

Magnetoplasmonic Photonic Arrays for Rapid and Selective Colorimetric Detection of Chloride Ions in Water

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Chemicals

Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$), sodium acetate (CH_3COONa , NaAc), silver nitrate (AgNO_3), sodium chloride (NaCl), magnesium chloride (MgCl_2), nickel(II) chloride (NiCl_2), ammonium chloride (NH_4Cl), zinc chloride (ZnCl_2), cobalt chloride (CoCl_2), barium chloride (BaCl_2), strontium chloride (SrCl_2), sodium nitrite (NaNO_2), sodium fluoride (NaF), copper(II) sulfate (CuSO_4), magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$), zinc sulfate (ZnSO_4), and ethylene glycol (EG) were purchased from Sigma-Aldrich Inc. (Yong-In, South Korea). Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was purchased from Hayashi Pure Chemical Ind., Ltd. (Japan). Nylon filter membrane (0.2 μm pore size, 47 mm diameter) was purchased from Whatman (UK). Deionized (DI) water ($>18 \text{ M}\Omega\text{cm}^{-1}$) was used for all solution preparations and experiments. All chemicals were analytical grade reagents and used as received without further purification.

Synthesis of Ag@Fe₃O₄ NPs

To synthesize NP₁₇₅, 0.1 M of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was fully dissolved in 40 mL of Ethylene Glycol (EG), followed by the addition of 0.875 M of Sodium Acetate (NaAc) and 14.75 mM of AgNO_3 . This mixture was subjected to rigorous stirring for 60 minutes and then sealed in a Teflon-lined stainless-steel autoclave (50 mL in volume). The autoclave was heated to 210 °C for 12 hours before cooling to room temperature. The resulting black products were washed multiple times with ethanol and deionized (DI) water, then dried under vacuum conditions at 60 °C for 6 hours. NP₁₅₀, NP₁₈₅, NP₂₀₀, and NP₂₃₄ were synthesized using the same procedure, but altering the Fe^{3+} precursor concentration. To make porous NP₂₃₄, oxalic acid was added individually to solutions of the Ag@Fe₃O₄ NPs (1 mg mL⁻¹). The mixtures were sonicated for 90 min in a sonication bath and then washed with DI water (with the help of a magnet) at least

thrice. For citric stabilization of NPs, 15 mg of NPs were combined with 15 ml of 3 mM citric acid, followed by 2 hours of sonication using an ultrasonic probe. The NPs were collected and washed with DI water using a magnetic stirrer. The samples were then refrigerated (4 °C) for 6 hours before utilization.

