Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary information for

Nickel Coating on Plasmonic Copper Nanoparticles Lowers Cytotoxicity and Enables Colorimetric pH Readout for Antibacterial Wound Dressing Application

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SUPPORTING EXPERIMENTAL AND CALCULATIONS

1. Finite-Difference Time-Domain Simulations

Finite-difference time-domain (FDTD) calculations were performed using Ansys Lumerical (v222). Dielectric constant data for bulk copper and nickel were taken from CRC handbook. Calculations were performed using a mesh size of 1 nm. The particle was placed in a uniform background medium with a dielectric constant of 1.33. Total-field scattered-field method with linearly polarized incident plane wave was used to simulate the absorption and scattering spectra; the un-polarized spectrum is the sum of the spectra with 0 and 90 degree polarizations.

2. Antibacterial Quantitative Analysis

Antibacterial properties were quantified by using the three parameters: bacterial growth value (BG), bacteriostatic activity (BS), and bactericidal activity (BC). These values were calculated according to JIS L 1902/2008.[1] BG is a measure of bacterial growth over time and is defined as:

$$BG = \log\left(\frac{T_{18h\ (untreated)}}{T_{0\ (untreated)}}\right)$$

where $T_{18h\ (untreated)}$ is the number of colonies (CFU/mL) of the bacteria after being incubated with untreated fabric for 18 hours; $T_{0\ (untreated)}$ is the number of colonies (CFU/mL) of the bacteria at the beginning.

BS pertains to the ability of materials to inhibit the growth of bacteria and is defined as:

$$BS = \log\left(\frac{T_{18h\ (untreated)}}{T_{18h\ (treated)}}\right)$$

where $T_{18h\ (treated)}$ is the number of colonies (CFU/mL) of the bacteria after being incubated with NP-coated fabric for 18 hours.

BC denotes the capacity of materials to eliminate bacteria and is defined as:

$$BC = \log\left(\frac{T_{0\ (untreated)}}{T_{18h\ (treated)}}\right)$$

3. Calculation of crystallite size using Scherrer equation

The Scherrer equation[2] was used to estimate the size of crystallites in CuNPs from the X-ray diffraction (XRD) diffraction peaks. The equation is

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos\theta}$$

where D is the crystallite size, k is the shape factor (0.94), λ is the wavelength of the X-ray source (0.15406 nm), β is the full width at half maximum (FWHM) of the peak, and θ is the Bragg angle.

The three diffraction peaks from Figure 1d (CuNP XRD) at 2θ of 43.2, 50.4 and 74.1 degrees yielded crystallite sizes of 16.1 nm,13.7 nm, and 14.3 nm, respectively. The average crystallite size of CuNPs was then 14.7 nm.

SUPPORTING FIGURES

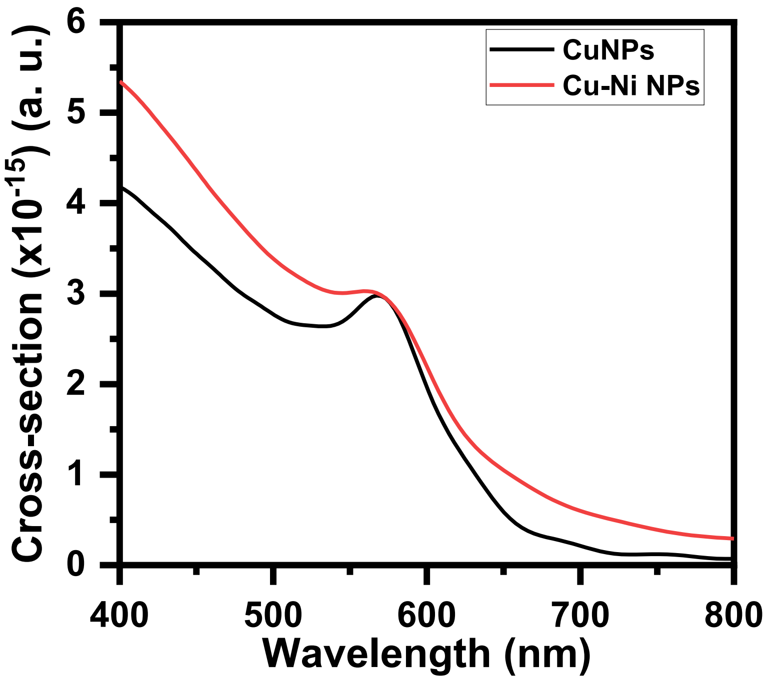

Figure S1. FDTD simulated extinction spectra of 45-nm CuNPs (black) and Cu-Ni NP with 45-nm copper core and 5-nm Ni shell. Ni shell dampens LSPR; however, actual thickness of Ni for the synthesized Cu-Ni NPs could not be determined via simulation.

