Author Manuscript

Title: Thermal Transition of Bimetallic Metal-Phenolic Networks to Biomass-Derived Hierarchically Porous Nanofibers

Authors: Gao Xiao; Wei Chen; Fan Tian; Joseph J. Richardson; Blaise L. Tardy; Minghua Liu; Neel Joshi; Junling Guo, Ph.D.

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.

To be cited as: Chem. Asian J. 10.1002/asia.201800284

Link to VoR: <https://doi.org/10.1002/asia.201800284>

Thermal Transition of Bimetallic Metal-Phenolic Networks to Biomass-Derived Hierarchically Porous Nanofibers**

Gao Xiao, Wei Chen, Fan Tian, Joseph J. Richardson, Blaise L. Tardy, Minghua Liu, Neel Joshi,* and Junling Guo*

Abstract: The development and utilization of biomass resources could contribute to explore novel materials for long-term sustainable energy storage and environmental applications, reduce environmental impacts, and meet the urgent need for green and sustainable development strategies. Herein, a bimetallic metal-phenolic networks (MPN) was applied to incorporate different metallic element species into cattle skin and fabricate collagen fiber-derived complex oxide nanofibers using natural polyphenols (*Myrica* tannins). Direct thermal transition of these biomass-MPN composites generates hierarchically porous nanofibers possessing micro- and mesoporous architectures along with a well-preserved macroscopic structure. The pore system and complex oxide composition provide excellent photocatalytic performance. This low-cost, simple and readily scalable MPN-based approach provides a straightforward route to synthesize nanostructured materials directly from biomass, which could play important roles in a wide range of potential applications.

The conversion of biomass into valuable porous inorganic materials for energy storage and environmental applications has attracted increasing attention because of the ever-increasing demand to eliminate petrochemical derivatives and other hazardous precursors by using natural, abundantly available, and renewable materials.^[1] The development of a sustainable route to prepare high-performance porous materials using low cost and highly abundant precursors is desirable for the widespread commercialization and large-scale applications.^[2] Various biomass products have been explored as starting materials to engineer porous inorganic materials for environmental applications.^[3] Nevertheless, porous materials derived from biomass generally show low functional performance owing to the limited variety of active atoms

(generally limited to naturally occurring carbon, nitrogen, sulfur, etc.) and the high yield of by-products.^[1b] To address these problems, different strategies have been developed to increase the functional performance of biomass-derived porous materials, such as incorporating different metallic or nonmetallic elements into the biomass during calcination to increase the compositional degree of metal oxides in the material skeleton.^[4] However, it can be costly and complicated to tether high concentrations of metal elements to biomass,^[5] and therefore it is still necessary to develop more versatile and facile methods to prepare biomass-derived porous materials with desirable functional performance.

Metal-phenolic networks (MPNs) are a versatile class of self-assembled materials constructed from polyphenols and metal ions through coordination bonds.^[6] The natural adherent properties of polyphenols enable MPN deposition onto various template materials, allowing for the rational design and engineering of diverse functional films and particles.^[7] The functionality of the MPN can be tuned through careful choice of the incorporated metal ions (Fe^{3+} , Al^{3+} , Cu^{2+} , Ti^{4+} , etc.).^[6b, 8] Therefore, the ability to incorporate multiple metals into MPN materials and transform the films into complex oxides provides new opportunities for engineering multifunctional systems for various applications.^[9]

In this study, bimetallic titanium/silver-phenolic networks (Ag/Ti-PN) and skin collagen fibers were used to fabricate high-performance complex oxide nanofiber with hierarchically porous architectures (*meso*-Ag/TiO₂). Skin-derived collagen fibers are one of the largest animal biomass resources and mainly originate from animal hide, the most abundant material in leather industry waste.^[10] Due to the highly ordered fibril microstructures and chemical properties of collagen fibers (**Figure 1a**), this material has been demonstrated to be an ideal biomass framework for engineering multifunctional materials for diverse applications.^[11] Collagen is a highly favorable substrate for the formation of MPNs owing to the high affinity between collagen and tannins.^[12] To our knowledge, this is the first time that a bimetallic MPN coating method has been used for the preparation of hierarchically porous nanofibers. This judicious transformation of organic-rich waste not only addresses the disposal issue, but also generates valuable functional inorganic porous materials from the discard. Our as-synthesized bimetallic porous materials will certainly be believed to be a trend setter and have greater economic ramifications by creating value-added materials from waste.

