Electronic Supplementary Material (ESI) for ChemComm.

Photonic Metal-Polymer Resin Nanocomposites with Chiral Nematic Order

Vitor M. Zamarion, [a,b] Mostofa K. Khan, [a] Maik Schlesinger, [a] Anas Bsoul,[c,d] Konrad Walus,[c] Wadood Y. Hamad,[e] and Mark J. MacLachlan[a*]

[a] Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1

[b] Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Avenida Professor Lineu Prestes, 748, São Paulo, SP, CEP 05508-000, Brazil. [c] Department of Electrical and Computer Engineering, University of British Columbia, 2332 Main Mall, Vancouver, BC, V6T 1Z4 (Canada). [d] Department of Computer Engineering, Jordan University of Science and Technology, Irbid, Jordan. [e] FPInnovations, 2665 East Mall, Vancouver, BC, Canada V6T 1Z4. Corresponding author: mmaclach@chem.ubc.ca

SUPPORTING INFORMATION

Experimental Section

Reagents

All compounds were used without further purification as received from the suppliers. Phenol (BDH, 99%), formaldehyde solution (Fisher, 36.5%; containing 12-15% methanol as a preservative), and sodium hydroxide (Fisher, 98.9% Certified ACS grade) were used as received without purification. The preparation of phenol-formaldehyde resin (CNMP) and CNC suspensions were conducted according to published procedures.[1,2] $HAuCl_4 \cdot 3H_2O$, $PdCl_2$ and $AgNO_3$ were all purchased from Aldrich.

Characterization

UV-visible-near infrared spectra were obtained on a Cary 5000 UV-Vis/NIR spectrophotometer in transmission mode by placing the films between a glass microscope slide and a cover slide to ensure the uniformity of heights in the films. The all set was put perpendicular to the beam path. CD spectroscopy was performed using a JASCO J-710 spectropolarimeter by mounting the films in the same procedure applied for UV-Vis-NIR measurements. Extra care were taken to acquire spectra in the same spot / side of the films before and after nanoparticles formation. Polarized optical micrographs were recorded on an Olympus BX41 microscope with crossed polarizers. Scanning electron microscopy (SEM) images were collected using a Hitachi S4700 electron microscope on samples sputter-coated with gold-palladium alloy prior to imaging. Critical point drying using $scCO_2$ was achieved with an autosamdri-815 critical point dryer (Tousimis Research Corporation, Rockville, Maryland, USA). Infrared spectra were obtained with a Nicolet 6700 FT-IR equipped with a Smart Orbit diamond attenuated total reflectance (ATR) attachment.

Preparation of chiral nematic mesoporous polymer (CNMP) films

An aqueous suspension of CNCs (4% w/v, pH 2.4), prepared by H_2SO_4 hydrolysis of wood pulp,[2] was diluted to 3% w/v and used as the chiral nematic liquid crystalline template.

This suspension was placed into an ultrasonic bath for 15 min to form a homogeneous suspension. 100 μL of phenol-formaldehyde ethanolic solution (35% w/v, pH 7) was added and the resulting suspension stirred for 1 h at room temperature, which was then poured into polystyrene Petri dishes and dried under ambient conditions, resulting in iridescent composite films. The films were then cured in an oven for 24 h and 75 °C. Finally, CNCs were removed using a caustic treatment. In a representative procedure, about 200 mg of the composite films were placed in a beaker containing 100 mL of 16% (w/v) NaOH solution at 70 °C for 12 h, stirring only occasionally to homogenize the solution. Then, the solution containing the films was cooled to room temperature and the films were transferred to a beaker containing deionized water at room temperature. To remove excess NaOH, the films were washed with copious deionized water until the washings were neutral by pH paper. Films were allowed to air-dry at ambient conditions. For supercritical drying using supercritical CO_2, the water was solvent-exchanged with methanol by sequentially transferring the films into water/methanol 75/25, 50/50, 25/75, and 0/100 (v/v) solvent mixtures and allowing the film to soak in each solvent mixture for at least 6 h, then finally soaking the film in pure ethanol for 6 h.

