Electronic Supporting Material

A novel double metal-dithizone functionalized polyurethane electrospun nanofiber and film for colorimetric determination of hexavalent chromium

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Experimental

Instrumentation

The NF was spun using a lab-made electrospinning instrument comprising a 25 kV high-voltage power supply (PHYWE, Germany), a syringe pump (NewEra, USA), and a flat plate collector covered with aluminium foil. The morphology of the membrane was studied by a scanning electron microscopy (SEM, FEI Quanta 400, USA) operating at an accelerating voltage of 20 kV and a magnification of 5000×. The SEM image was recorded on secondary electron signal. ImageJ image program (ImageJ, National Institutes of Health, 1.46, Maryland, USA) processed the average fiber diameter. The thermalgravimetric analysis was conducted on the DTG 60H analyser (Shimadzu, Japan), using an alumina crucible in nitrogen gas with a flow rate of 50 mL min^{-1}, a heating rate of 10°C min^{-1} and a temperature range of 30-900°C. Colour digital images were captured with an iPhone 8 Plus camera (USA) and RGB values were assessed by the ColorValue version 1.0.0 application (Withtec Co., Ltd., Korea).

Results and discussion

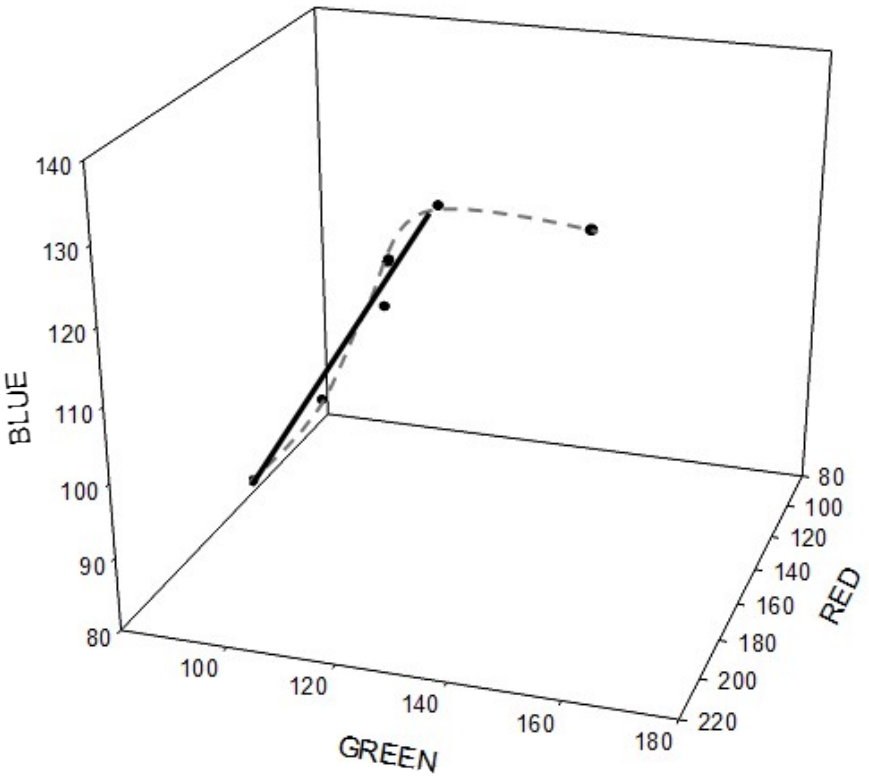

Fig. **S1** The red, green, blue values 3D plot by SigmaPlot of the Cr(VI) standard in microwell plate system.