Bimetallic Ag/Ti-PN was first formed on skin collagen fiber (**Figure 1b**), and due to the dense *ortho*-phenolic hydroxyls in polyphenols, *Myrica* tannins can coordinate with high amounts of both Ti^{4+} and Ag^+ ions forming a supramolecular network around the collagen fibers. Through thermal transitioning, the coordinated Ti^{4+} ions can be transformed into TiO_2 species, and the presence of Ag^+ ions will lead to the formation of complex oxides Ag_xTiO_2 , where x is the seeded molar fraction of $\text{Ag}^+:\text{Ti}^{4+}$ (**Figure 1c**). The high binding affinity and conformational nature of Ag/Ti-PN complexes meant that the naturally occurring

[*] Dr. Gao Xiao, Wei Chen, Prof. Minghua Liu
Department of Environmental Science and Engineering, College of Environment and Resources, Fuzhou University, Fuzhou 350108 (China)
Dr. Gao Xiao, Prof. Neel Joshi, Dr. Junling Guo
Wyss Institute for Biologically Inspired Engineering, School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, (USA)
E-mail: junling.guo@wyss.harvard.edu; njoshi@seas.harvard.edu
Dr. Gao Xiao, Harvard-MIT Division of Health Sciences and Technology, Massachusetts Institute of Technology, Cambridge, MA, 02139 (USA)
Fan Tian, Department of Applied Mathematics and Statistics, Johns Hopkins University, Baltimore, Maryland 21287 (USA)
Dr. Joseph J. Richardson, Department of Materials Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
Dr. Blaise L. Tardy, Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P. O. Box 16300, FI-00076 (Finland)

[**] We gratefully acknowledge the financial supports provided by the National Natural Science Foundation of China (Grant No. 21506036) and the Natural Science Foundation of Fujian Province, China (Grant No. 2017J01412). This work was also supported by the Scientific Research Foundation of the Education Department of Fujian Province, China (Grant No. JA15099). J. Guo is grateful for the Fellowships from C.H. Foundation (Grant No. 161102) and Wyss Institute at Harvard University. We acknowledge Yana Klyachina, Dr. Peter Nguyen for the preparation of scheme models

Supporting information for this article is given via a link at the end of the document.

hierarchical structures of the biotemplate were retained and replicated into the *meso*-Ag_{0.2}/TiO₂.

Figure 1. a-c, Schematic of the fabrication process where collagen fibers are used as a starting material for the synthesis of bimetallic Ag/TiO₂ nanofibers with mesoporous structures. The use of bimetallic silver-titanium phenolic networks (Ag/Ti-PN) based on *Myrica* tannins provides a metal source for the thermal transition to complex oxides (b,c). d-i, SEM images of the *meso*-Ag_{0.2}/TiO₂ (d) and (e, g, h) TEM and HRTEM images of the *meso*-Ag_{0.2}/TiO₂. Scale bars are (d) 1 μ m, (e) 50 nm, (f) 200 nm, (g,h) 5 nm. (f) EDS mapping analysis of *meso*-Ag_{0.2}/TiO₂, (i) the corresponding SAED pattern of *meso*-Ag_{0.2}/TiO₂. All *meso*-Ag_{0.2}/TiO₂ were synthesized at the optimized calcination temperature determined at 500 $^{\circ}$ C.