In situ synthesis of gold, silver and palladium nanoparticles by the CNMP matrix

For gold nanoparticles (AuNPs), an aqueous stock solution of $HAuCl_4$ (10 mmol L^{-1}) was prepared and shielded from light. Dry CNMP films with dimensions of 1 cm x 1 cm were placed inside glass vials, one in each vial, and then 4 mL of $HAuCl_4$ was added (diluted from the stock solution depending on the desired concentration for each film). In a typical procedure, the films were kept in contact with $HAuCl_4$ solution for 2 h without stirring and without the addition of a reducing agent. The films were then washed with copious deionized water, followed by acetone and dried at ambient conditions, resulting in red, iridescent films.

For silver (AgNPs) and palladium (PdNPs) nanoparticles, solutions of $PdCl_2$ and $AgNO_3$ salts were prepared in the concentrations of 0.1 and 1 M, respectively. CNMP films were also able to reduce such metals, but extended times and higher concentrations of metal ion were necessary to visibly see changes in the films. Keeping the same procedure used for CNMP-Au, the resulting iridescent films were yellow (for AgNPs) and brown (for PdNPs).

Inkjet Printing

Photonic patterns were printed by a custom-made inkjet printer using CNMP films as substrates. A novel piezoelectric-driven inkjet dispenser is used to dispense 1 M HCl solution on our substrates for printing the photonic pattern (Figure 5b) as per our previous publication.[3] The sample was then immersed in 0.5 mM $HAuCl_4$ for 1 h. To print the patterns of gold nanoparticles (Figure 5d), 10 mM aqueous solution of $HAuCl_4$ was used as ink instead of HCl. AuNPs were visible within 5-10 mins after printing. After printing, the resin films were preserved undisturbed for an hour before rinsing with water to remove unreacted (if there was any) Au^{3+} ions. Unlike many inkjet dispensers that made of glass and/or silicon, these dispensers are made of two widely used materials in microfluidics, namely polydimethylsiloxane (PDMS) and SU-8, which are well-known for their chemical stability. The dispensers have a modular design that allowed us to optionally dispose the microfluidic module (to avoid the cleaning process) for different inks (HCl (aq) vs. $HAuCl_4$ (aq) in present case) and to reuse the piezoelectric actuation unit. A computer-controlled XY-stage (carrying the substrate) synchronized with dispensed droplets was programmed to form the patterns. The dispensed droplets' diameters were about 120 μm. Further details about the inkjet dispensers' fabrication process and the experimental setup are discussed elsewhere.[4]

References

(1) M. K. Khan, M. Giese, M. Yu, J. A. Kelly, W. Y. Hamad and M. J. MacLachlan, *Angew. Chem. Int. Ed. Engl.*, **2013**, *52*, 8921-8924.

(2) W. Y. Hamad and T. Q. Hu, *Can. J. Chem. Eng.* **2010**, *88*, 392-402.

(3) M. K. Khan, A. Bsoul, K. Walus, W. Y. Hamad and M. J. MacLachlan, *Angew. Chem. Int. Ed. Engl.*, **2015**, *54*, 4304-4308.

(4) A. Bsoul, S. Beyer, A. Ahmadi, B. Stoeber, E. Cretu and K. Walus, "Molded Biocompatible and Disposable PDMS/SU-8 Inkjet Dispenser," The 17th International Conference on Miniaturized Systems for Chemistry and Life Sciences, pp. 636-638, 2013.

