomitantly attracted considerable attention. Among different polymeric nanoparticles, the PANI is considered preferable due to biocompatibility, low cost, mechanical flexibility, and the strong NIR absorption that demonstrated photothermal effect in various reports.<sup>14,15</sup> Although considerable effort has been devoted to this perspective and significant achievement has been made in both academic and industrial research, a number of challenges still remain for the implementation of rapid eradication agents/methods, especially for material surface cleaning and protection.<sup>15,16</sup> The development of such NIR-active photothermal coating agents to which bacteria are susceptible would allow users to control the bacteria cleaning/killing process.

In this study, 2-chloro-3',4'-dihydroxyacetophenone (CCDP) conjugated poly(vinylpyrrolidone) sulfobetaine (PVPS) was designed for use as an antibacterial adhesive coating agent. To incorporate broadband NIR light absorption properties, polyaniline (PANI) was subsequently assembled with the PVPS by ionic complex. The final design resulted in conducting antibacterial coating materials that could absorb broadband NIR light (650–900 nm region) to emit photothermal heat. Our reported coating material (PVPS:PANI) can therefore be used as an NIR-active, photothermal, self-cleaning conducting surface for the rapid killing of surface bacteria.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Polyvinylpyrrolidone (PVP,  $M_w$ : 40 000), 2-chloro-3',4'-dihydroxyacetophenone (CCDP), 1, 3-propanesultone, ethanol, tetrahydrofuran (THF), HCl, polyaniline ( $M_n$ : 10 000), trizma base (99%), trizma HCl (99%), diethyl ether, hexane, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenylterazolium bromide (MTT), MRS, lysogeny broth (LB), agar, deuterium oxide ( $D_2O$ ), and [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] (MTT) were purchased from Sigma-Aldrich, Korea. Propidium iodide (PI) and SYTO 9 were purchased from Molecular Probe, Life Technologies (Invitrogen).

**2.2. Characterization.** Scanning electron microscopy (SEM) was carried out with an SNE-3000 M (SEC). For the SEM analysis, samples were prepared by solution surface coating. The UV–vis–NIR spectra of the samples were recorded with a UV–vis absorption

spectrometer (Optizen 2020UV, Mecasysy Co.). Transmission electron microscopy (TEM) pictures were taken using FE-TEM, 200 kV, Technai F-20 (FEI, Netherlands). XPS spectra were obtained on an Omicrometer ESCALAB (Omicrometer, Taunusstein, Germany). Zeta potential data were obtained using a particle size analyzer (ELS-Z) from Otsuka Electronics Corp. The NIR laser was 808 nm (PSU-III-LRD, CNI Optoelectronics Tech. Co. LTD, China).

**2.3. Synthesis of Poly(vinylpyrrolidone)sulfobetaines [PVPS] through Betainization.** 2-Chloro-3',4'-hydroxyacetophenone (CCDP, catechol) quaternized polyvinylpyrrolidone (C-PVP) was synthesized following a method similar to that of our previous work.<sup>2</sup> Briefly, 3 g of C-PVP and 1,3-propane sultone (1.43 g) was dissolved in cosolvent THF/ethanol in a 1:1 ratio at room temperature. The solution was then stirred for 24 h at 40 °C. After being stirred, the solvent was evaporated using a rotary evaporator and precipitated using *n*-hexane. The resulting PVPS was dried under vacuum. The yield of the product was 91%.

**2.4. Formation of PVPS:PANI via Ionic Complex.** The PVPS:PANI composite was prepared by the formation of ionic complexes in the presence of PVPS and polyaniline. Briefly, PVPS (0.01 g) and polyaniline (0.1 g) were dispersed in 10 mL of 0.1 M HCl solution by sonication for 30 min. The solutions were then mixed together, the pH was controlled to be between pH 3–4 with 0.1 M HCl solution, and stirring was carried out for 24 h at room temperature. Finally, the PVPS:PANI composite obtained was purified by dialysis (molecular weight cutoff: 3500; Spectrum Laboratories, Inc.). The resulting polymer was freeze-dried and analyzed. The yield was 81% (Figure S1, Supporting Information).