The *meso*-Ag_{0.2}/TiO₂ obtained at 500 $^{\circ}$ C presented an ordered hierarchical fibrous structure with outer diameter of around 2-4 μ m which is similar to the original diameter of the bundle of natural collagen fiber used for templating (Figure 1d). Moreover, the fibrous morphology of collagen fibers was well preserved during the preparation of *meso*-Ag_{0.2}/TiO₂ (Figure S1a) and the nanoscale fibers self-assembled into multilevel *meso*-Ag_{0.2}/TiO₂ structures (Figure S1b). Fibrous materials are generally recognized to have mechanical flexibility, excellent mass transfer properties, and high surface areas.^[13] TEM and high-angle annular dark-field (HAADF-STEM) images showed the mesoporous structures of these *meso*-Ag_{0.2}/TiO₂ (Figure 1e, 1f and Figure S2a). The crystal nanostructures align along the longitudinal axis of the collagen fiber, which resulted from replicating the natural nanostructures into the *meso*-Ag_{0.2}/TiO₂ (Figure S2a, 2b). Energy-dispersive X-ray spectroscopy (EDS) mapping revealed that the Ag map had a shape similar to that of both Ti and O elemental maps, which directly confirmed the high distribution of Ag-containing species in the *meso*-Ag/TiO₂.

HAADF-STEM images of the cross-sectional scan (Figure S3) and EDS elemental analysis spectra of the surface of the *meso*-Ag_{0.2}/TiO₂@500 $^{\circ}$ C (Figure S4) demonstrated that the Ag loading was 0.5 mol % at all sub-layers of the fibers, however the elemental analysis showed a lower Ag concentration of 0.095 mol % on the surface. This suggested that only a small amount of Ag deposited on the surface of the nanofibers and the majority of the Ag (I) ions were well integrated into the crystal structures of *meso*-Ag_{0.2}/TiO₂.

Figure 1g and Figure S2b showed that metallic Ag nanoparticles with a size of 3-10 nm were evenly coated on the surface of the *meso*-Ag_{0.2}/TiO₂, and no AgNP aggregation was observed. In addition, compared with the pure TiO₂, a thin layer with a thickness of 3-5 nm could be attributed to the formation of Ag (I)-doped TiO₂. At a relatively low preparation temperature (500 $^{\circ}$ C), a limited diffusion length of Ag (I) into TiO₂ could result to the formation of Ag (I)-doped TiO₂. HRTEM images of an individual *meso*-Ag_{0.2}/TiO₂ (Figure S2c) and its corresponding fast Fourier transform (FFT) patterns (Figure S2d) showed the polycrystalline structure. It is generally accepted that metallic Ag nanoparticles function as electron sinks to accept photo-generated electrons from excited semiconductors, facilitating dioxygen reduction.^[14] In Figure 1h, the HRTEM image of the *meso*-Ag_{0.2}/TiO₂ shows clear lattice fringes with an interplanar spacing of 0.352 nm and 0.264 nm, which correspond to the 101 plane of TiO₂ anatase and 111 plane of Ag, respectively.^[16] Figure 1i confirms the successful formation of the anatase TiO₂ crystals and Ag nanoparticles.

Figure 2. (a) XRD patterns of the *meso*-Ag_{0.2}/TiO₂ at different calcination temperatures (400 $^{\circ}$ C, 500 $^{\circ}$ C, 600 $^{\circ}$ C; A, anatase), (b) Nitrogen adsorption/desorption isotherms of the samples, (c) BJH pore-size distributions of the samples, (d) BET and BJH surface area, pore volume of the *meso*-Ag_{0.2}/TiO₂ at different calcination temperatures.

Figure 2a showed the XRD patterns of the *meso*-Ag_{0.2}/TiO₂ at different calcination temperatures (400 $^{\circ}$ C, 500 $^{\circ}$ C, 600 $^{\circ}$ C). Although, all the diffraction peaks of the samples could be indexed to the TiO₂ anatase phase (JCPDS84-1286), the sample calcined at low temperature had a weak peak, which indicating a poor degree of crystallization degree for *meso*-

$\text{Ag}_{0.2}/\text{TiO}_2@400^\circ\text{C}$. This was also verified by surface area analysis in **Figure 2**. $\text{meso-Ag}_{0.2}/\text{TiO}_2@400^\circ\text{C}$ had no obvious mesoporous structure, while the other two samples had obvious hysteresis loops, indicating they replicate the template's natural mesoporous structure (**Figure 2b**). $\text{meso-Ag}_{0.2}/\text{TiO}_2@500^\circ\text{C}$ possessed the largest specific surface area and pore volume (**Figure 2c and 2d**). Therefore, the intermediate calcination temperature of 500°C was found to be optimal. This conclusion was also demonstrated in the subsequent UV-Vis Diffuse Reflection (DR) spectra of $\text{meso-Ag}_{0.2}/\text{TiO}_2$ at different calcination temperature (**Figure S7**) and photocatalytic degradation experiments (**Figure S8**).