Supporting Figures

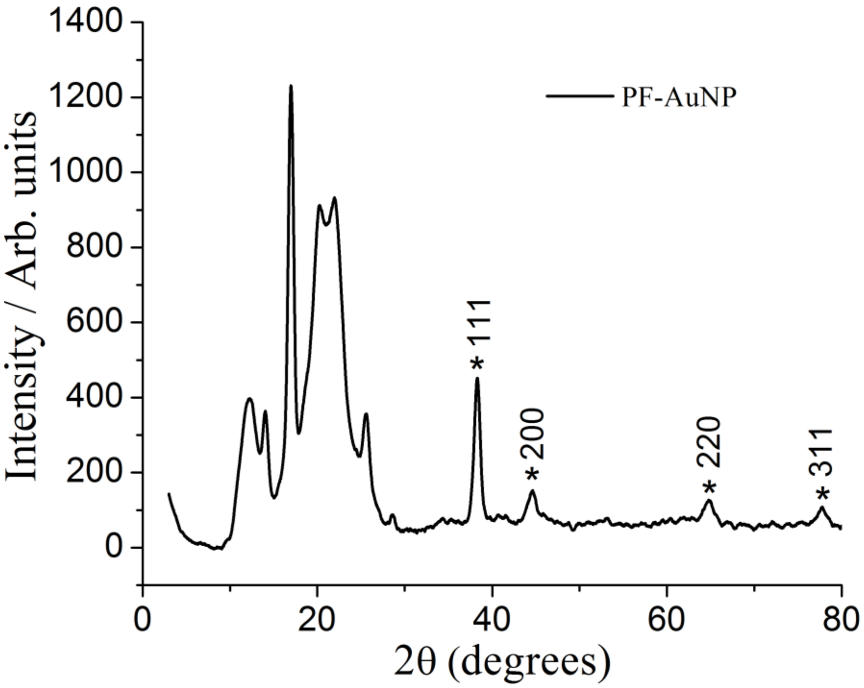

Figure S1. X-ray diffraction pattern of the CNMP-Au composite film. [$HAuCl_4$] = 0.5 mM, after 120 min of reaction with the Au^{3+} solution. *(hkl) Values are from the ICDD reference in the main manuscript text.

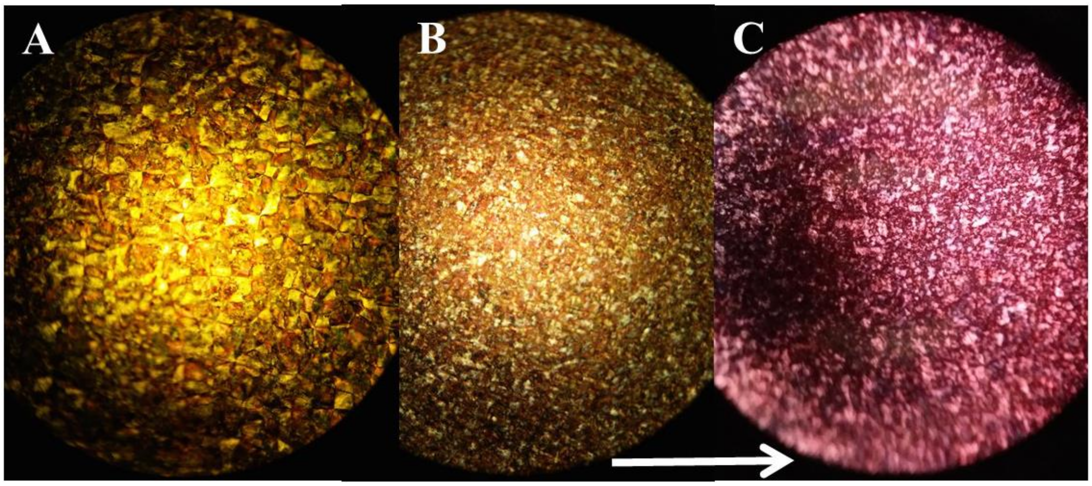

Figure S2. Polarized optical microscopy (POM) images of PF (A, B) and PF-AuNP (C). The image A illustrates a sample with bigger domains while B and C show small domains. The arrow indicates the sample used before and after gold deposition. [$HAuCl_4$] = 0.5 mM, after 120 min of reaction with the Au^{3+} solution.