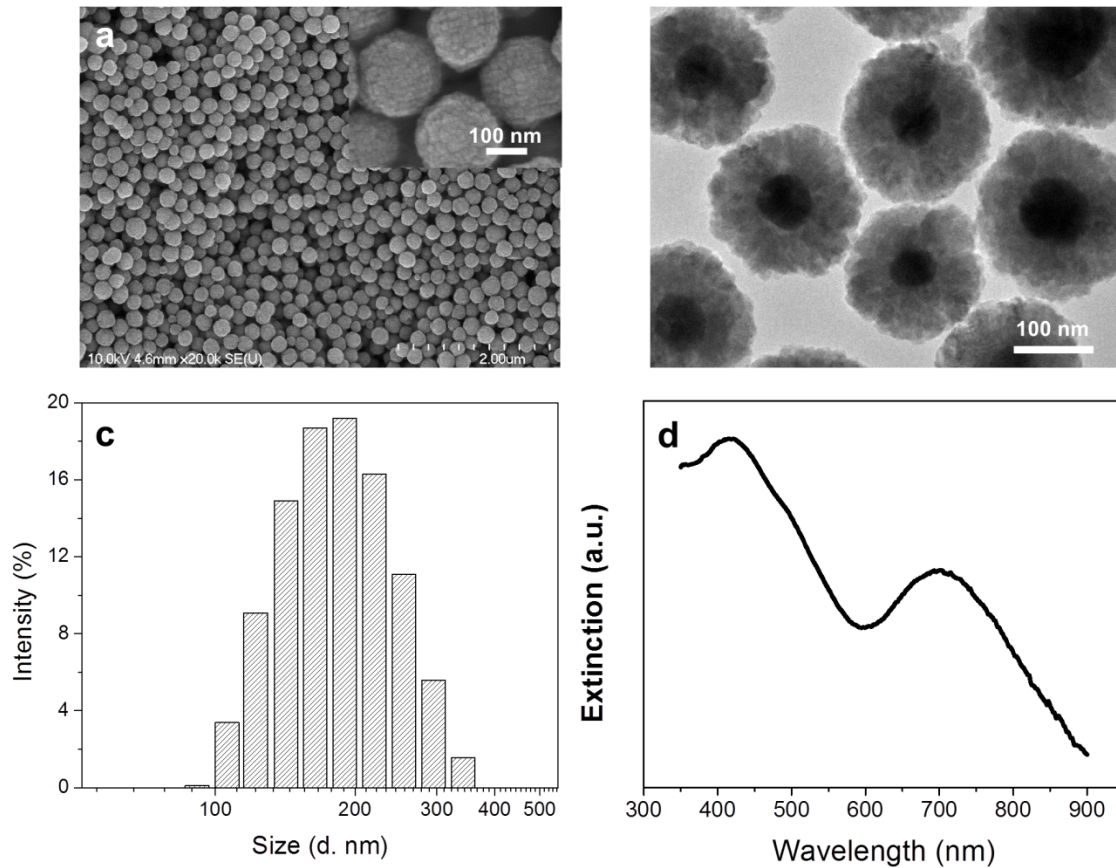


Figure S1. A) SEM, b) TEM images, c) size distribution histogram, and d) extinction spectra of NP₁₇₅.

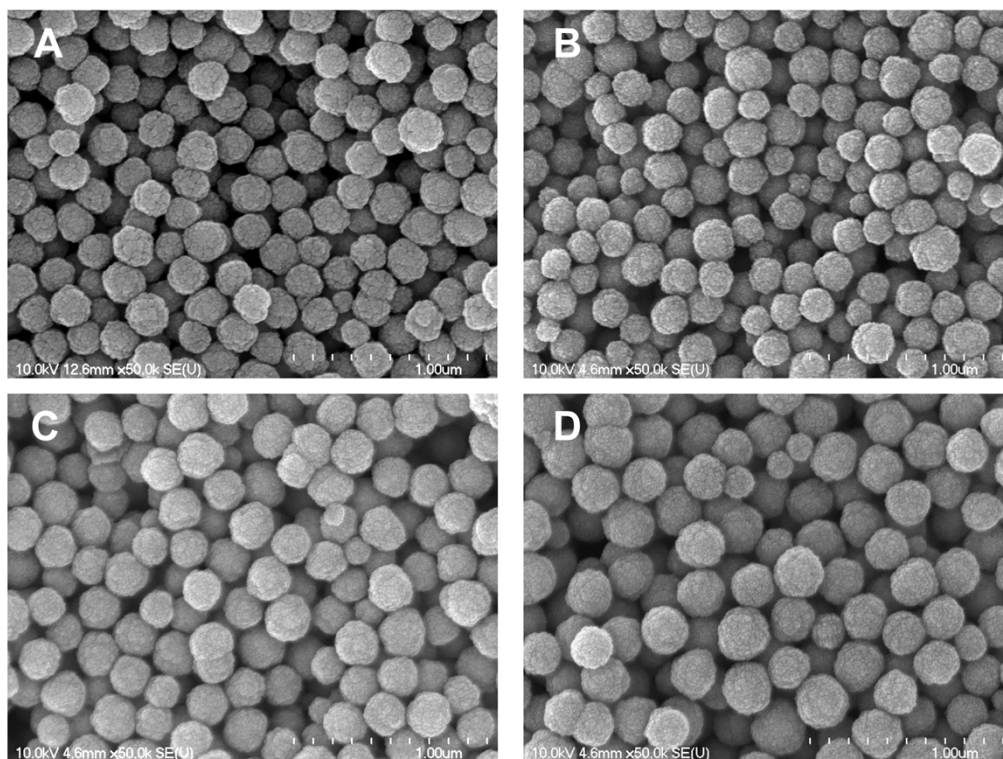


Figure S2. SEM images of different sized MagPlas NPs: a) NP₁₅₀, b) NP₁₇₅, c) NP₁₈₄, and d) NP₂₀₀.

