



## Photonic Metal-Polymer Resin Nanocomposites with Chiral Nematic Order

|                               |   |
|-------------------------------|---|
| Journal:                      | <i>ChemComm</i>   |
| Manuscript ID                 | CC-COM-04-2016-003147.R1  |
| Article Type:                 | Communication   |
| Date Submitted by the Author: | 16-May-2016   |
| Complete List of Authors:     | Zamarion, Vitor; University of Sao Paulo, Inst Quimica<br>Khan, Mostofa; University of British Columbia, Chemistry<br>Schlesinger, Maik; UBC Chemistry, Chemistry Department<br>Bsoul, Anas; The University of British Columbia, Electrical and Computer Engineering<br>Walus, Konrad; University of British Columbia, Electrical and Computer Engineering<br>Hamad, Wadood; FPInnovations, CNC-Biomaterials Group; UBC, Chemistry<br>MacLachlan, Mark; UBC Chemistry, Chemistry Department |
|                               |   |

## COMMUNICATION

# Photonic Metal-Polymer Resin Nanocomposites with Chiral Nematic Order

Cite this: DOI: 10.1039/x0xx00000x

Vitor M. Zamarion,<sup>†,a,b</sup> Mostofa K. Khan,<sup>†,a</sup> Maik Schlesinger,<sup>a</sup> Anas Bsoul,<sup>c,d</sup> Konrad Walus,<sup>c</sup> Wadood Y. Hamad,<sup>e</sup> and M. J. MacLachlan<sup>a,\*</sup>

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

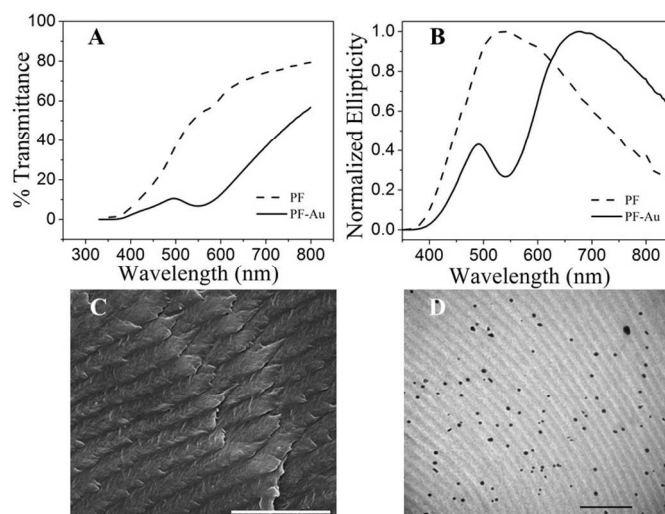
**Mesoporous resins with chiral nematic order were used as a scaffold to construct novel iridescent metal-polymer composites. Gold, silver and palladium nanoparticles were formed by an *in situ* reduction reaction. We have investigated the effects of concentration and time on the deposition. As a proof-of-concept, we demonstrate that this process can be extended to patterning photonic resins by inkjet printing.**

Metal nanoparticles, especially those based on precious metals, are of great interest for sensing, catalysis, and other applications.<sup>1–3</sup> Recently, there has been intense interest in the optical properties of gold and silver nanoparticles incorporated into environments with chiral structures.<sup>6–8</sup> These have typically been prepared by the borohydride reduction of metal ions in pre-formed hosts that have chiral nematic order,<sup>9–12</sup> or by co-assembly of mesogens into chiral nematic structures in the presence of metal nanoparticles.<sup>13–15</sup> The incorporation of metal nanoparticles clearly influences the optical properties of the host matrix.