**2.5. Antibacterial Activity.** Stock solutions of *S. aureus* (Gram-positive, strain ATCC 25323) and *E. coli* (Gram-negative, strain ATCC 25922) were prepared in LB and MRS broth (50 mL) medium, respectively, and incubated at 37 °C for 12 h at  $10^8$  cells/mL with varying concentrations of PVPS:PANI. At the end of the incubation period, the PVPS:PANI treated *S. aureus* and *E. coli* strains were irradiated with the 808 nm NIR laser for 1–5 min. The bacterial cells were then spread in Petri dishes for evaluation of the growth inhibition. Bactericidal effect was defined as a decrease in the CFU/mL after 24 h. For the control, both types of cells were used without addition of PVPS:PANI.

**2.6. SEM Evaluation of Bacterial Morphology.** The morphological changes to *S. aureus* and *E. coli* were investigated by scanning electron microscopy (SEM), following a procedure similar to that reported by Obonyo et al.<sup>17</sup> The bacterial cells were incubated for 1 h with 0.10 mg/mL [PVPS:PANI], and then visualized by SEM. For preparation of the SEM samples, untreated and treated bacteria were centrifuged to remove the supernatant, and the remaining pellet was quickly fixed with 2% glutaraldehyde for 2 h at 4 °C. The samples were then centrifuged to remove the glutaraldehyde and resuspended in water. The bacterial suspensions were dropped onto a polished silicon wafer and allowed to dry at room temperature. The dried samples were then sputter coated with platinum before SEM imaging.

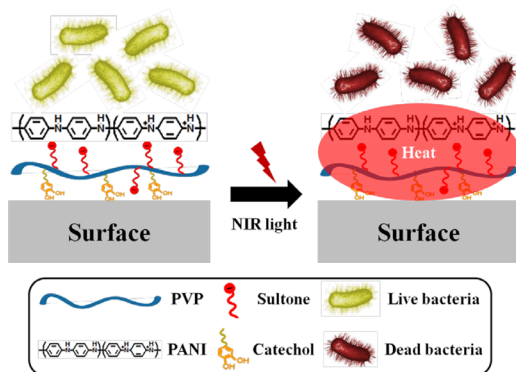
**2.7. Fluorescence Microscopy.** A live/dead bacterial viability kit (L-7007, Invitrogen, Carlsbad, CA) was used to determine the bacterial cell viability. PVPS:PANI-coated PET surfaces were prepared by the same procedure as described above, except that PET surfaces with an original size of 2.0 cm × 2.0 cm were used. A solution of mixed SYTO 9 and PI dyes was prepared according to the manufacturer's instructions. Bacterial suspensions (1 mL,  $5 \times 10^5$  CFU/mL) were then mixed with the fluorescent dyes (10  $\mu$ L) for 15 min. The bacterial suspensions with dyes (10  $\mu$ L) were dropped onto PVPS:PANI-coated or untreated (control) PET surfaces, and a glass coverslip (2.0 cm × 2.0 cm) was placed over the droplet. The slides were then incubated with shaking at 200 rpm for 1 h at 37 °C. The slides were also placed in the dark to avoid bleaching of the fluorescent dyes by ambient light. Examination was carried out with a fluorescence microscope (LSM 510, Carl-Zeiss). Images were obtained using an oil immersion 20× objective lens.

### 3. RESULTS AND DISCUSSION

Gaining a proper understanding of the characteristics of individual materials and evaluating their native behavior from different points of view has facilitated the exploration of new applicable sites.<sup>18</sup> For this purpose, composited polymers that are widely used as biomaterial can also have the additional possibility to be utilized as hyperthermic coating agents if they show optical absorption properties conducive to photo-activation for conversion to photothermal heat, simply by incorporating adhesive properties.<sup>1,5</sup> Thereafter, a cytotoxic NIR-active hyperthermic coated surface can be designed for the promising user control of rapid bacterial killing.

