

SUPPLEMENTARY INFORMATION

Optimization and antibacterial response of *N*-halamine coatings based on polydopamine

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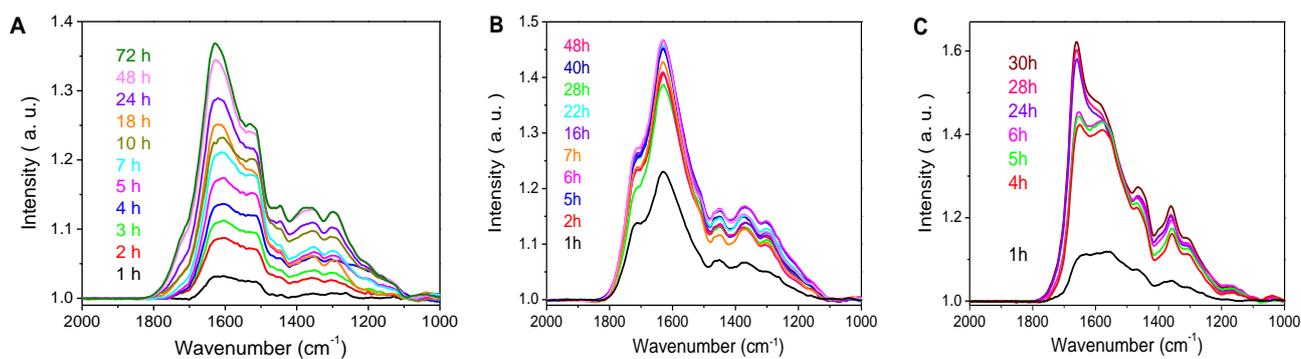


Figure S1. PM-RAIRS spectra of gold surfaces functionalized with (A) PDA-O₂ film by immersion in 0.5 mg·mL⁻¹ dopamine solution, (B) PDA-IO₄⁻ film by immersion in 0.5 mg·mL⁻¹ dopamine + 20 mM sodium periodate solution and (C) PDA-PEI film by immersion in 0.5 mg·mL⁻¹ dopamine + 0.25 mg·mL⁻¹ PEI solution, for various times.

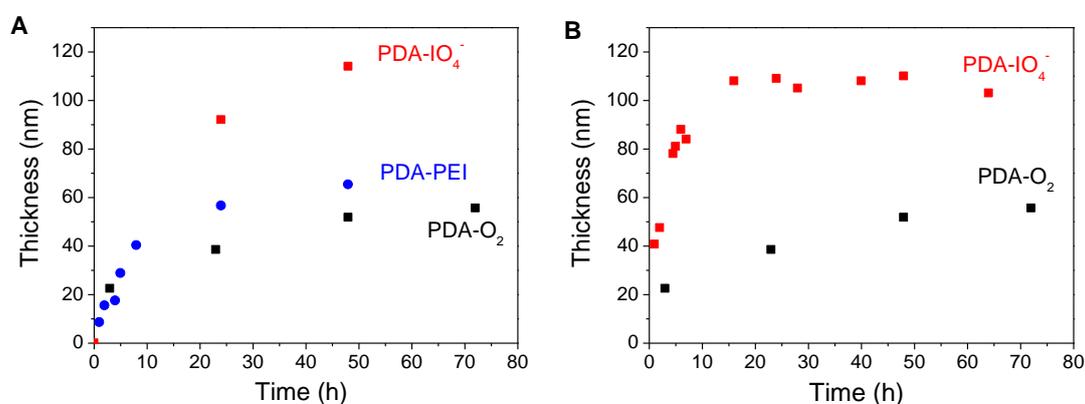


Figure S2. PDA-O₂, PDA-IO₄⁻ and PDA-PEI films thickness evaluated by (A) SEM observations and (B) Ellipsometry measurements.