Optimization of electrospinning conditions for PU-NF

During the electrospinning process, charges formed on the jet surfaces repel each other, stretching the electrospinning solution, to form nanofibers. The voltage is applied above a critical value to overcome the surface tension of the solution and allow a continuous spinning fiber jet to form.[1]

Effect of concentration of PU and applied voltage

PU concentrations of 10, 15, 20, and 25% (w/v) were electrospun at applied voltages of 15 and 20 kV. At 15 kV, 10-20% PU solutions produced smooth nanofiber but the 20% solution produced fibers that presented some spots like beads trapped inside the membrane (Fig. S2A). Moreover, 15% PU produced a larger area of the membrane than 10% PU. The polymer solution concentration is correlated with viscosity. Viscosity is a key parameter that affects the entanglement of the polymer molecules during electrospinning. A less viscous solution produces smoother, finer, and less beaded fibers. The diameters of electrospun PU-NFs were investigated (Fig. S3). With the increment in PU solution concentration from 15% to 20%, the fiber size increased from 758.33 ± 268.19 nm to 872.84 ± 481.56 nm. Since the viscosity of the 20% PU solution was greater, the jet of the PU solution was stretched less, and the fiber diameter increased. Moreover, 25% PU was too viscous to be spun which caused the solution to obstruct the flow through the tip of the needle, and subsequently, a localized gel was formed, giving a ribbon-like fiber.

When applying 20 kV (Fig. S2B), 10-20% PU produced fibers that were free of beads and smoother than the fibers produced at 15 kV, but not when 25% PU was used. Normally, the greater coulombic forces at higher voltage stretch the solution more, producing finer fibers.[2] As expected, the fibers PU spun at 20 kV (758.33 ± 268.19 nm) were smaller than fibers spun at 15 kV (895.56 ± 336.28 nm) but the 25% PU solution yielded poor fibers with beads or droplets. Hence, the best PU-NF was produced by electrospinning the 15% PU solution at 20 kV.

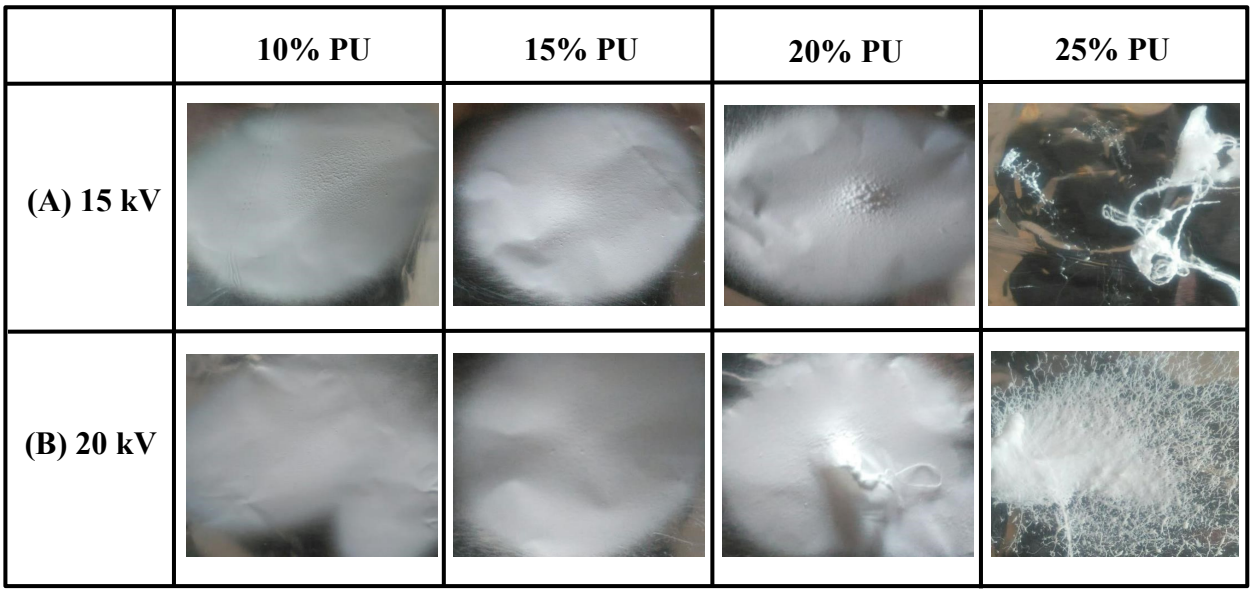

Fig. S2 Photographs are of PU-NF during electrospinning with different concentrations of PU at (A) 15 kV and (B) 20 kV voltage.