Utilizing the broad NIR absorption properties of polyaniline (PANI), the adhesive catechol (CCDP)-conjugated polyvinylpyrrolidone (PVP) with sultones was combined by ionic complex to yield the composite material [PVPS:PANI] for use as an NIR-absorbing stable adhesive coating agent.<sup>19,20</sup> The overall design is illustrated in Scheme 1.

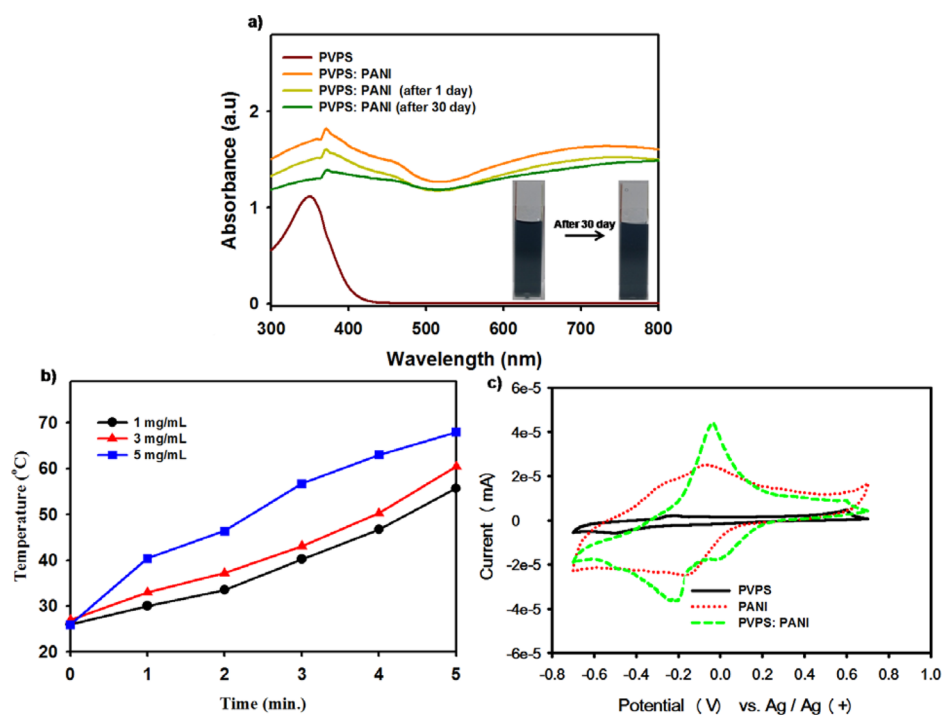
**Scheme 1. Illustration of the Preparation and Application of PVPS:PANI Coating and NIR Irradiation for the Photothermolysis of Surface Bacteria**