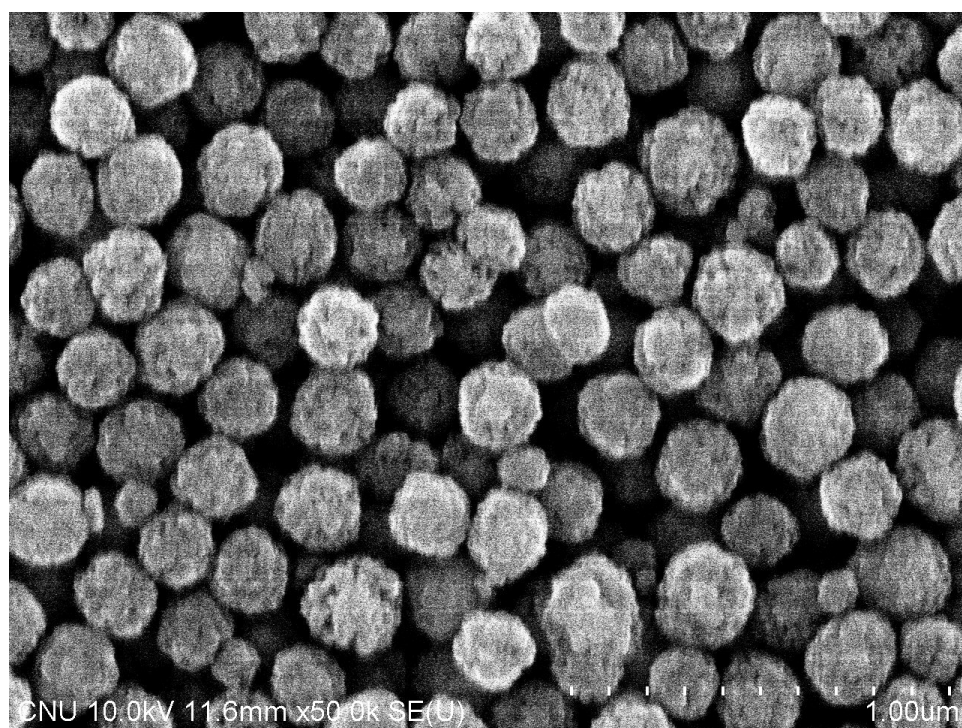


Figure S3. SEM image of porous 234 nm MagPlas NPs - NP_{234P}.

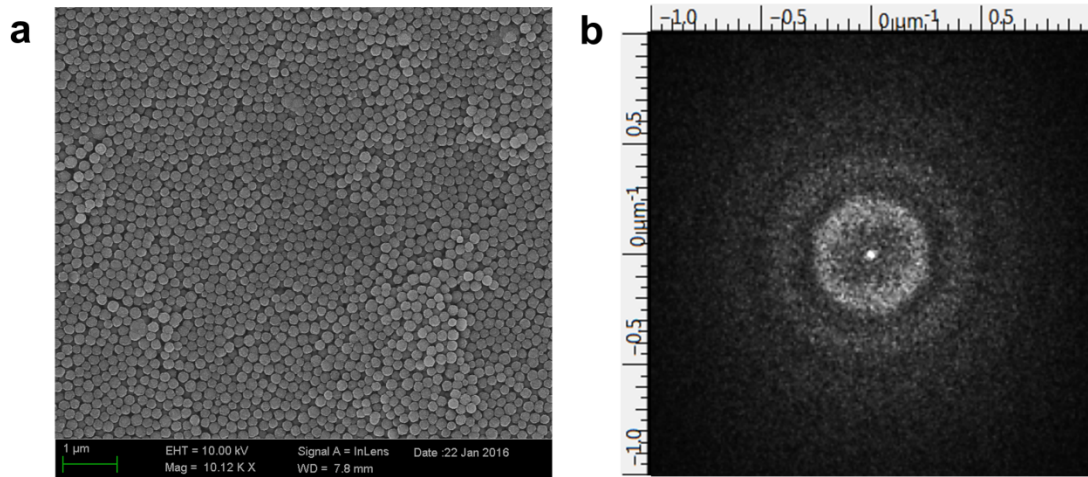


Figure S4. a) SEM image of MagPlas APAs and b) its corresponding fast Fourier transform (FFT) pattern.