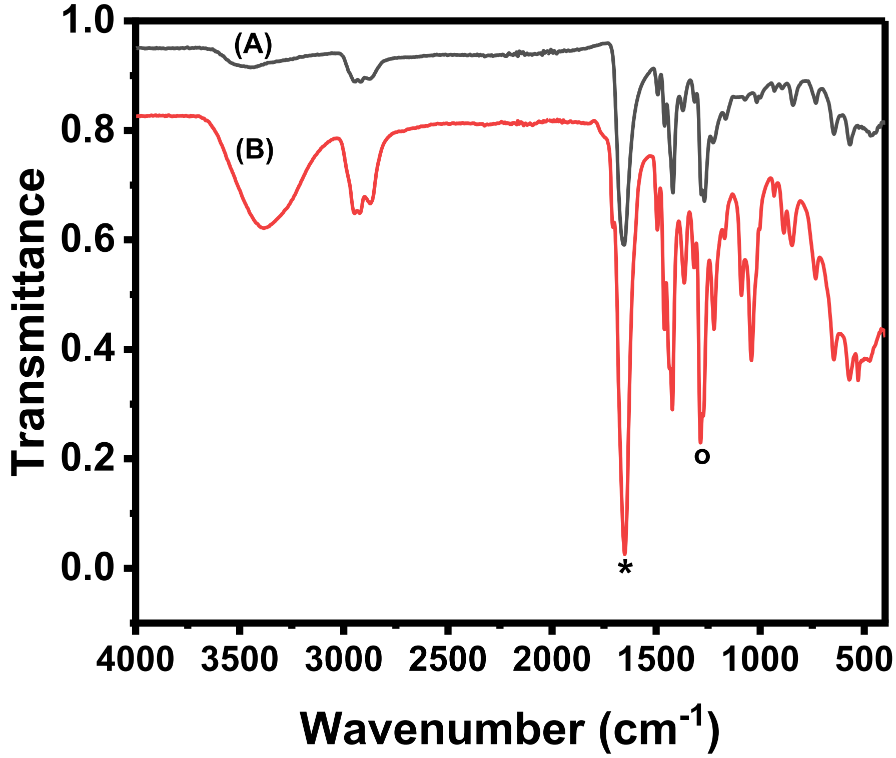

Figure S2. The FT-IR transmission spectra of (A) PVP and (B) purified CuNPs (vertically shifted for clarity). The C=O and C-N stretching vibrational modes observed at 1650 cm^{-1} and 1269 cm^{-1} are indicated by * and °.