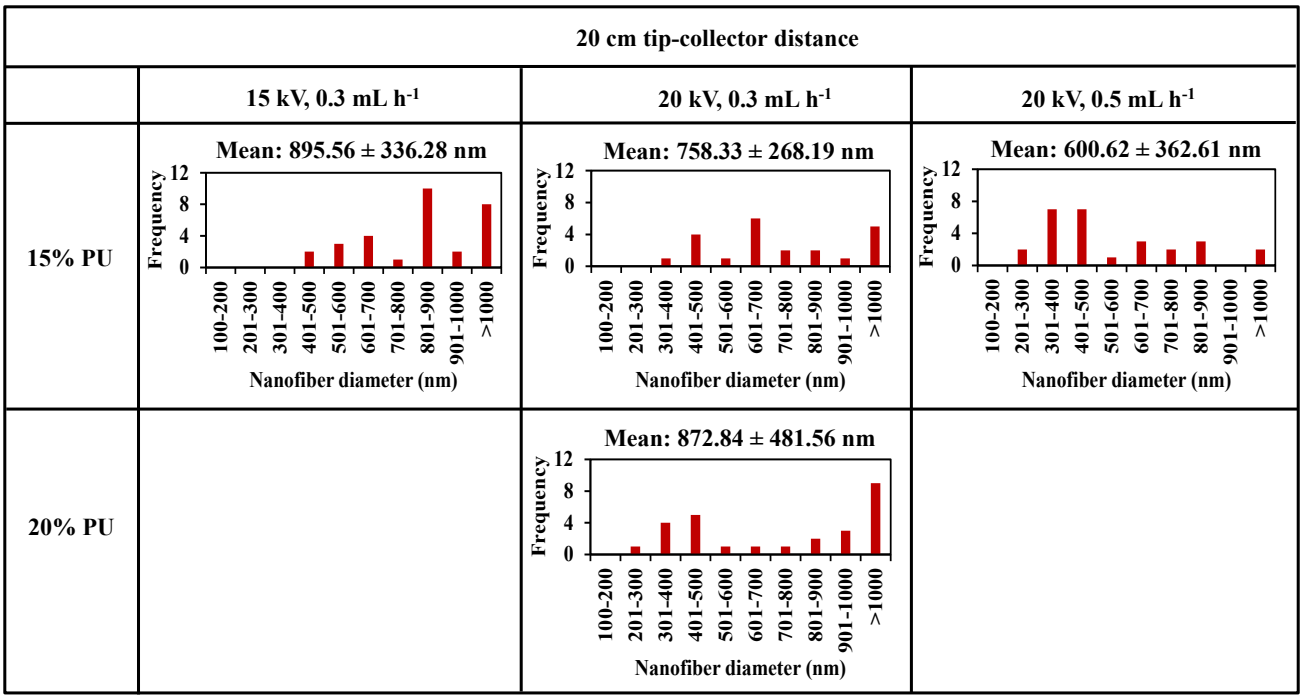

Fig. S3 The charts show fiber diameter distributions of PU-NF produced using different concentrations of PU, different applied voltages and different flow rates at a constant tip-collector distance of 20 cm.

Effect of flow rate and tip-collector distance

After PU concentration and voltage had been optimized for the electrospinning process, flow rate and tip-collector distance were studied. The flow rate of the polymer solution from the syringe can influence the jet velocity and transfer rate.[2] Fig. S4 shows the effect of flow rate (0.3 and 0.5 mL h^{-1}) on the PU-NF electrospinning at a constant 15 cm tip-collector distance. At 0.3 mL h^{-1}, a smoother membrane was produced that showed no beads since the solvent had enough time to evaporate.[2] At the higher flow rate, beads were formed in the center and outer membrane and fiber diameter decreased from 758.33 ± 268.19 nm to 600.62 ± 362.61 nm.