Most of the chiral nematic environments for metal nanoparticle studies have been constructed from cellulose nanocrystals (CNCs)<sup>13,16</sup> themselves, or from materials constructed using CNCs as a template.<sup>9–12,17</sup> CNCs spontaneously self-assemble into a film with chiral nematic order upon drying.<sup>18–20</sup> In 2013, we reported that co-condensation of resol precursors with CNCs yielded (after curing) phenol-formaldehyde (PF) resins that contain CNCs organized in a chiral nematic structure.<sup>21</sup> The CNCs are removed by alkaline treatment, affording mesoporous, iridescent PF materials. Treating these materials with HCl or formaldehyde changes the degree of swelling in the polymers and allows for the release of latent images due to polymer crosslinking.<sup>22</sup> Here we demonstrate that chiral nematic mesoporous PF resins are excellent hosts for the surprising *in situ* deposition of nearly monodisperse metal nanoparticles without the use of a reducing agent. The NPs are firmly anchored to the PF resin.

Chiral nematic mesoporous polymer (CNMP) based on PF was synthesized according to the literature procedure.<sup>21</sup> The film showed a reflection peak at 581 nm in the UV-vis spectrum and a broad CD signal around the same region, confirming that the film retained the chiral nematic order of the CNCs. We observed that upon treatment of the film with Au<sup>3+</sup> ions, the films became red. UV-Vis

spectroscopy of a film treated with 0.5 mM HAuCl<sub>4(aq)</sub> for 120 min showed a broad band assigned to the reflection peak of the chiral nematic structure and the SPR band of gold nanoparticles at 544 nm, Fig. 1a. The CD spectrum of the film (Fig. 1b) still showed the reflection band, but the absorption of the AuNPs leads to a splitting of the band, as previously observed in chiral nematic Prussian blue composites<sup>23</sup> and AuNP / CNC composites.<sup>17</sup> This verifies that the chiral nematic structure of the polymer is retained in the composite. Powder X-ray diffraction of the film (Fig. S1) verified that Au(0) had formed in the structure. Polarized optical microscopy (POM) images of CNMP and CNMP-Au composites show domains with different orientations (Fig. S2).



**Fig. 1** (A) UV-Vis spectroscopy of CNMP-Au composite material. (B) CD spectrum of CNMP-Au. (C) SEM (scale = 2 μm) and (D) cross-sectioned TEM (scale = 500 nm) image of CNMP-Au. (Samples prepared with [AuCl<sub>4</sub>]<sup>-</sup> = 0.5 mmol L<sup>-1</sup>).

Scanning electron microscopy (SEM) of the CNMP-Au (Fig. 1C and S3) showed a typical periodic chiral nematic ordering. Transmission electron microscopy (TEM) of the cross-sectioned composite film showed the presence of AuNPs very well dispersed

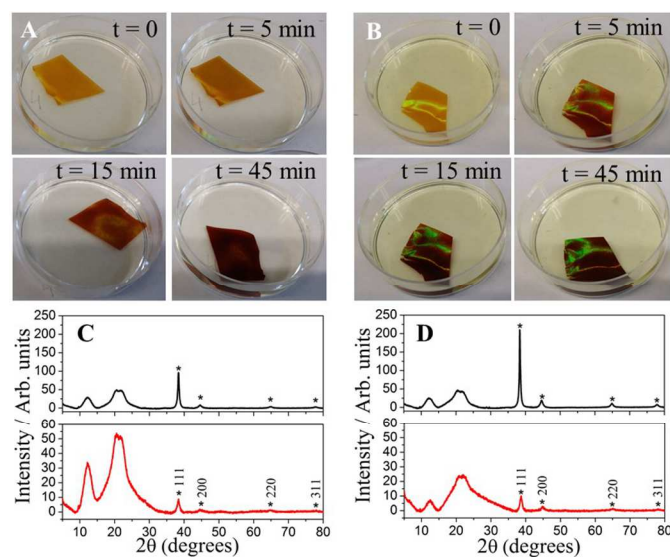
on the aligned PF layers, Fig. 1d and Fig. S4, with an average size of 27 nm from TEM.

The particles present shapes ranging from spheres to prisms and small rods (Fig. 1d and S4). From the TEM images, the AuNPs appear embedded in the PF resin. Stirring and sonicating the CNMP-Au composite in two different thiols (2,4,6-trimercapto-1,3,5-triazine and mercaptopropionic acid) led to no decoloration of the film even in high concentration of gold and thiol, indicating that the AuNPs are bonded strongly to the PF resin. This is an interesting observation and suggests possible future experiments to functionalize the AuNPs inside the material.