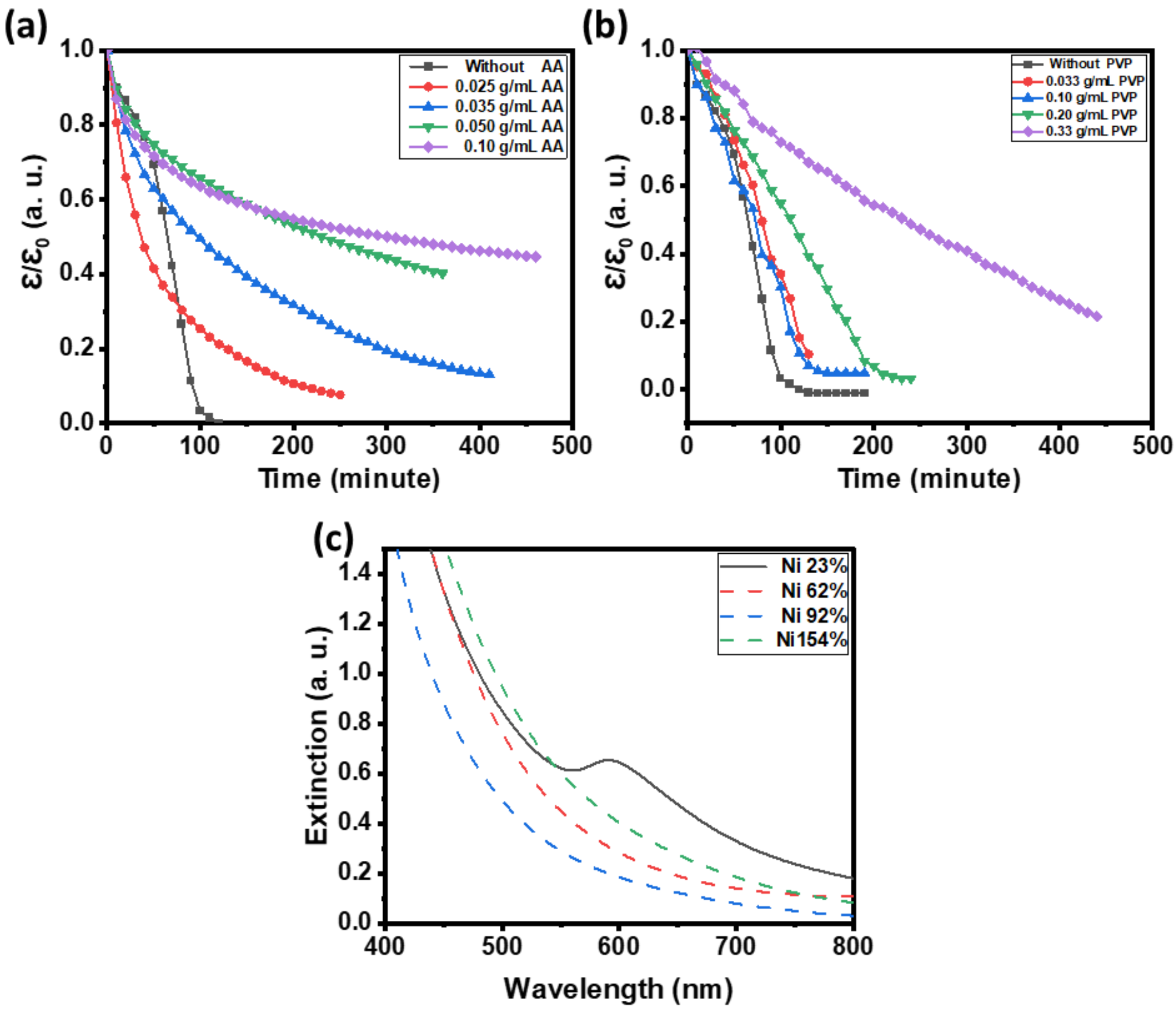

Figure S3. Relative changes in extinction at 570-590 nm for purified CuNPs in water with different concentrations of (a) PVP and (b) AA. (c) UV-vis extinction spectra of as-synthesized Cu-Ni NP solutions with different molar percentages of Ni precursor.