Film thickness measurements by ellipsometry for the PDA-O₂ and PDA-IO₄⁻ coatings and SEM observations for the PDA-PEI composite, reveal a logarithmic growth of the film as a function of the immersion time of the substrate (Figure S2). For the PDA-O₂ coating, the ellipsometry data confirms the kinetic deposition profile obtained by PM-RAIRS analysis, namely that the thickness of the PDA film progressively reaches a maximum value of around 50 nm in accordance with the data reported by Messersmith *et al.*¹. This stationary phase can be attributed to the depletion of the monomer in the supernatant solution, being able to crosslink on the PDA film, in favor of non-reactive quinone molecules². Regarding the PDA-IO₄⁻ coating, a faster deposition kinetics than during a conventional deposition is observed, for this a logarithmic kinetics leading to thicknesses up to 100 nm is observed. This faster growth rate can be explained by the strong oxidizing power of periodate leading more quickly to the oxidation of dopamine and the formation of PDA particles in solution. The appearance of the coating after 24 hours of deposition observed by SEM reveals a very dense and very rough coating due to bulky PDA aggregates deposited on the surface of the coating (Figure S3).

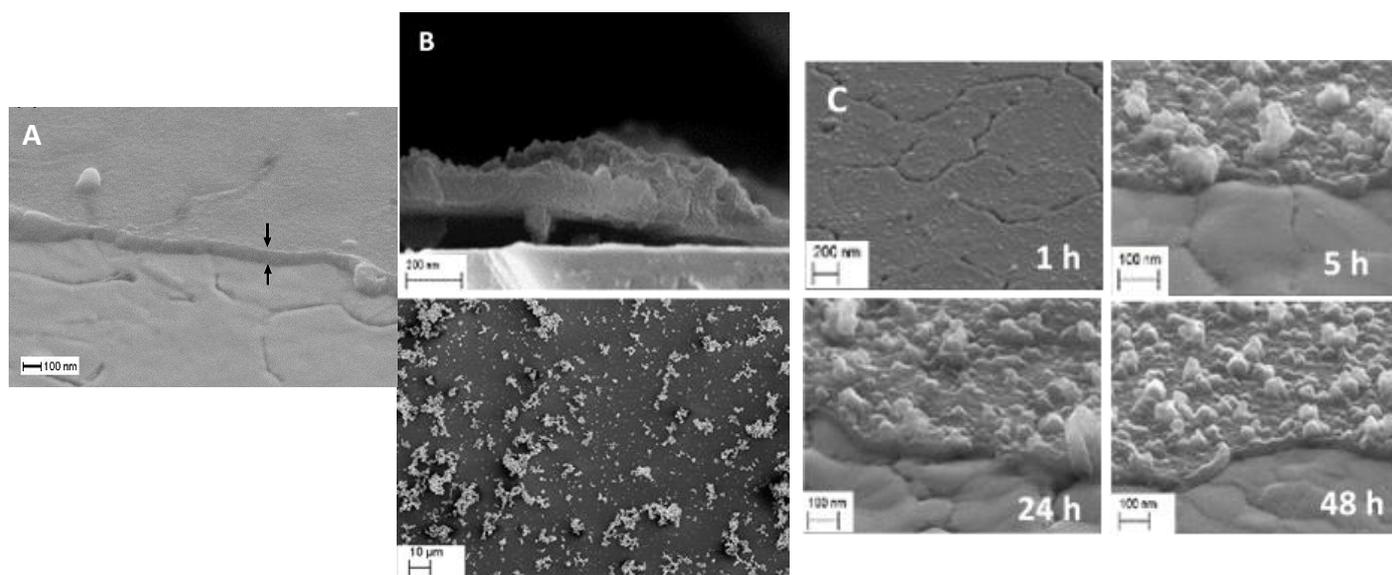


Figure S3. SEM micrographs of (A) PDA-O₂ coating on a gold substrate after 24 h of immersion in 0.5 mg mL⁻¹ dopamine solution, (B) PDA-IO₄⁻ coating on a gold substrate after 24 h of immersion in 0.5 mg mL⁻¹ dopamine + 0.20 mM of sodium periodate solution and (C) PDA-PEI coatings on gold substrates after 1 h, 5 h, 24 h, and 48 h of immersion in 0.5 mg mL⁻¹ dopamine + 0.25 mg mL⁻¹ PEI solution.