Figure 3a shows the wide-angle XRD patterns of $\text{meso-Ag}_x/\text{TiO}_2$ ($x = 0, 0.05, 0.1, 0.2, 0.5$, and 1). All the characteristic diffraction peaks of the TiO_2 anatase phase (JCPDS file No.21-1272) can be observed, confirming the highly crystalline nature of the $\text{meso-Ag}_{0.2}/\text{TiO}_2$.^[17] The average anatase crystallite size was subsequently estimated using the Scherrer equation. The results summarized in **Figure S5** showed that $\text{meso-Ag}_{0.2}/\text{TiO}_2$ sample had a relatively smaller crystal size ($8.1\text{--}6.1\text{ nm}$) than those of pure TiO_2 (9.7 nm). The crystal size decreased with increasing silver content from the ratios of 0 to 0.5 . Additionally, when the silver content was low, the peaks corresponding to Ag_2O or metallic Ag nanoparticles cannot be identified, since the ionic radius of Ag^+ ($1.26\text{ \AA}$) is larger than that of Ti^{4+} ($0.68\text{ \AA}$) it is difficult for Ag^+ to replace Ti^{4+} in the crystal lattice. Thus, the Ag atoms were preferably located at the grain boundaries and grain junctions of titania crystallite growth through the formation of Ag-O-Ti bonds. Potentially, this increased the diffusion barrier at the titania grain junctions and then inhibited the crystallite growth of TiO_2 during calcination.^[18] However, when the amount of silver was increased to match that of titanium, the characteristic peaks of metallic Ag (JCPDS04-0783), suggesting that the metallic Ag nanoparticles could be deposited on the surface of TiO_2 nanoparticles leading to an increase of the average grain size of $\text{meso-Ag}_{0.2}/\text{TiO}_2$.^[19]

distributions of the $\text{meso-Ag}_x/\text{TiO}_2$ with calcination temperatures of 500°C , (d) BET and BJH surface area, pore volume of the $\text{meso-Ag}_x/\text{TiO}_2$ with calcination temperatures of 500°C .

Figure 3b shows the N_2 adsorption-desorption isotherms of $\text{meso-Ag}_x/\text{TiO}_2$ displaying the hysteresis loop characteristic to mesoporous materials. **Figure 3c** shows that the pore diameter distributions of $\text{meso-Ag}_x/\text{TiO}_2$ are in the range of $3\text{--}10\text{ nm}$, which supports the formation of the mesoporous structure. The BET surface area, BJH surface area, and pore volume are summarized in **Figure 3d**. $\text{meso-Ag}_{0.2}/\text{TiO}_2@500^\circ\text{C}$ exhibited the highest surface area ($111.65\text{ m}^2/\text{g}$) and pore volume ($0.182\text{ cm}^3/\text{g}$). In addition, the BJH surface area was higher than that of BET suggesting that there were almost no micropores in the $\text{meso-Ag}_x/\text{TiO}_2$ samples.