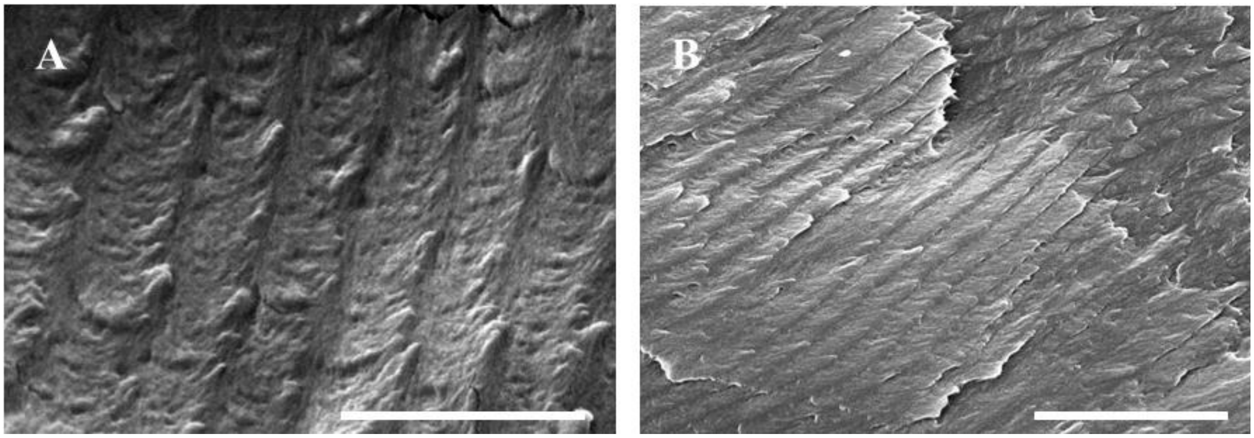

Figure S3. Scanning electron microscopy (SEM) images of the CNMP-Au composite film. A) Scale bar = 1 μm, B) Scale bar = 2 μm. [$HAuCl_4$] = 0.5 mM, after 120 min of reaction with the Au^{3+} solution.