Finally, for the PDA-PEI coating, the monitoring of the thickness, carried out by SEM observations, again reveals a logarithmic change in the thickness of the deposit over time, confirming the PM-RAIRS observations. A maximum deposit thickness is reached around 60 nm of deposit after 24 hours of immersion, which shows a deposit kinetics similar to the so-called conventional coating, namely the PDA-O₂ coating. The SEM observations on a gold surface reveal that after 5 hours of deposition, the topography of the gold surface is no longer visible (grain boundary still visible after 1 hour of immersion time) unlike the PDA-O₂ coating for which it is still visible there after 48 h of deposition, which clearly shows a greater thickness of this composite. These observations also reveal a deposit exhibiting two distinct morphological layers. A dense layer formed after 5 hours of deposition then an upper layer composed of aggregates providing greater roughness to the surface compared to a coating of PDA-O₂. It would therefore seem that during the early stages of deposition, a compact layer is formed with a density comparable to that of conventional PDA-O₂, then PDA-PEI aggregates formed in solution following the polymerization of the composite are grafted on the surface, these aggregates are not removed during the sonication step.

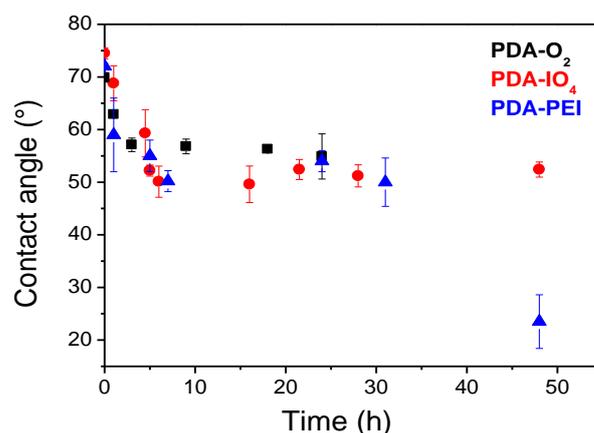


Figure S4. Evolution of the contact angle with water as a function of the immersion time of a gold surface in various PDA solutions. Films: PDA-O₂ (black square), PDA-IO₄⁻ (red circle) and PDA-PEI (blue triangle).

Contact angle measurements with water were used to assess the wettability of the surface and to demonstrate a change in the chemistry of the latter following deposition. Indeed, PDA-O₂ is a hydrophilic coating exhibiting a contact angle with water close to 60°³, unlike bare gold for which an angle close to 75° is generally observed. A monitoring of wettability with water as a function of the deposition time of the PDA was carried out, the results are presented in Figure S4. It is noted that the contact angle decreases over time to reach a plateau after 3 h of deposition, level around 55° which approaches the value of the contact angle reported in the literature. It can thus be seen that this monitoring of wettability makes it possible to have, in a simple and rapid way, an indication of the time at the end of which the coating becomes homogeneous at the macroscopic level in terms of coverage of the substrate and thus completes the monitoring by PM-RAIRS and ellipsometry.

Concerning the PDA-IO₄⁻ coating, the evolution of the contact angle formed between the coating and the water matches the profile obtained for the PDA-O₂ coating. In fact, a sharp reduction in the angle is observed during the first 10 hours, then a plateau is observed, thus testifying to a homogeneous coating on the gold surface which is completely covered by the deposit. Note that this change is similar to the profile found when monitoring the thickness of the deposit. Thus, just as with the PDA-O₂ coating, the kinetic monitoring of the deposit by measuring the contact angle turns out to be a simple method of monitoring the PDA deposit over time.