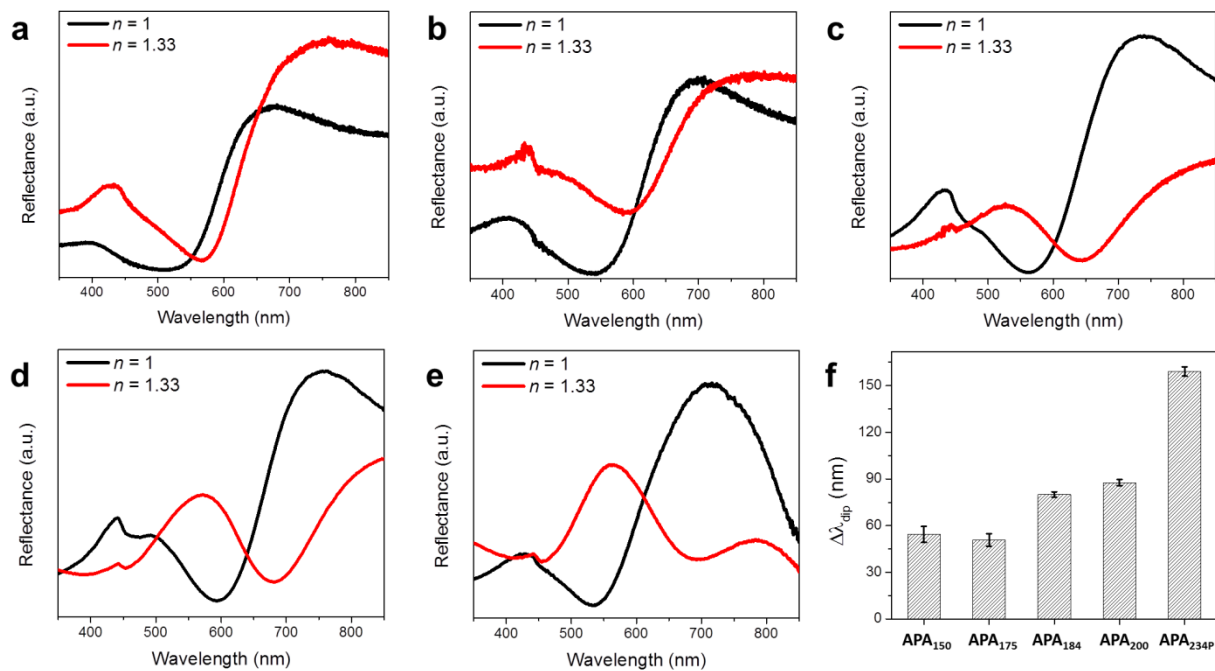


Figure S5. Reflectance spectra of APAs in dry ($n = 1$) and wet ($n = 1.33$) states: a) APA₁₅₀, b) APA₁₇₅, c) APA₁₈₄, d) APA₂₀₀, and e) APA_{234P}. f) Wavelength shifts of reflectance dip of the APAs after wetting.