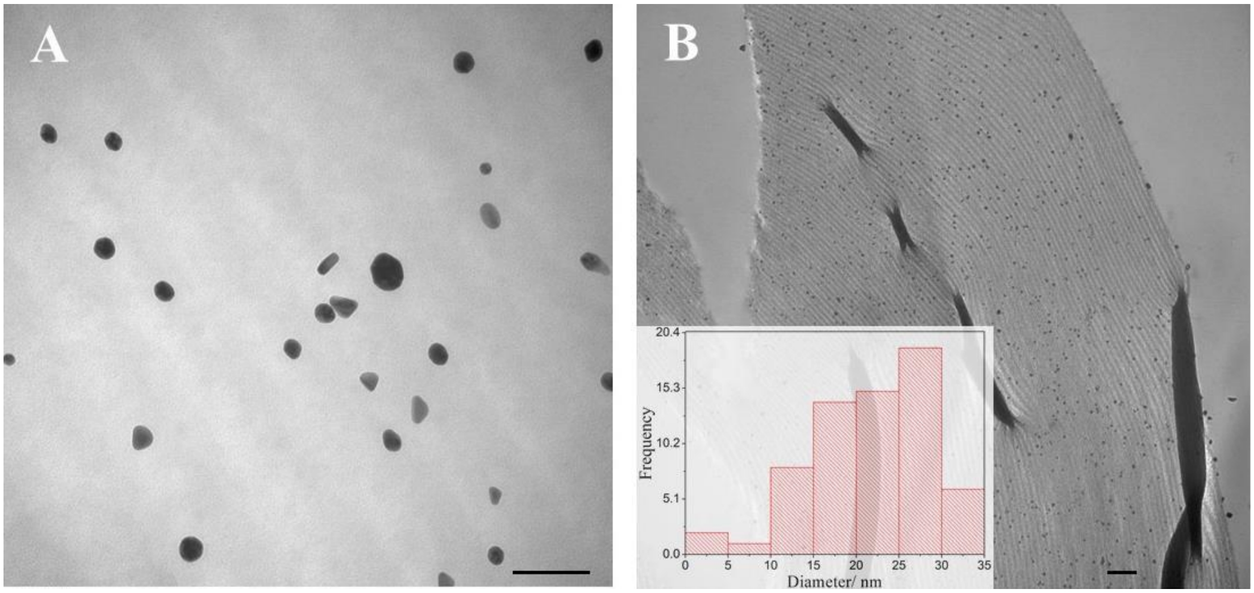

Figure S4. Cross-sectioned transmission electron microscopy (TEM) images of the CNMP-Au composite film with different magnifications A) scale bar = 100 nm, B) scale bar = 500 nm. Inset on B: Histogram of size distribution for AuNPs in CNMP-Au. [$HAuCl_4$] = 0.5 mM, after 120 min of reaction with the Au^{3+} solution.

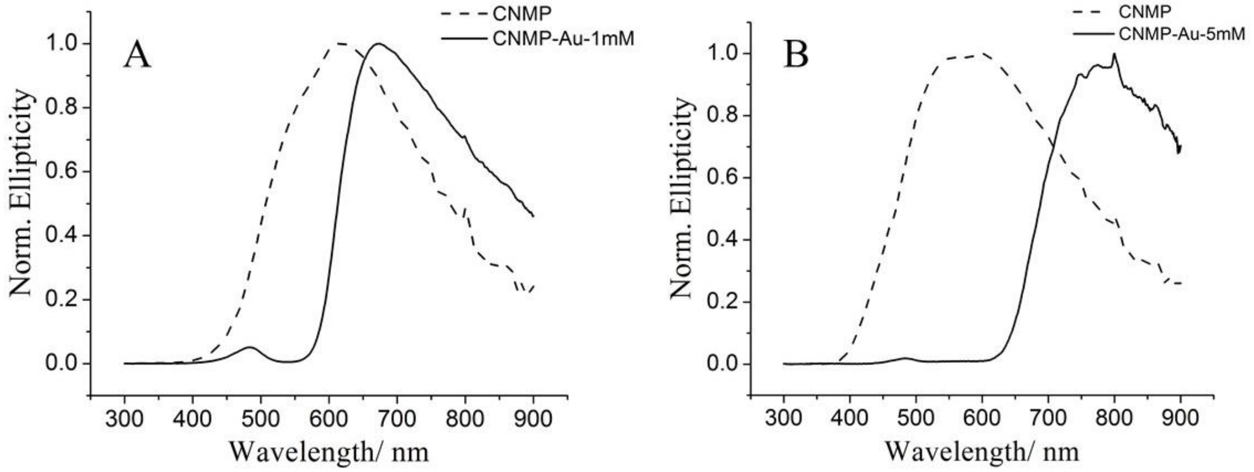

Figure S5. Normalized CD spectra of CNMP and CNMP-Au composite films. A) [$HAuCl_4$] = 1 mM, after 120 min of reaction with the Au^{3+} solution. B) [$HAuCl_4$] = 5 mM, after 120 min of reaction with the Au^{3+} solution.

Figure S6. Photographs of two CNMP films treated with 0.1 mmol L^{-1} $HAuCl_4$ for 120 min (left) and 24 h (right).