Finally, it is noted that the PDA-O₂ and the PDA-PEI composite have the same evolution profile of wettability during the first 30 hours of deposition. Indeed, the contact angle with water decreases over time to reach a plateau after 5 hours of deposition, around 50° which is slightly lower than the value obtained from pure PDA. Nevertheless, a very sharp drop in this wettability is observed after 30 hours of deposition, suggesting an enrichment of the surface in PEI, which is more hydrophilic than PDA, in favor of the PDA-PEI composite (PEI having been introduced in excess). We can thus see that this wettability monitoring made it possible to highlight different stages of deposition and surface evolution of the film over time, supplementing the PM-RAIRS, XPS and SEM observations.

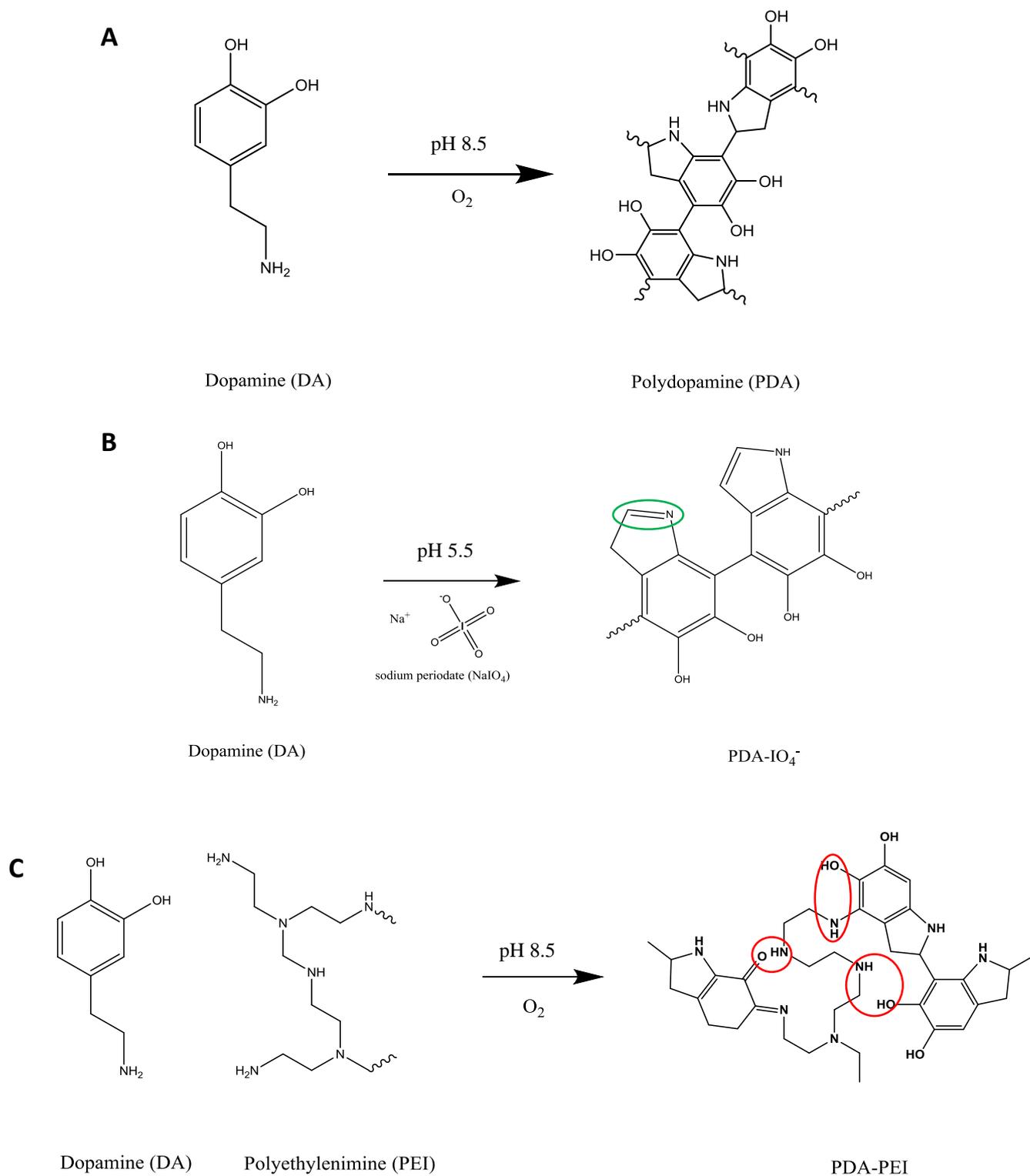


Figure S5. Representative structural components: (A) in PDA-O₂ film, (B) in PDA-IO₄⁻ film with the presence of tertiary amine (in green) and (C) in PDA-PEI films with the presence of hydrogen bonds (in red).

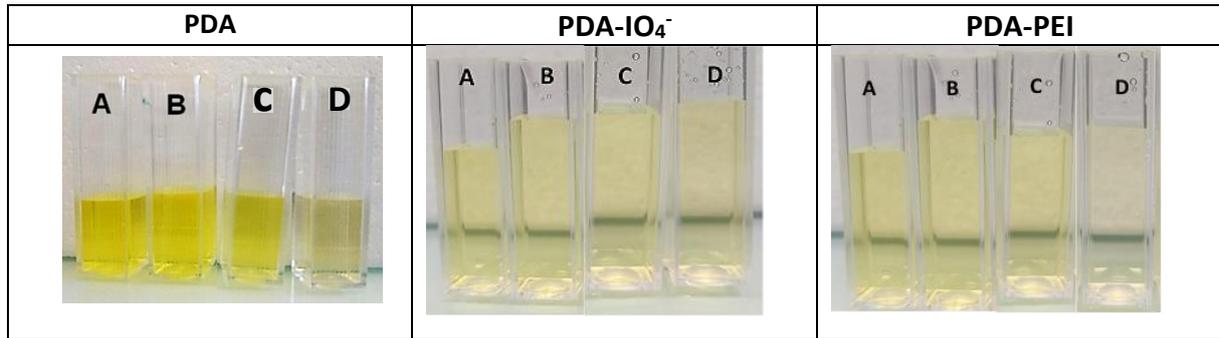


Figure S6. Demonstration of the presence of chloramine functions using TNB. Optical images of cuvettes (1 cm) containing the TNB solution after 24 hours of immersion. (A) un-modified TNB solution, after immersion of (B) Au substrate, (C) PDA-XX film, (D) PDA-XX-Cl film.

