Electronic supplementary information

Fabrication of monodisperse Au@Ag bimetallic nanorods loaded nanofibrous membrane with fast thermo-responsiveness and its use as a smart freestanding SERS substrate

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Scheme S1. Intermolecular crosslinking reaction between NMA units of PNN



Scheme S2. Intermediates proposed for 4-NTP to 4-ATP reduction (top: direct route via a hydroxylamine intermediate; bottom: condensation route through the formation of 4,4'-dimercaptoazobenzene (4,4'-DMAB)





Figure S1. ¹H NMR spectrum of PNN (a) and temperature dependent absorbance of PNN aqueous solution (b)





(b)

Figure S2. TEM image of Au@AgNRs (a) and UV-vis-NIR spectrum of Au@AgNRs aqueous dispersion (inset is

its optical image) (b)





(c)

(d)

Figure S3. Optical images of control sample (a) and Au@AgNRs/PNN composite nanofibrous membranes

(HNF-1 (b), HNF-2 (c), HNF-3 (d))





(b)

Figure S4. Optical images of control sample and Au@AgNRs/PNN composite nanofibrous membranes in

water before (a) and after (b) oscillation $~(100 \ \text{rpm}{\times}2 \ \text{h})$



Figure S5. FTIR spectra of uncrosslinked PNN nanofibrous membrane and HNF-2







(c)

Figure S6. (a) SERS spectra of 10⁻⁷ M 4-NTP aqueous solution based on Au@AgNRs/PNN composite nanofibrous membranes (HNF-2) as substrate at three different excitation wavelengths (532 nm, 633 nm, 785 nm); (b) SERS spectra of 10⁻⁷ M 4-NTP aqueous solution based on the composite nanofibrous membranes with three different Au@AgNRs contents as the substrates, respectively (785 nm excitation); (c) The plot of the 1334 cm⁻¹ peak intensity against the Au@AgNRs concentration in the spinning solution of the composite nanofibrous membranes.







(c)





(e)



Figure S7. (a) SERS spectra of different concentrations of 4-NTP in aqueous solution based on HNF-1 as substrate with 785 nm excitation; (b) Amplified SERS spectra of low concentrations of 4-NTP in (a); (c) Plot of

the 1334 cm⁻¹ peak intensity in (a) vs. log (c) of 4-NTP; (d) SERS spectra of different concentrations of 4-NTP in aqueous solution based on HNF-3 as substrate with 785 nm excitation; (e) Amplified SERS spectra of low concentrations of 4-NTP in (d); (f) Plot of the 1334 cm⁻¹ peak intensity in (d) vs. log (c) of 4-NTP.