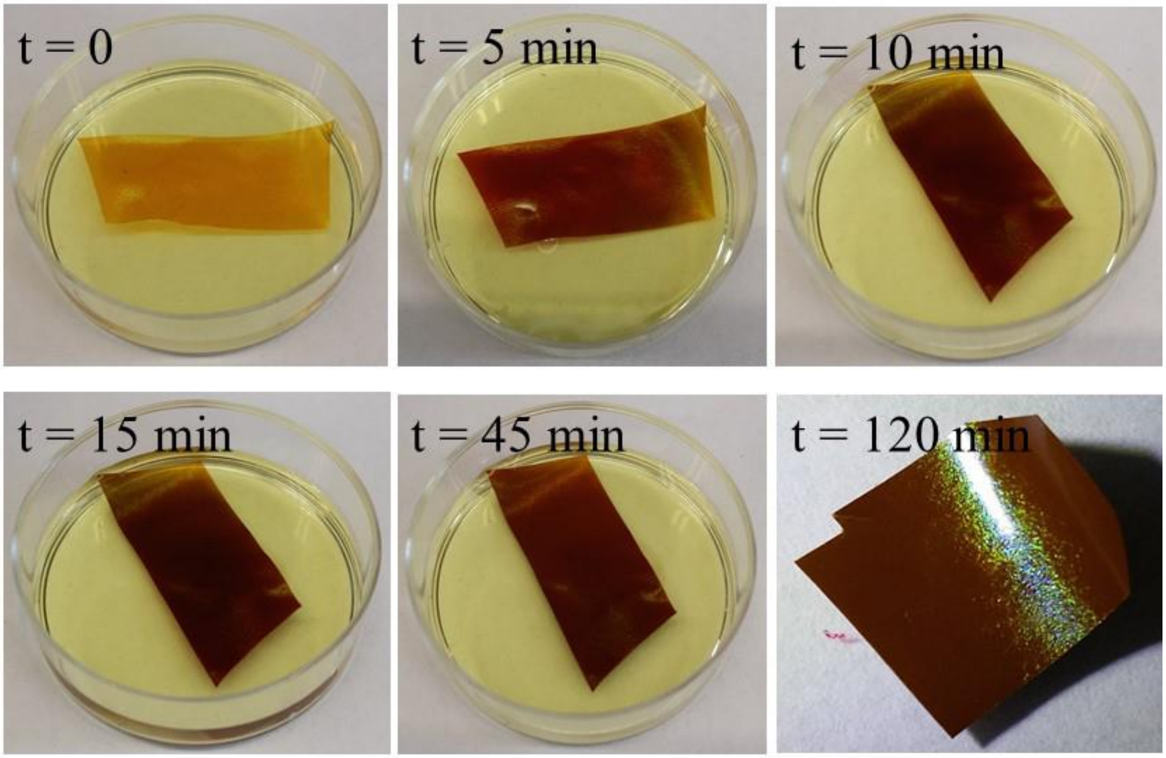

Figure S7. Sequence of photographs of a CNMP film treated with 10 mM $HAuCl_4$ from 0 to 120 min.