The *in situ* formation of AuNPs in the mesoporous PF resin without a sacrificial reducing agent likely involves reduction of the PF resin. In fact, various carbohydrates and polyphenols have been used to reduce gold or silver in the past, and we recently showed that non-porous aminophenol formaldehyde resin spheres could be used to form core-shell Au/polymer structures.<sup>24</sup>

We investigated the concentration and time dependence of the Au<sup>3+</sup> reduction by the resin. Fig. 2a and 2b show photographs of the resin films with 1 and 5 mM concentration of HAuCl<sub>4</sub>, respectively, in different times, where it is possible to see the yellow films turning red. PXRD of the films after 2 h (Fig. 2c,d) confirm the Au(0) formation, with the peak intensities depending on Au<sup>3+</sup> concentration, which also affects the observed CD spectrum (Fig. S5). Fig. S6 shows photographs of two films treated with 0.1 mM HAuCl<sub>4</sub> for 120 min and 24 h, showing the kinetic control of the redox reaction. When a film was treated with 10 mM HAuCl<sub>4</sub>, the reaction was much faster; Fig. S7 shows a photograph of the film treated at 10 mM for 120 min.

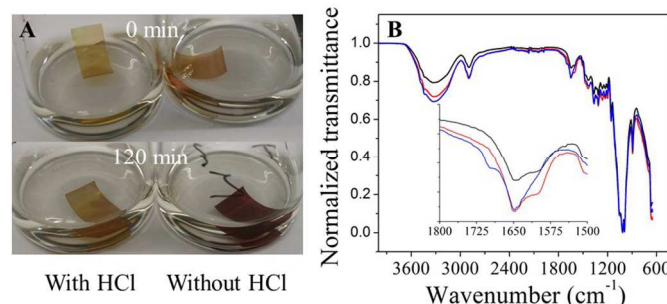
To probe the mechanism of the reduction and the anchoring of AuNPs to the CNMP, we treated the CNMP sample with 0.1 M HCl. When the CNMP film is treated with HCl, the polymer crosslinks more and reduces the concentration of formyl groups on the film.<sup>24c</sup> Fig. 3 shows photographs of two films (one previously treated with HCl) in contact with 1 mM HAuCl<sub>4</sub> for 120 min. The film treated with HCl showed less ability to reduce the AuNPs compared with the untreated film. We believe that residual formyl groups are responsible for the Au<sup>3+</sup> reduction, which explains the disappearance of the band at 1597 cm<sup>-1</sup>, which is assigned to ν C=C aromatic ring of free phenol upon treating the film with 1 mM HAuCl<sub>4</sub> (Fig 3).



**Fig. 2** Top: Photos showing the evolution of AuNP formation in the CNMP depending on [AuCl<sub>4</sub><sup>-</sup>] concentration. (A) 1 mM HAuCl<sub>4</sub> and (B) 5 mM HAuCl<sub>4</sub>. (C) PXRD of CNMP-Au film treated with 1 mM HAuCl<sub>4</sub> for 15 min (red) and 120 min (black).

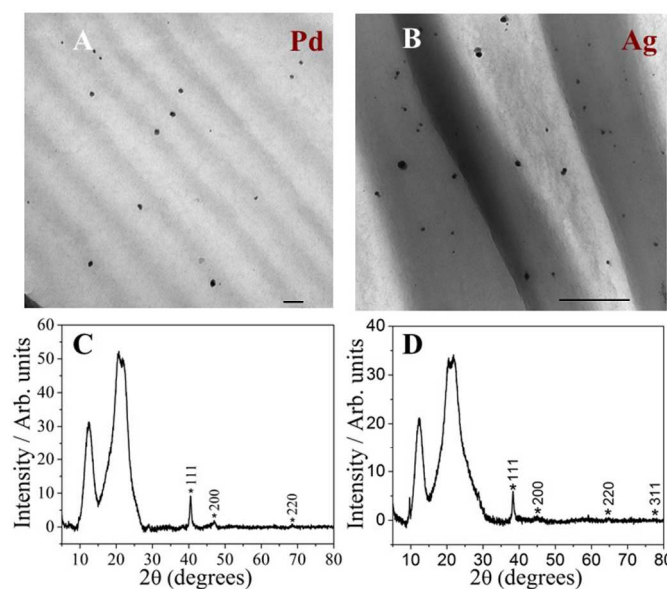
(black). (D) PXRD of CNMP-Au film treated with 5 mM HAuCl<sub>4</sub> for 15 min (red) and 120 min (black). \* (hkl) Values for Au(0) are from reference 25.