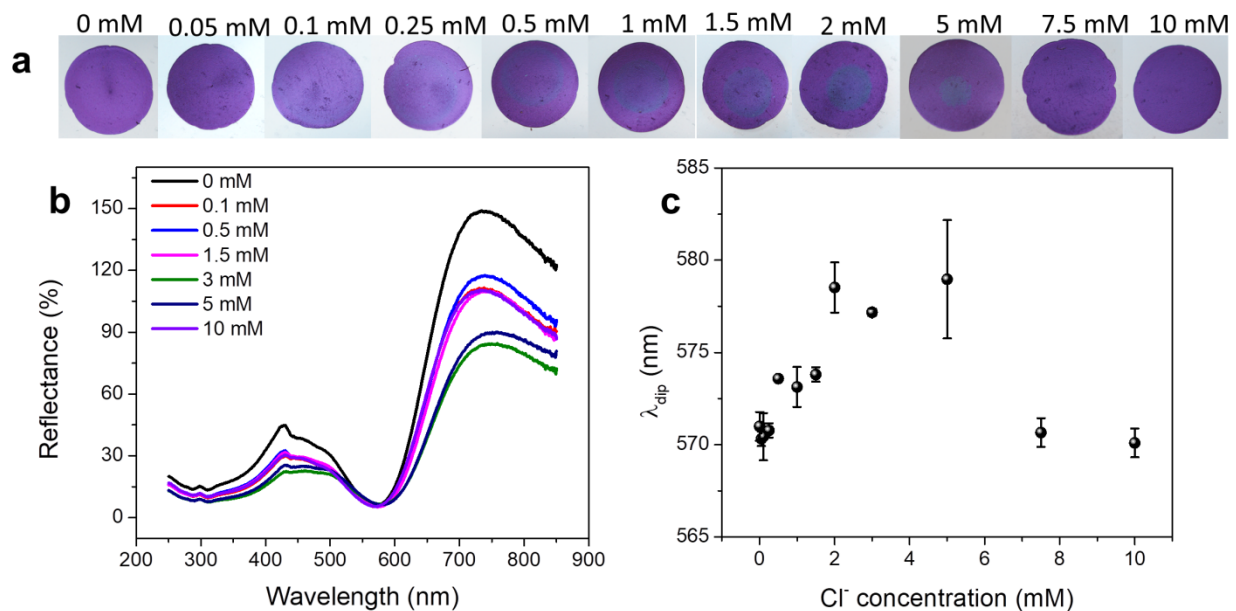


Figure S6. a) Photographs and b) reflectance spectra of MagPlas APA₁₈₄ impregnated with 50 mM AgNO₃ after adding solutions with different Cl⁻ ion concentrations (C_{Cl}). c) The dependence of λ_{dip} on Cl⁻ ion concentrations of MagPlas APA₁₈₄ impregnated with 50 AgNO₃ concentration.

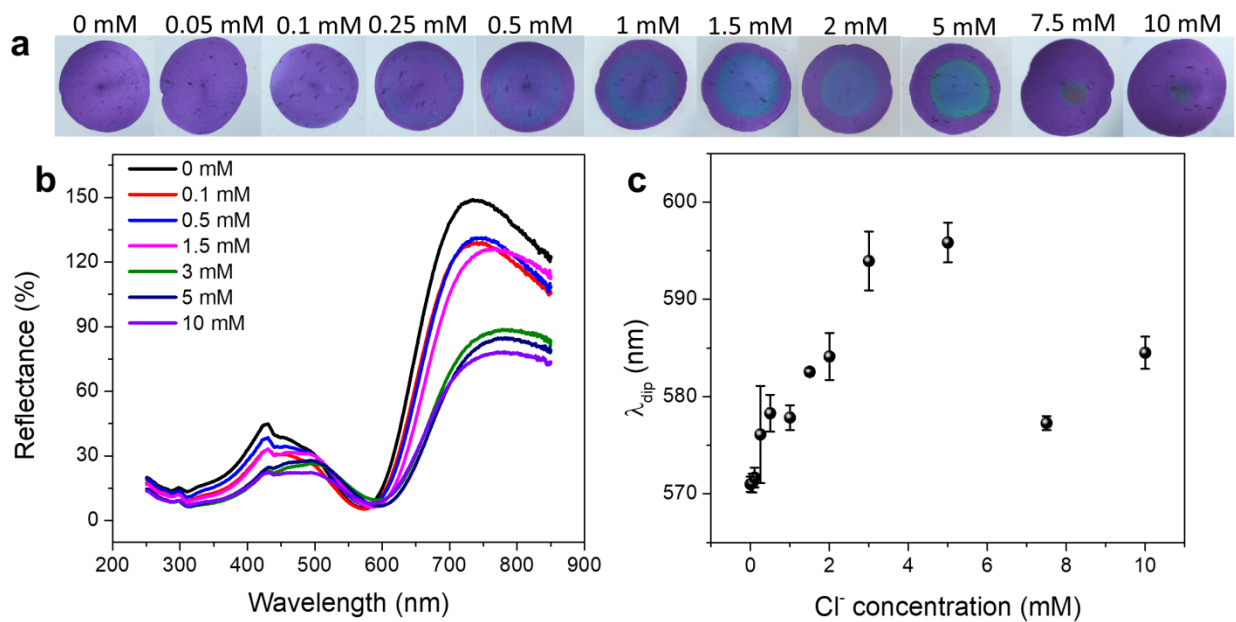


Figure S7. a) Photographs and b) reflectance spectra of MagPlas APA₁₈₄ impregnated with 100