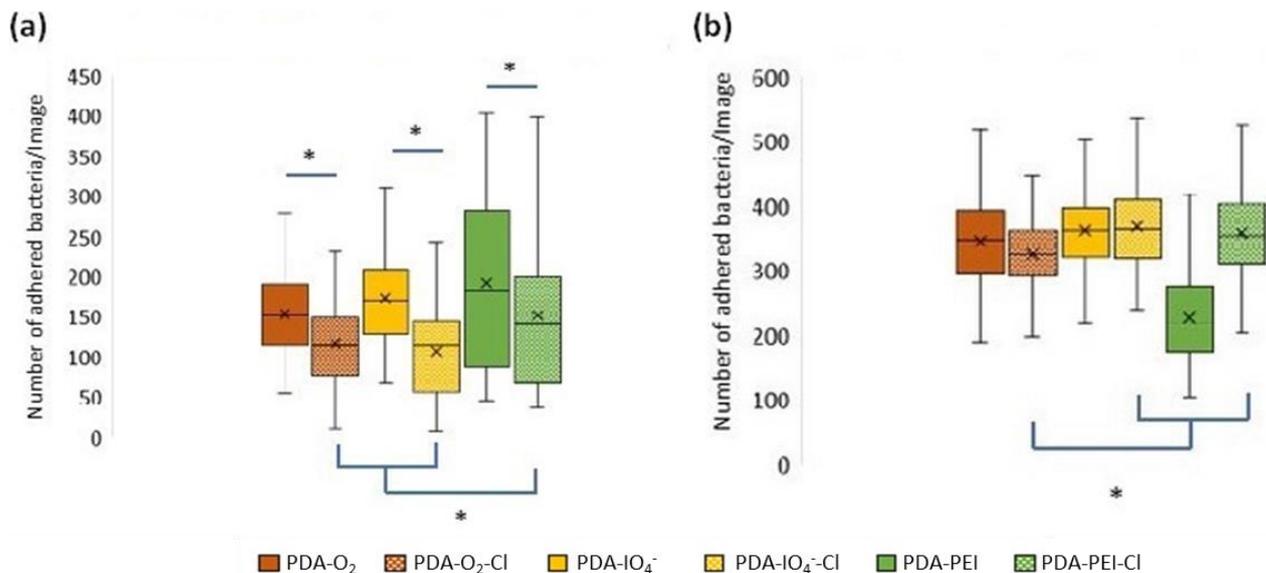


Figure S7. Statistical analyses of bacterial adherence. (a) for *E. coli*, all chlorinated coatings showed statistically significant differences (*) in bacteriological count values compared with control ($p < 0.01$). In addition, PDA-O₂-Cl and PDA-IO₄⁻-Cl coating show significant differences (*) compared to PDA-PEI-Cl ($p < 0.01$). (b) for *S. epidermidis*, no such tendency is observed between chlorinated and non-chlorinated coating; however, PDA-O₂-Cl shows significant difference (*) compared to PDA-IO₄⁻-Cl and PDA-PEI-Cl ($p < 0.01$).