The approach to metal NP / PF resins was extended to other metals. In addition to gold, it was possible to construct silver, and palladium metal nanoparticles in the CNMP (TEM images, Fig. 4A-B; PXRD, Fig. 4C-D).



**Fig. 3** (A) FTIR of: CNMP (black line), CNMP-Au-0.5 mM (red line) and CNMP-Au-10 mM (blue line). Inset: 1800 – 1500 cm<sup>-1</sup>. (B) Photographs of AuNPs formation inside CNMP previously treated with HCl (left) and not treated with HCl (right).

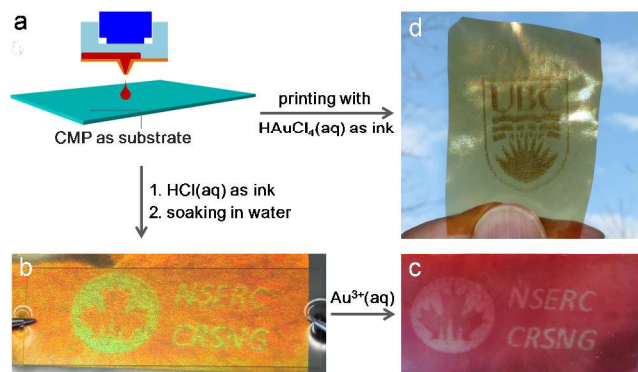
In comparison with gold, silver and palladium formed metal NPs much more sluggishly. In fact, it was necessary to use a concentration of 10 times more for silver and 100 times more for palladium in an overnight reaction to obtain well-dispersed nanoparticles (Fig. 4, Fig. S8-S9). PdNPs have irregular square shapes resembling distorted cubes, while AgNPs are spherical and present a wide size distribution including very small particles.



**Fig. 4** Top: TEM of (A) CNMP-PdNPs and (B) CNMP-AgNPs. Bottom: PXRD of (C) CNMP-PdNPs and (D) CNMP-AgNPs. Scale bars: CNMP-PdNP = 100 nm, CNMP-AgNP = 500 nm. \* (hkl) Values for Pd and Ag are from references 26 and 27, respectively.

We employed two different strategies to pattern AuNPs in the CNMP films. As mentioned above, treating films with HCl enhances crosslinking of PF via condensation of surface hydroxymethyl groups. The region treated with acid is consequently less hydrophilic and therefore swells less in aqueous solvents compared to as-synthesized CNMP, leading to a contrast in photonic colour. Thus,

inkjet printing using  $\text{HCl}_{(\text{aq})}$  as ink generates an image that remains latent in the dry state and is revealed upon swelling in water (Figure 5a,b).<sup>22</sup> In one procedure, we used this pre-patterned CNMP film as a substrate for site-specific deposition of AuNPs by soaking in an aqueous solution of  $\text{HAuCl}_4$ . Formation of AuNPs was hindered in the  $\text{HCl}$ -treated regions due to the lack of reducing hydroxymethyl groups. Plasmonic colour contrast that arises from the differences in the density of AuNPs resulted in an explicit image (Figure 5c). As an alternative approach, we used 10 mM aqueous solution of  $\text{HAuCl}_4$  as “ink” for inkjet printing of patterns onto the CNMP film. Upon printing,  $\text{Au}^{3+}$  solution infiltrates into the mesopores leading to the formation and highly localized placement of AuNPs and hence constitutes the explicit pattern (Figure 5d). The mesoporous nature of the substrate facilitated quick absorption of the ink and prevented its spreading by ambient disturbances. Moreover, relatively fast nucleation and growth led to anchoring of AuNPs in the polymer matrix and prevented lateral diffusion, resulting in high resolution images. We anticipate that this approach can be extended to printing of programmable gradient patterns and patterns of mixed-metal nanoparticles with tunable compositions using inkjet dispensers integrated with multichannel microfluidic components.