The coexistence of Ag(I) and metallic Ag was also verified by X-ray photoelectron spectroscopy (XPS) analysis. $\text{Ti } 2s/2p/3s/3p$ and $\text{O } 1s$ can be observed in the spectra, which can be attributed to the TiO_2 phase (**Figure 4a**). Compared with the pure TiO_2 , the new peaks of $\text{Ag } 3d$ are clearly observed, which can be ascribed to both metallic Ag and/or Ag(I) doped in the TiO_2 .^[20] In the sample of $\text{meso-Ag}_1/\text{TiO}_2$, the intense peaks of $\text{Ag } 3d_{5/2}$ and $\text{Ag } 3d_{3/2}$ at 368.3 and 374.3 eV , respectively, can be assigned to metallic Ag (**Figure 4b**). In the sample of $\text{meso-Ag}_{0.1}/\text{TiO}_2$, the $\text{Ag } 3d$ region showed a weak XPS peaks at 368.0 eV and 374.0 eV , which corresponded to the $\text{Ag } 3d_{5/2}$ and $\text{Ag } 3d_{3/2}$ peaks of Ag(I) . As for the $\text{meso-Ag}_{0.2}/\text{TiO}_2$ sample, more detailed XPS spectra are available in **Figure S6**, the binding energy of $\text{Ag } 3d$ at 368.1 eV and 374.1 eV can be assigned to the metallic Ag phase and Ag(I) phase.^[20]

UV-Vis absorption spectra of $\text{meso-Ag}_x/\text{TiO}_2$ with different ratios of $\text{Ag}^+/\text{Ti}^{4+}$ ions are shown in **Figure 4c**. The absorption edge wavelength and band gap were calculated and summarized in **Figure 4d**. After the formation of bimetallic Ag/Ti oxide species, $\text{meso-Ag}_x/\text{TiO}_2$ exhibits a wide visible-light absorption in the range of $400\text{--}800\text{ nm}$. The absorbance edge of the $\text{meso-Ag}_x/\text{TiO}_2$ shifted from 396 to 506 nm when the mole ratio of Ag/Ti increased from 0 to 0.2 . Meanwhile, the band gap gradually decreased from 3.130 eV to 2.446 eV , likely due to the strong localized surface plasmon resonance of Ag nanoparticles and the additional energy level of the Ag(I) ion. When the molar ratio of Ag/Ti was increased above 0.2 , the visible light absorption ability of the $\text{meso-Ag}_x/\text{TiO}_2$ decreased to 446 nm and the band gap increased to 2.78 eV . The UV-Vis results are in good agreement with the band-gap trends observed by XPS. To further illustrate the structural merits of this unique pore architecture, methyl orange (MO) degradation was used as a probe reaction to evaluate the photocatalytic activity of the $\text{meso-Ag}_x/\text{TiO}_2$ under visible light irradiation. As shown in **Figure 4e**, the catalytic degradation rate could be enhanced with increasing silver content, as all $\text{meso-Ag}_x/\text{TiO}_2$ exhibited relatively higher activity when compared with the pure meso-TiO_2 . The overall influence of silver content (Ag/Ti mole ratio) on the catalytic activity follows the order of $0.2 > 0.5 > 0.1 > 1 > 0.01 > 0$. **Figure 4f** shows the rapid change of the UV-Vis spectrum of $\text{meso-Ag}_{0.2}/\text{TiO}_2$ suspensions with MO. Among the catalysts with different ratios of Ag/Ti , $\text{meso-Ag}_{0.2}/\text{TiO}_2$ showed the highest photocatalytic activity with a decomposition rate of

Figure 3. (a) XRD patterns of $\text{meso-Ag}_x/\text{TiO}_2$ with different ratios of Ag/Ti ions ($x = 0, 0.05, 0.1, 0.2, 0.5$, and 1) at the optimum calcination temperature (500°C) (A, anatase; S, rutile), (b) nitrogen adsorption/desorption isotherms of the $\text{meso-Ag}_x/\text{TiO}_2$ with calcination temperatures of 500°C , (c) BJH pore-size