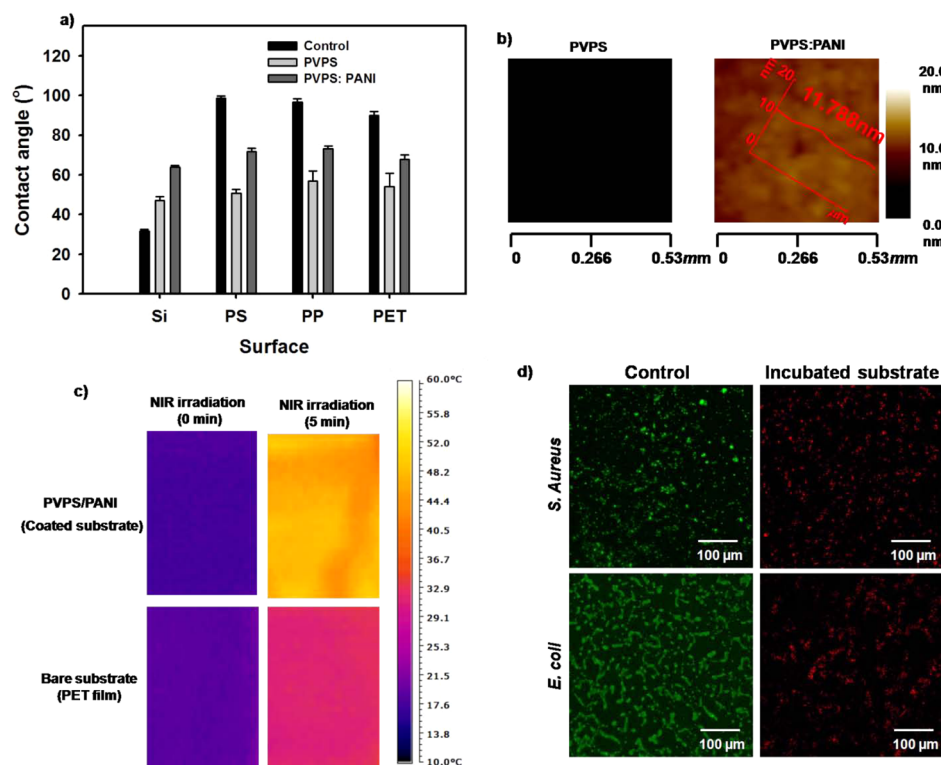
The UV-vis to NIR spectra of PVPS and PVPS:PANI composite materials were recorded to investigate the light absorption properties, as shown in Figure 1a. The spectrum of PVPS:PANI was dominated by a broad absorption band from the UV-vis to NIR region. The electronic properties of  $\pi$ - $\pi^*$  transition of the polymeric backbone benzenoid ring with excited quinoid ring arose from charge transfer to the adjacent benzenoid rings, with each side contributing broad absorption specifically near the NIR area.<sup>21</sup> Moreover, UV-vis-NIR absorption on PET (polyethylene terephthalate) substrate coated PVPS:PANI film has also shown a similar NIR band in that area (Figure S2, Supporting Information). As the stability of composite materials is an important issue during application, the PVPS:PANI was evaluated for 30 days, during which the stability of the broad NIR absorption band was maintained. Furthermore, the thermo gravimetric analysis (TGA) demonstrated the concentration of PVPS and PANI suggesting a 1/5 ratio in PVPS:PANI composite (Figure S3, Supporting Information). The PVPS:PANI composite materials are highly sensitive to NIR light absorption, which follows the characteristic properties of hyperthermal-based NIR-responsive photothermal agents.<sup>19</sup> As expected, the NIR-irradiated PVPS:PANI composite agent showed a sharp rise in heat as a function of laser exposure from 1 to 5 min. For 1–3 mg/mL solutions of the PVPS:PANI composite, NIR agent generated temperatures of 52–67 °C (Figure 1b). Therefore, this may

suggest that the light absorbed by NIR-active PVPS:PANI composite can efficiently be converted into thermal energy.<sup>15,19</sup> The effects of pH on ionic complexed PVPS:PANI composite were studied for photothermal performance where acidic condition maintained a slightly better photothermal efficiency than basic pH (Figure S4, Supporting Information). At the same time, the potential native properties of the PVPS:PANI, as a conducting material, were also tested by standard cyclic voltammetry (CV). Figure 1c shows the cyclic voltammetry (CV) of PVPS, PANI, and PVPS:PANI electrodes of the same respective weight. The CV curve of the PVPS:PANI electrode exhibited a much larger rectangular area than that of the pure PANI electrode with a reversible redox process, mainly due to the electrostatic ionic complex and ordered morphology.<sup>22</sup> The electrostatic ionic interaction between PANI and sultones ( $\text{SO}_3^-$ ) facilitated charge transfer, consequently resulting in improvement of the electrochemical performance. In the study conditions of pH 7.4, the PVPS:PANI composite showed a surface charge of +18 mV, which indicated substantial colloidal stability and dispersibility.<sup>23</sup>