mM AgNO₃ after adding solutions with different Cl⁻ ion concentrations (C_{Cl}). c) The dependence of λ_{dip} on Cl⁻ ion concentrations of MagPlas APA₁₈₄ impregnated with 100 mM AgNO₃ concentration.

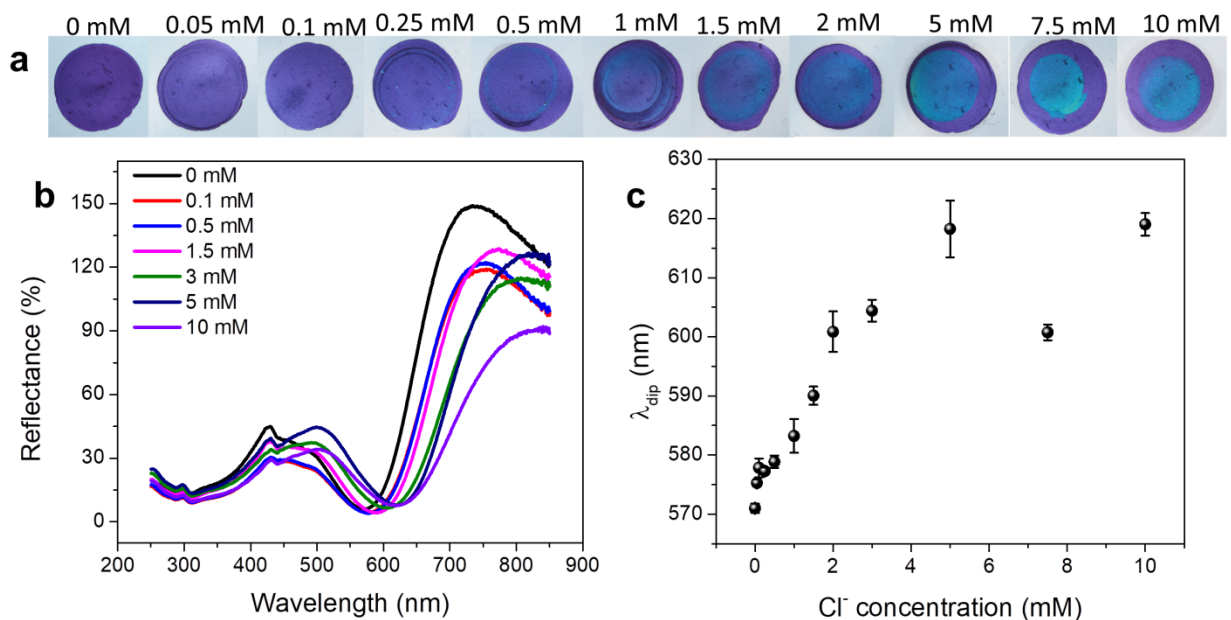


Figure S8. a) Photographs and b) reflectance spectra of MagPlas APA₁₈₄ impregnated with 500 mM AgNO₃ after adding solutions with different Cl⁻ ion concentrations (C_{Cl}). c) The dependence of λ_{dip} on Cl⁻ ion concentrations of MagPlas APA₁₈₄ impregnated with 500 mM AgNO₃ concentration.