**Fig. 5** (a) Schematic of the microfluidic nozzle of the custom inkjet printer used to print patterns on CNMP substrates. (b) Photograph of the pattern printed with  $\text{HCl}_{(\text{aq})}$  as ink and revealed by soaking in water. (c) Photograph of the same patterned CNMP film treated with  $\text{HAuCl}_{4(\text{aq})}$ . (d) Photograph of the explicit pattern obtained by direct writing using  $\text{HAuCl}_{4(\text{aq})}$  as ink.

In summary, we have demonstrated a convenient and facile synthesis of metal nanoparticles embedded in a mesoporous PF resin. The size and density of AuNPs encapsulated in the resin can be controlled through manipulation of the reagent concentration and deposition time. This concept was extended to other metal NPs, including silver and palladium. As well, the technique has allowed for the development of a novel high throughput method to pattern CNMP using an ink jet printer to embed metal NPs at specific sites. Our new approach to mesoporous membranes containing metal NPs will open up new opportunities for investigating catalytic and photonic properties. We are now investigating the catalytic and photonic properties, especially the chiroptical properties, of the new composites and will report these in due course.

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada. VMZ and MS are grateful to the São Paulo Research Foundation (FAPESP; Grant #2014/01025-0) and the German Academic Exchange Service (DAAD), respectively, for post-doctoral fellowships. We thank CelluForce and FPIInnovations for the donation of CNCs.

## Notes and references

- <sup>a</sup> Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1. mmaclach@chem.ubc.ca  
<sup>b</sup> Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Avenida Professor Lineu Prestes, 748, São Paulo, SP, CEP 05508-000, Brazil.  
<sup>c</sup> Department of Electrical and Computer Engineering, University of British Columbia, 2332 Main Mall, Vancouver, BC, V6T 1Z4 (Canada).  
<sup>d</sup> Department of Computer Engineering, Jordan University of Science and Technology, Irbid, Jordan.  
<sup>e</sup> FPIInnovations, 2665 East Mall, Vancouver, BC, Canada V6T 1Z4.

† These authors contributed equally to this work.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