The introduction of a catechol (CCDP) moiety in composite materials has benefits for use as an independent coating agent. The adhesion properties of catechol are therefore widely utilized for the fabrication of a wide variety of coating agents on various substrate properties.<sup>5</sup> To examine the surface coating efficiency, the CCDP conjugated PVPS:PANI composites were applied on silicon (Si), polystyrene (PS), polypropylene (PP), and poly ethylene terephthalate (PET) substrate. As can be seen in Figure 2a, the application of PVPS:PANI coating composite on Si substrate resulted in increased hydrophobicity, which was confirmed by the increase of the water contact angle from 25° to 64°. In contrast, polystyrene (PS), polypropylene (PP), and poly ethylene terephthalate (PET) coated substrates showed decreased water contact angles of 26°, 23°, and 20°, respectively. The decreased static contact angle was due to the higher hydrophobicity of these bare surfaces as compared to the coated surface. However, all of the coated substrates maintained 64°–67° static contact that revealed the uniformity of the surface modification with PVPS:PANI coating agents. As seen via atomic force microscopy (AFM) in Figure 2b, the PVPS:PANI-covered surfaces showed well-dispersed arrangement. In the AFM topography measurements, PVPS:PANI exhibited a 11.78 nm higher thickness as compared to the free PVPS surface. Having established that NIR excitation of the PVPS:PANI has photothermal conversion properties, it was then necessary to examine the photothermal sensitivity of this surface. Irradiation of the PVPS:PANI surface with the NIR laser demonstrated immense thermal elevation (52–55 °C) of the coated substrate (PET), strongly indicating photothermal conversion ability (Figure 2c). To evaluate the potential applicability of this NIR-active photothermal surface, bacterial photothermolysis using the PVPS:PANI coating was observed through fluorescence-based cell labeling assay. The fluorescence labeling of SYTO 9 (green color) for live cells and propidium iodide (red color) for dead bacterial cells allows the cytotoxic effects to be distinguished simultaneously.<sup>24</sup> As proof of concept, NIR exposure of the PVPS:PANI coated material treated with both bacterial strains (*S. aureus* and *E. coli*) showed red stain emissions from dead cells, demonstrating the bacterial killing efficiency, whereas only live bacteria were detected in the control groups (Figure 2d). Therefore, NIR-irradiated PVPS:PANI coating materials were proven to be a promising exploration into the new and exciting concept of clean and



**Figure 1.** (a) UV-vis-NIR absorption of PVPS and PVPS:PANI. The images included inside show the stability, as determined through solubility observation and UV-vis-NIR absorption from 1 to 30 days. (b) Photothermal heat conversion curve of NIR-irradiated [PVPS:PANI] at 1, 3, and 5 mg/mL. The NIR laser was 808 nm and 2 W/cm<sup>2</sup>. (c) Cyclic voltammetry (CV) curves of PVPS, PANI, and PVPS:PANI at a scan rate of 5 mV/s.



**Figure 2.** (a) Water contact angle measurements on silicon (Si), polystyrene (PS), polypropylene (PP), and polyethylene terephthalate (PET) substrate with application of [PVPS:PANI] coating material. (b) AFM topography images and height profiles of PVPS and PVPS:PANI coated Si wafers, respectively. (c) The near-infrared (NIR)-irradiated photothermal response of PVPS:PANI and PVPS-coated PET substrate. (d) Fluorescence microscopy images showing the photothermal cytotoxicity in *S. aureus* and *E. coli* after 5 min of 808 nm NIR irradiation on the PVPS:PANI (1 mg/mL) surface using SYTO 9 (live cells) and propidium iodide (PI) costain (dead cells). The control groups were examined in the absence of NIR exposure. The laser power density was 2 W/cm<sup>2</sup>.