	10 cm	15 cm	20 cm
0.3 mL h^{-1}			
0.5 mL h^{-1}			

Fig. S4 Photographs show the effect of flow rate on electrospinning efficiency (Electrospinning condition: 15% PU, 20 kV applied voltage, 15 cm tip-collector distance, 1 h electrospinning time) and tip-collector distance (electrospinning condition: 15% PU, 20 kV applied voltage, 0.3 mL h^{-1} flow rate, 1 h electrospinning time).

The tip-collector distance can also affect fiber morphology. At the optimal flow rate of 0.3 mL h^{-1}, we investigated the effect of tip-collector distances of 10, 15, and 20 cm (Fig. S4). In fact, the tip-collector distance provides a chance for the solvent to evaporate before reaching the collector.[3] At 10 cm, thicker fibers were formed and at 20 cm, PU-NF became rounder and produced the smoothest membrane. Thus, a flow rate of 0.3 mL h^{-1} and 20 cm tip-collector distance were selected as the optimal conditions.

To summarize the electrospinning optimization results: for 1 h of electrospinning, a 15% PU solution, under a 20 kV voltage, at a flow rate of 0.3 mL h^{-1}, with a 20 cm tip-collector distance, fiber was formed with a diameter of 758.33 ± 268.19 nm (Fig. 1A).

Table S1 Weight loss at different temperatures and degradation peaks of PU-NF, DTZ/PU-NF, and DPC/PU-NF

	Weight loss (%)							Degradation
Sample	100°C	200°C	300°C	400°C	500°C	600°C	700°C	temperature peak (°C)
15% PU-NF	0.86	1.53	6.16	70.53	84.17	89.33	95.45	600.00
5% DTZ/15%PU-NF	1.17	2.76	8.60	72.97	90.86	93.04	95.55	470.00
5% DPC/15%PU-NF	1.32	2.94	11.12	67.30	85.91	94.00	100.00	550.00

Table S2 Method validation results from this study in comparison to other colorimetric methods

Parameter	DTZ-Co^{2+}/ PU-NF (This study)	DTZ-Co^{2+}/ PU-MPF (This study)	DPC/Colorimetry (Lace, et al. 2019)[4]	Colorimetry (Li, et al. 2008)[5]	Colorimetry (Chamaraja, Mohesh & Kumar, 2021)[6]
Linearity range ($mg\ L^{-1}$)	0.001-1.0	0.01-5.0	0.03 – 3	0.008 – 1.25	0.00002 – 0.0008
LOD ($mg\ L^{-1}$)	0.001	0.018	0.023	0.0078	0.0000009
LOQ ($mg\ L^{-1}$)	0.007	0.060	0.076	-	0.000003

References

1) M. Dhanalakshmi, A. K. Lele and J. P. Jog, *Mater. Today Commun.*, 2015, **3**, 141-148.

2) N. Bhardwaj and S. C. Kundu, *Biotech. Adv.*, 2010, **28**, 325-347.

3) S. Thenmozhi, N. Dharmaraj, K. Kadirvelu and H. Y. Kim, *Mater. Sci. Eng. B*, 2017, **217**, 36-48.

4) A. Lace, D. Ryan, M. Bowkett and J. Cleary, Int. J. Environ. Res. Public Health, 2019, 16(10), 1803.

5) J. Li, H. Wei, S. Guo and E. Wang, Anal. Chim. Acta., 2008, 630, 181-185.

6) N. A. Chamaraja, B. Mahesh, C. B. Praveen Kumar, Environ. Nanotechnol. Monit. Manag., 2021, 16, 100471.