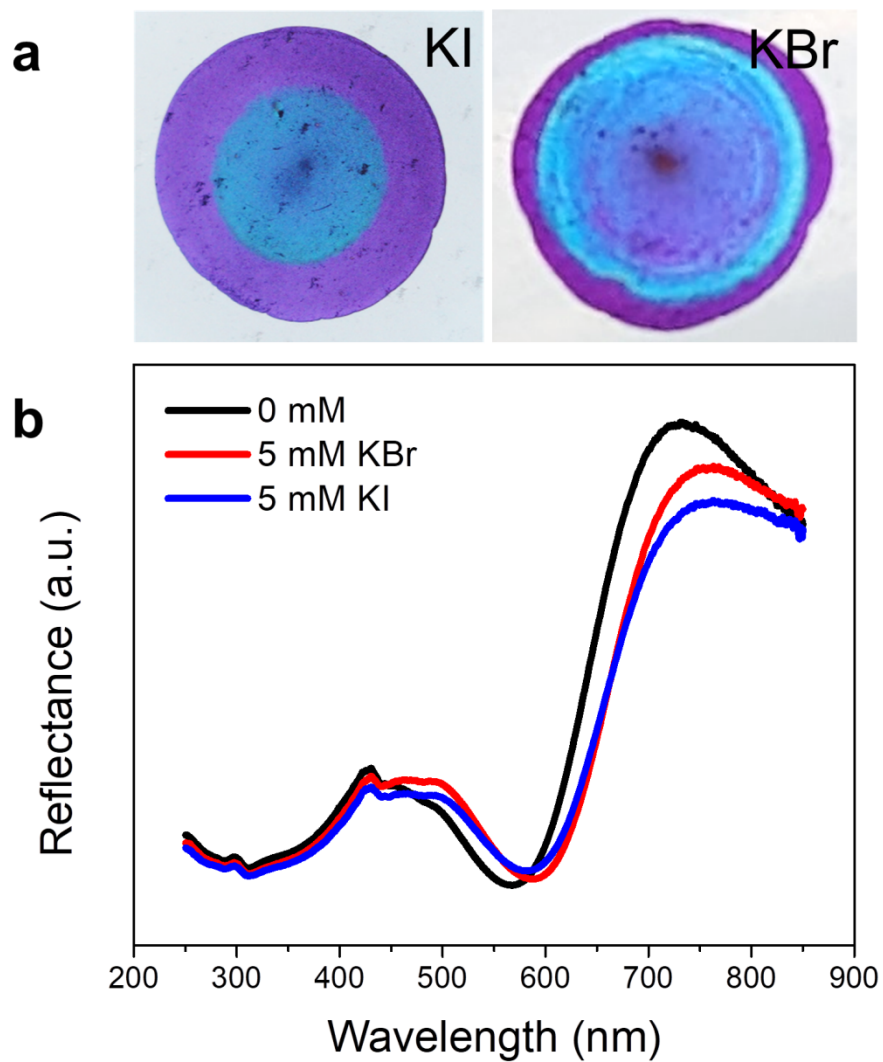


Figure S9. a) Photographs and b) reflectance spectra of MagPlas APA₁₈₄ impregnated with 250 mM AgNO₃ after adding 5mM KBr and 5 mM KI.

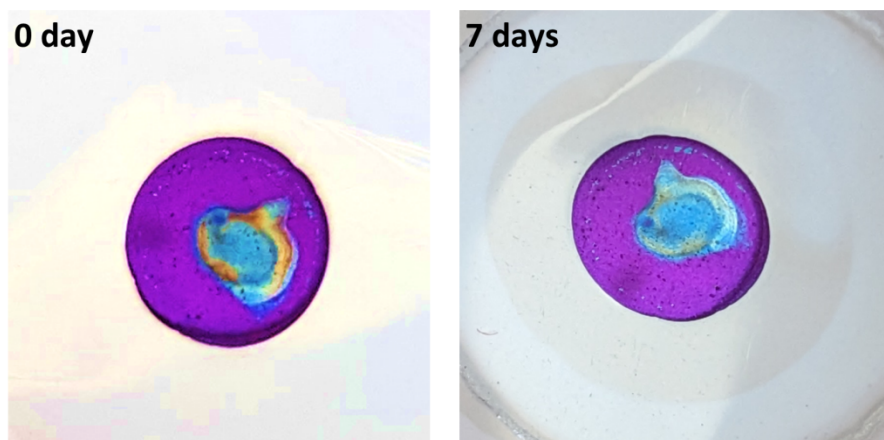


Figure S10. Photographs of MagPlas APA₁₈₄ impregnated with 250 mM AgNO₃: a) right after and b) after 7 days adding 5mM NaCl.