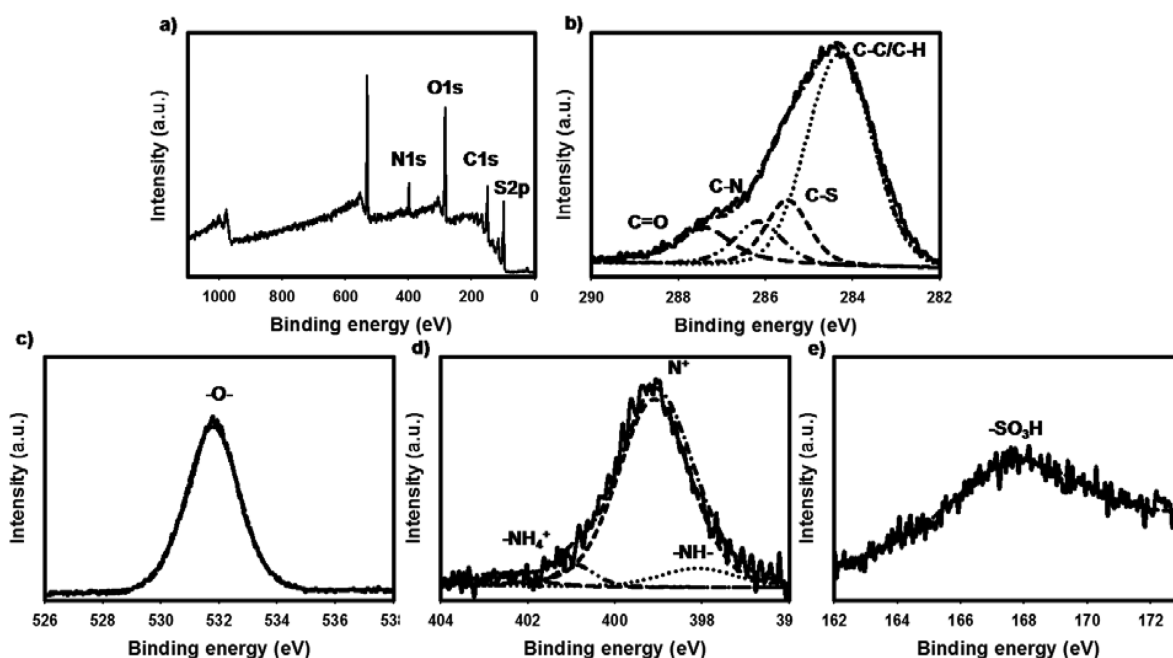


Figure 3. XPS measurements in (a) survey scan, and narrow scan of (b) C 1s, (c) O 1s, (d) N 1s, and (e) S 2p of PVPS:PANI composite material.