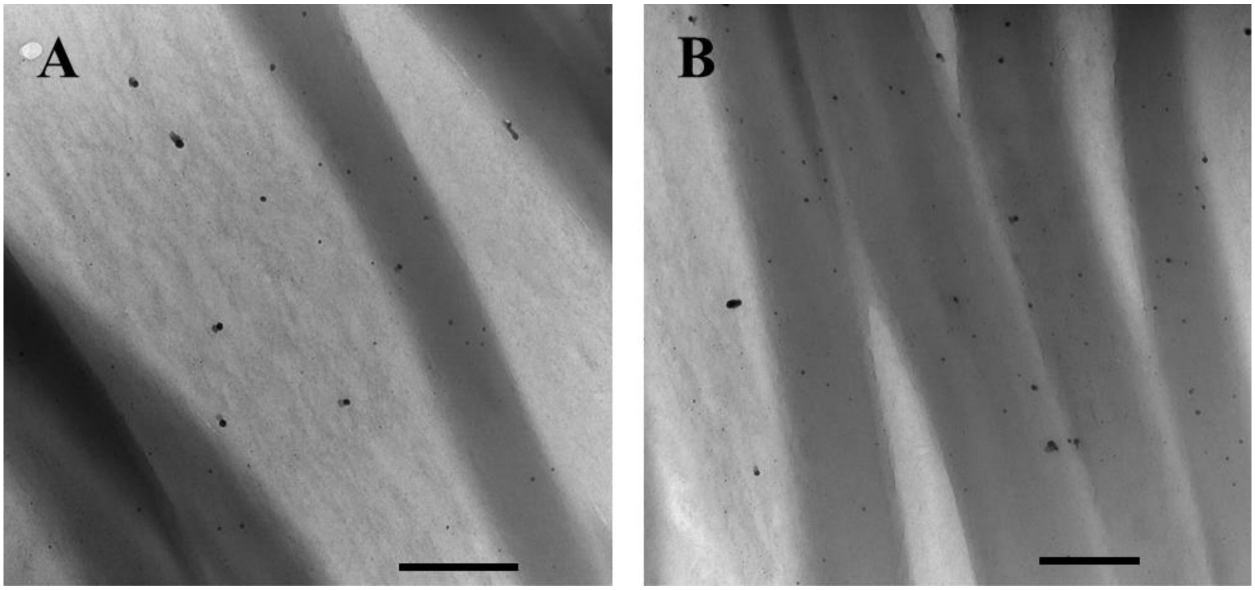

Figure S8. Cross-sectioned transmission electron microscopy (TEM) images of CNMP-Ag composite with different magnifications. A) and B) Scale bar = 500 nm. $[Ag^+]$ = 1 M, after 14 h of reaction with the Ag^+ solution.

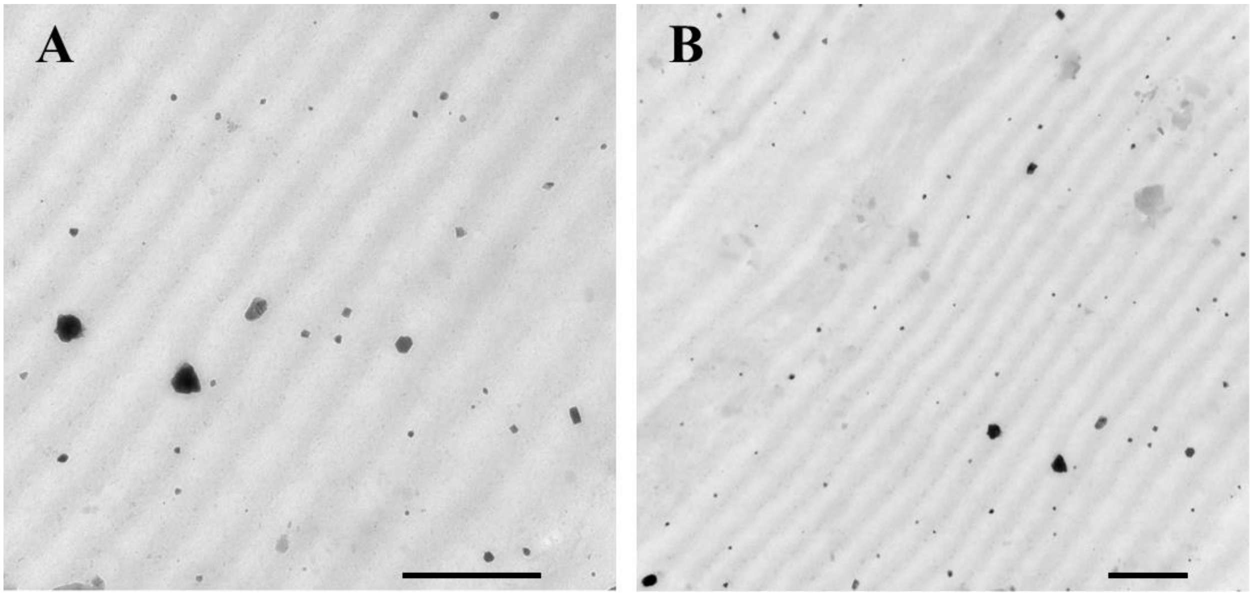

Figure S9. Cross-sectioned transmission electron microscopy (TEM) images of CNMP-Pd composite with different magnifications. A) and B) Scale bar = 500 nm. [Pd^{2+}] = 0.1 M, after 14 h of exposure to the Pd^{2+} solution.