90.3% at 40 min. The successful incorporation of Ag and Ti sources uniformly into the collagen fiber is the key to the preparation of high-performance catalysts. Moreover, the catalyst could be reused (**Figure S9**) which shows that the degradation amount only drops to 80.2% after five uses, showing good reusability. The high electron-hole recombination inhibition could be achieved with metallic Ag coatings on the surface of the nanoparticles according to *Schottky* barrier formation. Moreover, the photo-generated electrons are excited from the isolated energy level of Ag(I) doping due to the conduction band of TiO_2 to reduce oxygen, while the photo-generated holes remain on the Ag-doping energy level to oxidize organic substances.^[21] Finally, the doping of Ag(I) is usually accompanied by the formation of defects, which can play the role of trap centres to photoelectrons and will efficiently separate the photo-excited holes and electrons and prolong their lifetime.^[22]

oxygen. The nanostructures of *meso*- Ag_x/TiO_2 were replicated from the hierarchical structure and morphology of natural collagen fibers. Ag (I) and metallic Ag can be co-existed when the calcination temperature was 500 °C. The results indicate that the use of *Myrica* tannins for forming bimetallic Ag/Ti-PN to functionalize collagen fibers is a promising and efficient method for the preparation of complex oxide catalysts. The synergistic effect of Ag and Ag (I) significantly enhanced the visible light photocatalytic activity. As a result of the strong interactions between metal ions and polyphenols, MPN-based strategies could provide a new avenue for the preparation of other bimetallic combinations, such as $\text{Co}^{2+}/\text{Ti}^{4+}$, $\text{Bi}^{3+}/\text{Fe}^{3+}$, and $\text{Ce}^{3+}/\text{Ti}^{4+}$ for the synthesis of other metal (or metal oxide, metal carbide)/carbon composites used as supercapacitors, batteries, and catalysts.

Keywords: biomass • metal-phenolic networks • mesoporous • nanofibers • tannins

Figure 4. (a) XPS survey spectra of the *meso*- TiO_2 , *meso*- $\text{Ag}_{0.1}/\text{TiO}_2$, *meso*- $\text{Ag}_{0.2}/\text{TiO}_2$, *meso*- Ag_1/TiO_2 and (b) corresponding XPS spectra of Ag 3d. (c) UV-vis DR spectra of the *meso*- Ag_x/TiO_2 with different ratios of Ag/Ti ($x = 0, 0.05, 0.1, 0.2, 0.5$, and 1), (d) The gap energy (left axis) and the absorption edge (right axis) of the samples, (e) Photocatalytic degradation rate of MO in the presence of various kinds of photocatalysts in the aqueous dispersion under visible light irradiation (initial concentration 10mg/L, 100 mL, pH =6.53), (f) Temporal spectral changes of MO in aqueous *meso*- $\text{Ag}_{0.2}/\text{TiO}_2$ dispersion under visible irradiation. Inset shows the change of color during the degradation process. All *meso*- Ag_x/TiO_2 were synthesized under the optimal calcination temperature of 500 °C.

In summary, we provided a simple and sustainable method for the synthesis of mesoporous Ag/Ag(I) modified TiO_2 nanofibers (*meso*- Ag_x/TiO_2) by using bimetallic Ag/Ti-PN to coat skin-derived collagen, followed by calcination in the presence of