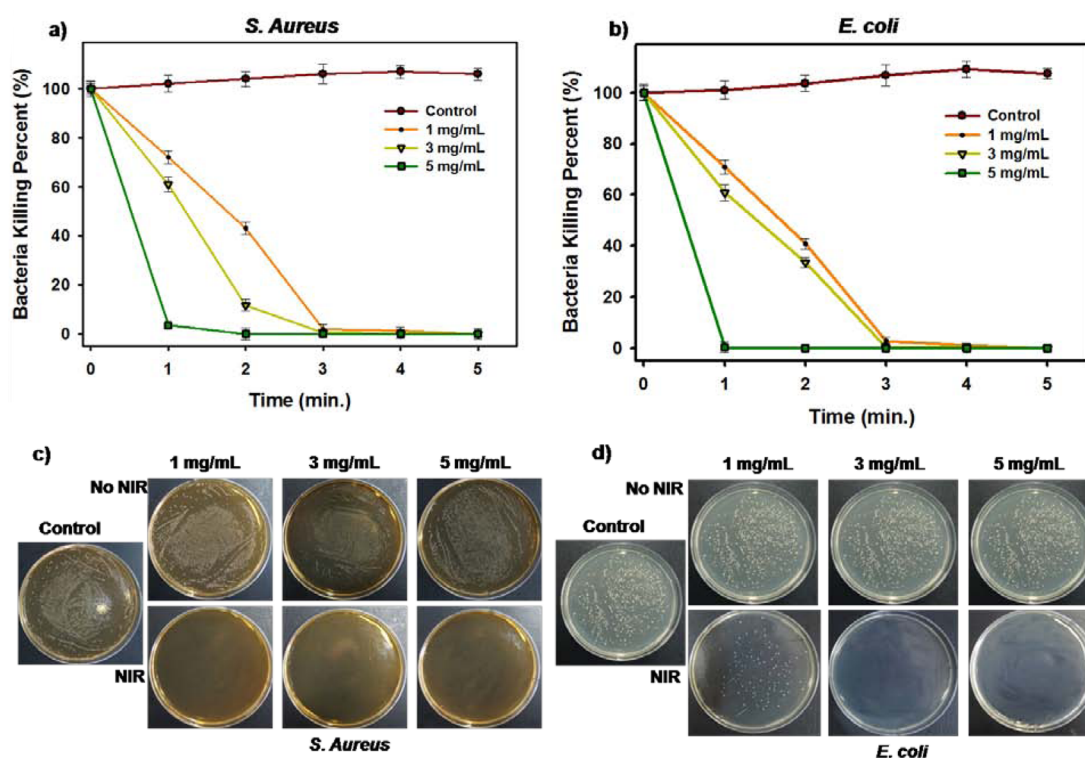


Figure 4. (a and b) The percentage of photothermal bacterial killing efficiency of [PVPS:PANI] at concentrations of 1, 3, and 5 mg/mL on Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria, respectively. (c and d) Photographs of *S. aureus* and *E. coli* colonies grown on LB agar plates of (a) and (b). The laser power density was  $2 \text{ W/cm}^2$ , with exposure for 5 min at 808 nm.

sustainable material surface protection, carried out more rapidly.

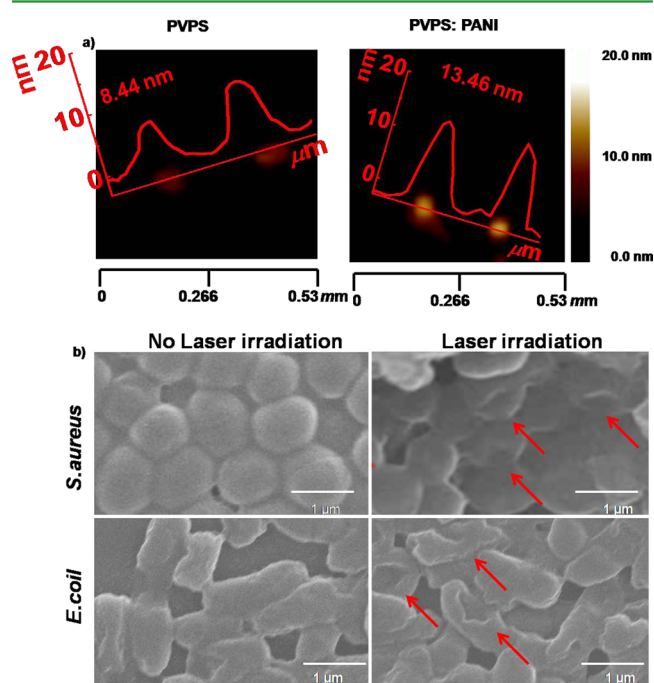
The XPS survey scan spectra (Figure 3a) and the narrow scan model fit spectra were determined for the C 1s, O 1s, N 1s, and S 2p, peaks, respectively (Figure 3b–e). The optimized fit parameters showed deconvoluted C 1s core peak positions of C–C/C–H (284.3 eV), C–S (285.5 eV), C–N (286.2), and C=O (287.4) components (Figure 3b). The peak centered at

532 eV represented the O 1s peak (Figure 3c). The area of the N 1s peak was fractioned into three components, the imine groups (398.1 eV), the cationic form of nitrogen (400.9 eV), and the protonated amine groups (402.6 eV), clearly demonstrating the integral structural parts of PANI (Figure 3d). The S 2p XPS signal at 168.8 eV described  $-\text{SO}_3\text{H}$  groups as a function of sulfone moieties (Figure 3e).<sup>25–27</sup> The overall

XPS peaks therefore reasonably denoted the integrated chemical composition of PVPS:PANI film.