- J. P. Camden, J. A. Dieringer, J. Zhao and R. P. Van Duyne, *Acc. Chem. Res.*, 2008, **41**, 1653.
- M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293.
- J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao and R. P. Van Duyne, *Nat. Mater.*, 2008, **7**, 442.
- A. R. Tao, S. Habas and P. Yang, *Small*, 2008, **4**, 310.
- V. M. Zamarion, R. A. Timm, K. Araki and H. E. Toma, *Inorg. Chem.*, 2008, **47**, 2934.
- I. Lieberman, G. Shemer, T. Fried, E. M. Kosower and G. Markovich, *Angew. Chem. Int. Ed. Engl.*, 2008, **47**, 4855.
- J. Sharma, R. Chhabra, A. Cheng, J. Brownell, Y. Liu and H. Yan, *Science*, 2009, **323**, 112.
- Z. Fan and A. O. Govorov, *Nano Lett.*, 2010, **10**, 2580.
- H. Qi, K. E. Shopsowitz, W. Y. Hamad and M. J. MacLachlan, *J. Am. Chem. Soc.*, 2011, **133**, 3728.
- J. A. Kelly, K. E. Shopsowitz, J. M. Ahn, W. Y. Hamad and M. J. MacLachlan, *Langmuir*, 2012, **28**, 17256.
- M. Schlesinger, M. Giese, L. K. Blusch, W. Y. Hamad and M. J. MacLachlan, *Chem. Commun.*, 2015, **51**, 530.
- M. Schlesinger, W. Y. Hamad and M. J. MacLachlan, *Soft Matter*, 2015, **11**, 4686.
- A. Querejeta-Fernández, G. Chauve, M. Methot, J. Bouchard and E. Kumacheva, *J. Am. Chem. Soc.*, 2014, **136**, 4788.
- A. Lukach, H. Thérien-Aubin, A. Querejeta-Fernández, N. Pitch, G. Chauve, M. Méthot, J. Bouchard and E. Kumacheva, *Langmuir*, 2015, **31**, 5033.
- Q. Liu, M. G. Campbell, J. S. Evans and I. I. Smalyukh, *Adv. Mater.*, 2014, **26**, 7178.
- For recent references on CNCs, see: (a) G. Chu, X. Wang, H. Yin, Y. Shi, H. Jiang, T. Chen, J. Gao, D. Qu, Y. Xu and D. Ding, *ACS Appl. Mater. Interfaces*, 2015, **7**, 21797; (b) M. Giese, L. K. Blusch, M. K. Khan and M. J. MacLachlan, *Angew. Chem. Int. Ed. Engl.*, 2015, **54**, 2888; (c) T. Abitbol, E. Kloser and D. G. Gray, *Cellulose*, 2013, **20**, 785; (d) X. Mu and D. G. Gray, *Langmuir*, 2014, **30**, 9256; (e) D. Liu, S. Wang, Z. Ma, D. Tian, M. Gu and F. Lin, *RSC Adv.*, 2014, **4**, 39322; (f) I. Usov, G. Nyström, J. Adamcik, S. Handschin, C. Schütz, A. Fall, L. Bergström and R. Mezzenga, *Nat. Commun.*, 2015, **6**, 7564; (g) J. P. F. Lagerwall, C. Schütz, M. Salajkova, J. Noh, J. Hyun Park, G. Scalia and L. Bergström, *NPG Asia Mater.*, 2014, **6**, e80; (h) M. Kaushik, K. Basu, C. Benoit, C. M. Cirtiu, H. Vali and A. Moores, *J. Am. Chem. Soc.*, 2015, **137**, 6124.
- A. Querejeta-Fernández, B. Kopera, K. S. Prado, A. Klinkova, M. Methot, G. Chauve, J. Bouchard, A. S. Helmy and E. Kumacheva, *ACS Nano*, 2015, **9**, 10377.
- Y. Habibi, L. A. Lucia and O. J. Rojas, *Chem. Rev.*, 2010, **110**, 3479.
- R. J. Moon, A. Martini, J. Nairn, J. Simonsen and J. Youngblood, *Chem. Soc. Rev.*, 2011, **40**, 3941.
- C. Miao and W. Y. Hamad, *Cellulose*, 2013, **20**, 2221.
- 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.

- 22 M. K. Khan, A. Bsoul, K. Walus, W. Y. Hamad and M. J. MacLachlan, *Angew. Chem. Int. Ed. Engl.*, 2015, **54**, 4304.
- 23 P.-X. Wang, V. M. Zamarion, W. Y. Hamad and M. J. MacLachlan, *Dalton Trans.* 2015, **44**, 14724.
- 24 (a) A. Sasikala, M. Linga Rao, N. Savithramma, T. N. V. K. V. Prasad, *Appl. Nanosci.*, 2015, **5**, 827; (b) Z. Shervani, Y. Yamamoto, *Carbohydr. Res.*, 2011, **346**, 651; (c) M. K. Khan and M. J. MacLachlan, *ACS Macro Lett.*, 2015, **4**, 1351.
- 25 H.E. Swanson and E. Tatge, *Natl. Bur. Stand., Circ. 539*, 1953, **1**, 33.
- 26 B Coles, *J. Inst. Met.* 1956, **84**, 346.
- 27 H.E. Swanson and E. Tatge, *Natl. Bur. Stand., Circ. 539*, 1953, **1**, 23.