- aJ. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D. W. Bahnemann, *Chem. Rev.* **2014**, *114*, 9919-9986; bJ. Wei, Y. Liang, Y. Hu, B. Kong, G. P. Simon, J. Zhang, S. P. Jiang, H. Wang, *Angew. Chem. Int. Ed.* **2016**, *128*, 1377-1381; cP. Q. Nguyen, Z. Botyanszki, P. K. R. Tay, N. S. Joshi, *Nat. Comm.* **2014**, *5*, dS. Dutta, A. Bhaumik, K. C.-W. Wu, *Energy Environ. Sci.* **2014**, *7*, 3574-3592; eL.-F. Chen, Z.-H. Huang, H.-W. Liang, W.-T. Yao, Z.-Y. Yu, S.-H. Yu, *Energy Environ. Sci.* **2013**, *6*, 3331-3338.
- aC. Mao, F. Zuo, Y. Hou, X. Bu, P. Feng, *Angew. Chem. Int. Ed.* **2014**, *53*, 10485-10489; bS. Wang, L. Pan, J.-J. Song, W. Mi, J.-J. Zou, L. Wang, X. Zhang, *J. Am. Chem. Soc.* **2015**, *137*, 2975-2983; cH. Guan, J. Lin, B. Qiao, X. Yang, L. Li, S. Miao, J. Liu, A. Wang, X. Wang, T. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 2820-2824; dM. J. Nalbandian, K. E. Greenstein, D. Shuai, M. Zhang, Y.-H. Choa, G. F. Parkin, N. V. Myung, D. M. Cwierny, *Environ. Sci. Tech.* **2015**, *49*, 1654-1663; eC. T. Dinh, H. Yen, F. Kleitz, T. O. Do, *Angew. Chem. Int. Ed.* **2014**, *53*, 6618-6623; fB. Liu, L.-M. Liu, X.-F. Lang, H.-Y. Wang, X. W. D. Lou, E. S. Aydil, *Energy Environ. Sci.* **2014**, *7*, 2592-2597; gJ. B. Joo, M. Dahl, N. Li, F. Zaera, Y. Yin, *Energy Environ. Sci.* **2013**, *6*, 2082-2092.
- aP. Chen, L.-K. Wang, G. Wang, M.-R. Gao, J. Ge, W.-J. Yuan, Y.-H. Shen, A.-J. Xie, S.-H. Yu, *Energy Environ. Sci.* **2014**, *7*, 4095-4103; bS. Gao, X. Wei, H. Fan, L. Li, K. Geng, J. Wang, *Nano Energy* **2015**, *13*, 518-526; cS. Gao, K. Geng, H. Liu, X. Wei, M. Zhang, P. Wang, J. Wang, *Energy Environ. Sci.* **2015**, *8*, 221-229; dX. Liu, Y. Zhou, W. Zhou, L. Li, S. Huang, S. Chen, *Nanoscale* **2015**, *7*, 6136-6142; eW.-J. Liu, K. Tian, Y.-R. He, H. Jiang, H.-Q. Yu, *Environ. Sci. Tech.* **2014**, *48*, 13951-13959; fW. Qian, F. Sun, Y. Xu, L. Qiu, C. Liu, S. Wang, F. Yan, *Energy Environ. Sci.* **2014**, *7*, 379-386; gJ. Xie, H. Xie, B. L. Su, Y. b. Cheng, X. Du, H. Zeng, M. Wang, W. Wang, H. Wang, Z. Fu, *Angew. Chem. Int. Ed.* **2016**, *55*, 3031-3035.
- S. Zhu, X. Gao, Y. Zhu, Y. Li, *Green Chem.* **2016**, *18*, 782-791.
- J. T. Korhonen, P. Hiekkataipale, J. Malm, M. Karppinen, O. Ikkala, R. H. Ras, *ACS nano* **2011**, *5*, 1967-1974.
- aH. Ejima, J. J. Richardson, F. Caruso, *Nano Today* **2016**; bJ. Guo, Y. Ping, H. Ejima, K. Alt, M. Meissner, J. J. Richardson, Y. Yan, K. Peter, D. von Elverfeldt, C. E. Hagemeyer, *Angew. Chem. Int. Ed.* **2014**, *53*, 5546-5551; cH. Ejima, J. J. Richardson, K. Liang, J. P. Best, M. P. van Koeverden, G. K. Such, J. Cui, F. Caruso, *Science* **2013**, *341*, 154-157.
- aJ. Guo, X. Wang, D. C. Henstridge, J. J. Richardson, J. Cui, A. Sharma, M. A. Febbraio, K. Peter, J. B. de Haan, C. E. Hagemeyer, *Adv. Healthc. Mater.* **2015**, *4*, 2170-2175; bJ. Y. Oh, Y. Jung, Y. S. Cho, J. Choi, J. H. Youk, N. Fechner, S. J. Yang, C. R. Park, *ChemSusChem* **2017**, *10*, 1675-1682; cJ. Guo, H. Sun, K. Alt, B. L. Tardy, J. J. Richardson, T. Suma, H. Ejima, J. Cui, C. E. Hagemeyer, F. Caruso, *Adv. Healthc. Mater.* **2015**, *4*, 1796-1801.
- J. Guo, B. L. Tardy, A. J. Christofferson, Y. Dai, J. J. Richardson, W. Zhu, M. Hu, Y. Ju, J. Cui, R. R. Dagastine, *Nat. Nanotech.* **2016**, *11*, 1105.
- S. J. Yang, M. Antonietti, N. Fechner, *J. Am. Chem. Soc.* **2015**, *137*, 8269-8273.
- J. Guo, H. Wu, X. Liao, B. Shi, *J. Phys. Chem. C* **2011**, *115*, 23688-23694.
- aJ. Guo, X. Wang, P. Miao, X. Liao, W. Zhang, B. Shi, *J. Mater. Chem.* **2012**, *22*, 11933-11942; bX. P. Liao, B. Shi, *Environ. Sci. Tech.* **2005**, *39*, 4628-4632.
- X. Liao, Z. Lu, X. Du, X. Liu, B. Shi, *Environ. Sci. Tech.* **2004**, *38*, 324-328.