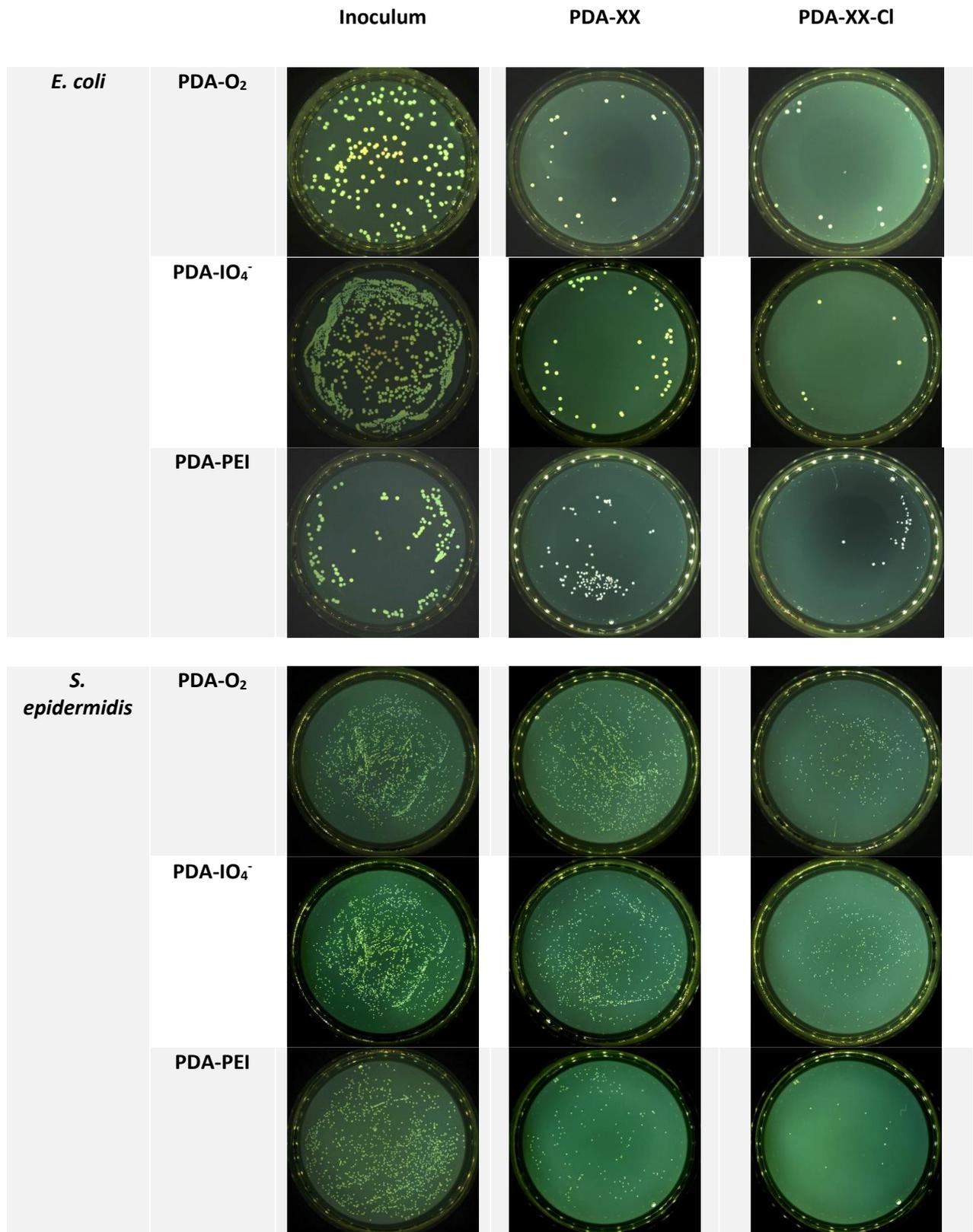


Figure S8. Optical photographs of agar plates presenting the killing test results for inoculum, PDA-XX, and PDA-XX-Cl coatings, after 3 h in contact with 20 μ L of an *Escherichia coli* or an *S. epidermidis* suspension.

Table S1. Average number of bacteria in CFU·mL⁻¹ after killing tests against the different PDA coatings.

		Inoculum	PDA-X	PDA-X-CI
<i>E. coli</i>	PDA-O ₂	2.5 10⁷ (± 6.1 10 ⁵)	3.58 10⁵ (± 4.6 10 ⁵)	2.36 10⁵ (± 2.7 10 ⁵)
	PDA-IO ₄ ⁻	2.0 10⁷ (± 2.2 10 ⁵)	5.1 10⁵ (± 8.5 10 ⁴)	4.4 10⁵ (± 2.9 10 ⁵)
	PDA-PEI	2.9 10⁶ (± 9.0 10 ⁵)	1.5 10⁶ (± 4.0 10 ⁵)	8.6 10⁴ (± 1.3 10 ⁴)
<i>S. epidermidis</i>	PDA-O ₂	1.4 10⁷ (± 1.2 10 ⁶)	1.1 10⁷ (± 9.0 10 ⁵)	4.6 10⁶ (± 1.2 10 ⁵)
	PDA-IO ₄ ⁻	1.5 10⁷ (± 1.1 10 ⁶)	1.0 10⁷ (± 8.5 10 ⁵)	2.6 10⁶ (± 3.6 10 ⁵)
	PDA-PEI	1.5 10⁷ (± 1.1 10 ⁶)	1.2 10⁷ (± 1.0 10 ⁶)	5.1 10⁶ (± 7.4 10 ⁵)

References

1. Lee. H.; Dellatore. S. M.; Miller. W. M.; Messersmith. P. B.. Mussel-Inspired Surface Chemistry for Multifunctional Coatings. *Science* **2007** 318 (5849) 426-430.
2. Nazi. N.; Humblot. V.; Debiemme-Chouvy. C.. A New Antibacterial N-Halamine Coating Based on Polydopamine. *Langmuir* **2020** 36 (37) 11005-11014.
3. Ponzio. F.; Barthès. J.; Bour. J.; Michel. M.; Bertani. P.; Hemmerlé. J.; d'Ischia. M.; Ball. V.. Oxidant Control of Polydopamine Surface Chemistry in Acids: A Mechanism-Based Entry to Superhydrophilic-Superoleophobic Coatings. *Chemistry of Materials* **2016** 28 (13) 4697-4705.