To study the hyperthermic-based surface bacteria killing properties of the prepared PVPS:PANI coating materials, Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria were treated with the PVPS:PANI agent. After NIR exposure, both PVPS:PANI-treated bacterial species displayed time-dependent killing. The widely dispersed PVPS:PANI composite at 1 mg/mL was capable of destroying all bacteria after 3 min of NIR irradiation (Figure 4a and b). This killing time can be decreased by increase of the PVPS:PANI concentration (Figure 4c and d).<sup>28</sup> Although PANI was proven to have antibacterial activity through disruption of the bacterial cell surface,<sup>8</sup> these results demonstrate a switchable rapid killing system from treated surface through utilization of the broadband NIR absorption property of polyaniline (PANI). This early destruction can have a significant impact on the prevention of bacterial resistance and strengthen the shelf life of material surfaces.<sup>29</sup> In addition to photothermal antibacterial activity, the toxicity of PVPS:PANI was evaluated by the well-known MTT assay method on mammalian MDCK cell line demonstrating biocompatibility (Figure S5, Supporting Information).<sup>30</sup>

AFM images were obtained to gain a visual understanding of the modification of the PVPS:PANI from PVPS. Figure 5a



**Figure 5.** (a) The AFM images and height profiles of a droplet of PVPS and PVPS:PANI on silicon wafer. (b) Scanning electron microscopy (SEM) images of *S. aureus* (top panel) and *E. coli* (bottom panel) after 5 min of NIR irradiation at 808 nm with [PVPS:PANI] treatment at 1 mg/mL. The control groups were examined in the absence of NIR irradiation. The laser power density was 2 W/cm<sup>2</sup>.

shows the average particle diameters of PVPS (8.44 nm) and PVPS:PANI (13.46 nm). In these images, the rising particle sizes are characteristic of electrostatic interaction, following assembly between PVPS and PANI. As could be expected, the external stimulus-controlled self-cleaning coating material has enormous potentiality in different biomedical fields.<sup>31,32</sup> Moreover, the transmission electron microscopic (TEM) image also supported the same morphological character as

those observed in AFM micrograph (Figure S6, Supporting Information). From this perspective, attachment and cell membrane lysis after NIR stimulus was confirmed through the study of bacteria with PVPS:PANI via scanning electron microscopy (SEM). Herein, the SEM images showed dispersibility of the PVPS:PANI particles to attach/capture the bacterial strain (Figure 5b). However, after 5 min of NIR exposure, all of the PVPS:PANI-treated bacteria (*S. aureus* and *E. coli*) were destroyed, demonstrating the rapid killing efficiency of this agent.

#### 4. CONCLUSION

By utilizing NIR absorption properties, we presented an NIR light-sensitive photothermal coating agent (PVPS:PANI). The compositional character was rectified through optical absorption study, showing that the coating agent efficiently absorbs in the UV–vis to NIR region. This broad NIR absorption was found to result in the rapid generation of eminent photothermal heat in a very short period. The static contact angle demonstrated uniform coating potentiality. Interestingly, both strains of PVPS:PANI-treated bacteria (*S. aureus* and *E. coli*) were destroyed within 3 min of NIR exposure of the coated surface. The colony counting and MTT assay simultaneously demonstrated antibacterial efficiency. In addition, the SEM image of 1 mg/mL PVPS:PANI-treated bacteria and fluorescence-labeling of live/dead cells by coated substrate imaging clearly demonstrated the potential of NIR irradiated PVPS:PANI photothermal coating agents. Photothermal-based surface protection strategies therefore promise exciting opportunities in the emerging field of surface coating.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

<sup>1</sup>H NMR spectrum, UV–vis–NIR absorption band, comparison of thermograms, heat generation curve, cell viability assays, and TEM images. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b04321.

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##### Notes

The authors declare no competing financial interest.

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