- [13] A. L. Wang, X. J. He, X. F. Lu, H. Xu, Y. X. Tong, G. R. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 3669-3673.
- [14] J. Fei, J. Li, *Adv. Mater.* **2015**, *27*, 314-319.
- [15] P. Wang, B. Huang, X. Qin, X. Zhang, Y. Dai, J. Wei, M. H. Whangbo, *Angew. Chem. Int. Ed.* **2008**, *47*, 7931-7933.
- [16] B. Qiu, M. Xing, J. Zhang, *J. Am. Chem. Soc.* **2014**, *136*, 5852-5855.
- [17] J. Yu, J. Low, W. Xiao, P. Zhou, M. Jaroniec, *J. Am. Chem. Soc.* **2014**, *136*, 8839-8842.
- [18] N. Feng, Q. Wang, A. Zheng, Z. Zhang, J. Fan, S.-B. Liu, J.-P. Amoureux, F. Deng, *J. Am. Chem. Soc.* **2013**, *135*, 1607-1616.
- [19] C. Jia, P. Yang, J. Li, B. Huang, K. Matras - Postolek, *ChemCatChem* **2016**, *8*, 839-847.
- [20] J. Guo, X. Wang, X. Liao, W. Zhanga, B. Shi, *J. Phy. Chem. C* **2012**, *116*, 8188-8195.
- [21] W. Li, Z. Wu, J. Wang, A. A. Elzatahry, D. Zhao, *Chem. Mater.* **2013**, *26*, 287-298.
- [22] H. Yin, X. Wang, L. Wang, Q. Nie, Y. Zhang, Q. Yuan, W. Wu, *J. Alloys. Compd.* **2016**, *657*, 44-52.

Entry for the Table of Contents

COMMUNICATION

Bimetallic metal-phenolic network was applied to converse collagen fibers from leather industry waste to functional hierarchically porous nanofibers

Prof. Gao Xiao, Wei Chen, Fan Tian, Dr. Joseph J. Richardson, Dr. Blaise L. Tardy, Prof. Minghua Liu, Prof. Neel Joshi,* and Dr. Junling Guo*

Page No. – Page No.

Thermal Transition of Bimetallic Metal-Phenolic Networks to Biomass-Derived Hierarchically Porous Nanofibers

Author Manuscript

Minerva Access is the Institutional Repository of The University of Melbourne

Author/s:

Xiao, G;Chen, W;Tian, F;Richardson, JJ;Tardy, BL;Liu, M;Joshi, NS;Guo, J

Title:

Thermal Transition of Bimetallic Metal-Phenolic Networks to Biomass-Derived Hierarchically Porous Nanofibers.

Date:

2018-04-16

Citation:

Xiao, G., Chen, W., Tian, F., Richardson, J. J., Tardy, B. L., Liu, M., Joshi, N. S. & Guo, J. (2018). Thermal Transition of Bimetallic Metal-Phenolic Networks to Biomass-Derived Hierarchically Porous Nanofibers.. Chem Asian J, 13 (8), pp.972-976. <https://doi.org/10.1002/asia.201800284>.

Persistent Link:

<http://hdl.handle.net/11343/283881>