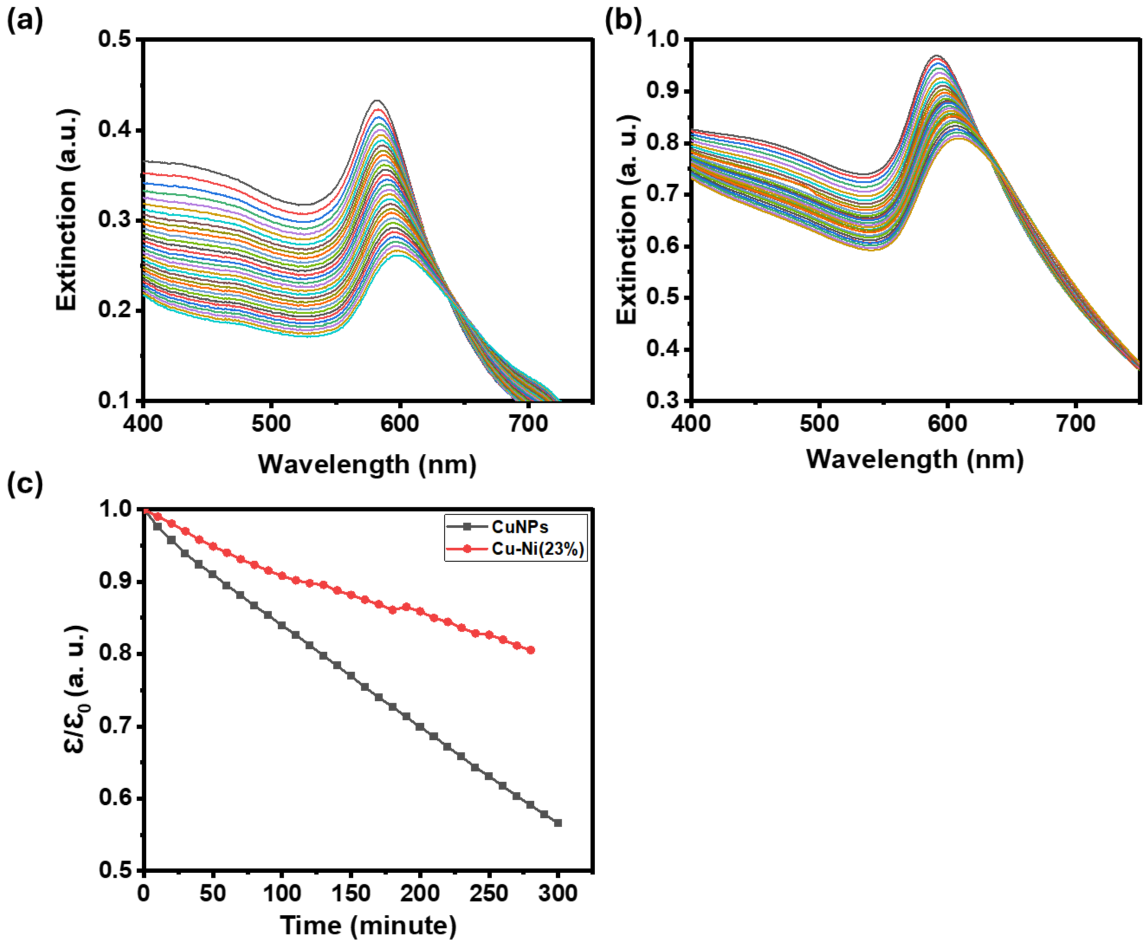

Figure S4. Evolution of UV-vis extinction spectra over time of (a) CuNPs and (b) Cu-Ni NPs in ethanol. (c) Relative extinction intensity at 583 nm vs time of CuNPs vs Cu-Ni NPs.

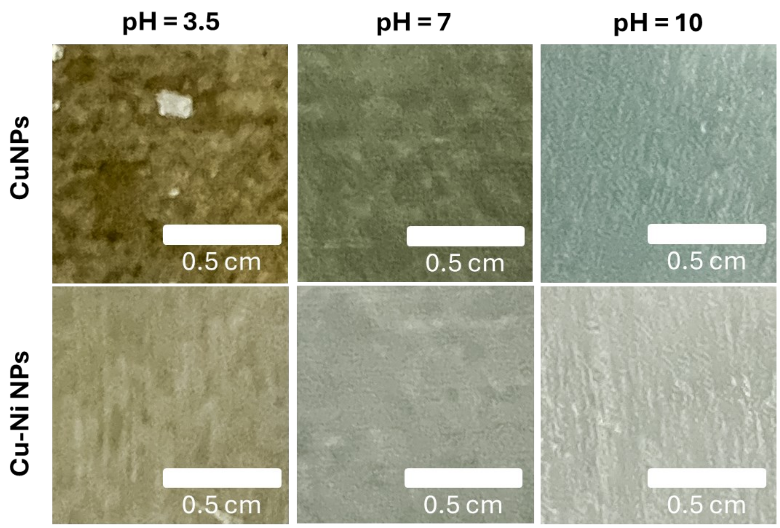

Figure S5. Photographs of CuNP- and Cu-Ni NP-coated fabrics in pH= 3.5, 7 and 10 after one month.

SUPPORTING TABLES

Table S1. Summary of diameters of CuNPs by DLS analysis at different reaction times.

Time	Z-Average (nm)
22s	107.4 ± 4.8
39s	93.0 ± 4.1
47s	90.8 ± 3.7
59s	86.2 ± 6.4
1 min 10 s	84.8 ± 5.0
1 min 30 s	82.0 ± 5.4
5 min	91.9 ± 4.2
10 min	87.7 ± 3.8
15 min	85.1 ± 3.2
20 min	87.8 ± 2.7
25 min	86.5 ± 2.2
30 min	87.8 ± 3.1

Table S2. Summary of quantitative antibacterial tests of CuNPs and Cu-Ni NPs.

NP loading (µmol)	BS[1]		BC[2]		BG[3]
	CuNPs	Cu-Ni NPs	CuNPs	Cu-Ni NPs	
1	-0.01	-0.33	-2.93	-3.21	
2	0.02	0.07	-2.90	-3.27	
4	0.15	0.14	-2.10	-3.20	> 1.50
6	+∞	0.33	+∞	-3.02	
8		1.09		-2.26	

[1] According to the antibacterial standard set by the Japanese Association for the Functional Evaluation of Textiles (JAFET), NP-coated fabrics are deemed significantly effective in inhibiting the growth of bacteria if the BS >2.2[1].
[2] BC > 0 is considered notably effective of NPs-coated fabric in killing bacteria[1].
[3] Bacteria are considered healthy when their growth value surpasses 1.5 in the negative control group[1].

SUPPORTING REFERENCES

1. Japan Textile Evaluation Technology Council, *JEC301. The Certification Standards of Antibacterial Finished Textile Products*, Japan Textile Evaluation Technology Council, Osaka, 2012.

2. F.T.L. Muniz, M.A.R. Miranda, C. Morilla dos Santos, and J.M. Sasaki, *Acta Cryst. A,* 2016, **72**, 385-390.