

COMMUNICATION

Facilely and efficiently tuning metal–organic nanostructures of a charge-transfer complex based on a water controlled nanoreaction and the chemistry of 7,7,8,8-tetracyanoquinodimethane (TCNQ)

Cite this: DOI: 10.1039/c3nr05108k

Received 24th September 2013
Accepted 21st December 2013

DOI: 10.1039/c3nr05108k

www.rsc.org/nanoscale

Jingyi Song,^{abcd} Zhuoyu Ji,^{abcd} Qiong Nie^{*abcd} and Wenping Hu^{*abcd}

Metal–organic charge-transfer complexes based on 7,7,8,8-tetracyanoquinodimethane (TCNQ) have received considerable attention because of their unique solid-state physical properties for potential applications in nanoscale opto-electronic devices. To address the challenge in preparing novel metal–TCNQ (MTCNQ) nanostructures, here we introduce a facile and efficient way for synthesizing MTCNQ, taking Ni[TCNQ]₂(H₂O)₂ as an example. By finely tuning the amount of water added into TCNQ solution, well-ordered and large-scale patterns of Ni[TCNQ]₂(H₂O)₂ were successfully obtained in a controllable manner. This facile method will not only be beneficial for the tailored preparation of nanoscale MTCNQ complexes, but also enrich the chemistry of TCNQ.

Introduction

Molecular materials of metal–organic charge-transfer complexes based on 7,7,8,8-tetracyanoquinodimethane (TCNQ), such as the charge-transfer complexes CuTCNQ and AgTCNQ,^{1–4} have attracted extensive attention for decades due to their unique solid-state physical properties. For example, CuTCNQ exhibits intriguing opto-electronic properties and demonstrates potential applications in electrical and optical memory devices, sensors, and magnetic devices.^{5–11} However, it remains a great challenge for the synthesis of novel MTCNQ compounds and further advancing them into practical applications.^{12,13} Here, we take a charge-transfer complex based on nickel and TCNQ as an example, introducing a facile and efficient way to prepare a binary complex of Ni[TCNQ]₂(H₂O)₂, and providing new insights into the binary M[TCNQ]₂(S) complexes (here M refers to the first-row transition metal (Mn, Fe, Co, Ni, etc.) and S represents a coordinating solvent). The water-

controlled synthesis, the characterization of the compounds and the patterning of the nanostructures are demonstrated in this communication.

Experimental section

TCNQ was purchased from Aldrich and re-crystallized twice prior to use. Nickel films were deposited on glass substrates or silicon wafers *via* vacuum evaporation. The substrates were cleaned with pure water, ethanol, acetone, dilute HCl and pure water successively before use. After nickel deposition, the substrates were immersed into a TCNQ/acetonitrile solution, followed by carefully adding deionized water into the solution. Finally, the substrates were removed from the solution, gently washed with excess acetonitrile to remove any residue TCNQ and blown dry under a stream of N₂. The products were characterized by UV-Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), *etc.*

Results and discussion

The generation of the target products is depicted by eqn (1). It is noteworthy that water is requisite for the reaction to take

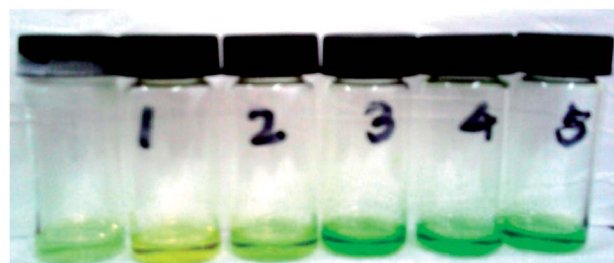


Fig. 1 The water controlled reaction of TCNQ on Ni in acetonitrile solution, after keeping nickel substrates in solution for 10 minutes. Water percent: (left) 0%, (1) 0.5%, (2) 1%, (3) 2%, (4) 3%, and (5) 5%.

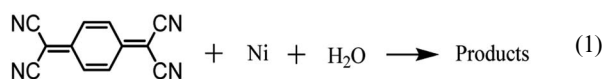
^aDepartment of Orthodontics, School and Hospital of Stomatology, Peking University, Beijing 100081, China

^bBeijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^cInstitute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, China

^dDepartment of Chemistry, Beijing Normal University, Beijing 100875, China. E-mail: nieqiong@pkuss.bjmu.edu.cn; huwp@iccas.ac.cn

place.¹⁴ As soon as water was dipped into the TCNQ acetonitrile solution and mixed homogeneously, the solution turned dark green as shown in Fig. 1. In fact there were two competing processes existing in solution: TCNQ molecules reacted with Ni and water to form products, and at the same time the generated products decomposed into TCNQ and water again. TCNQ is insoluble in water, but the target products are soluble. Probably the completion of the two opposite processes made the reaction highly sensitive to water. It was found that there was an optimum range of the added water. As shown in Fig. 1, 2–3% of water was the best to control the reaction. More water would be harmful to the reaction because of the increased solubility of the products.



The SEM images of the products after reaction are shown in Fig. 2, which tended to form “square columns” on nickel substrates (Fig. 2a and b). The dashed frame area is a vivid indication of the growth process. An individual square column structure was examined by transmission electron microscopy (TEM) and atomic force microscopy (AFM) as shown in Fig. 2c and d, respectively, suggesting both the width and thickness of the square columns were around 400 nm. After dipping the nickel substrate in TCNQ solution for 15 minutes, large-area and uniform nanostructures were formed on the substrate as shown in Fig. 2e. The chemical composition of the columns was determined by energy-dispersive X-ray diffraction (EDX). The EDX profile of the columns exhibited similar characteristics with identical peaks of C, N, O and Ni elements, confirming that the products were Ni[TCNQ]_x-based materials.

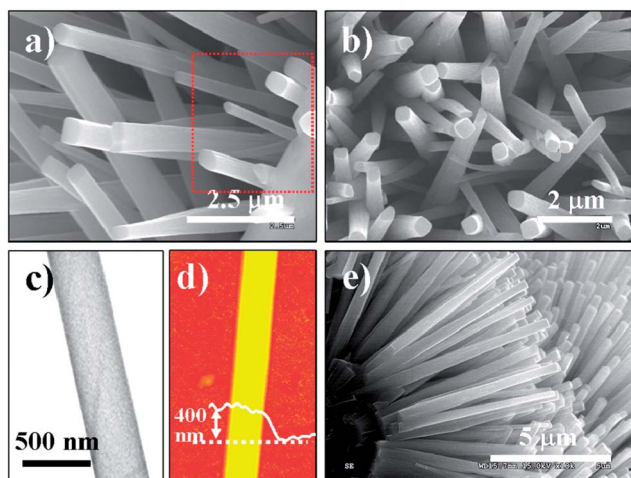


Fig. 2 (a and b) SEM images of the synthesized Ni(TCNQ)_x-based material, and the dashed frame area in (a) indicates the growth process of the nanometer-sized square columns, (c) TEM and (d) AFM images of an individual square column, indicating that both the width and thickness of the square columns were around 400 nm, and (e) large-area and uniform nanostructures of “square columns” formed on nickel substrates.

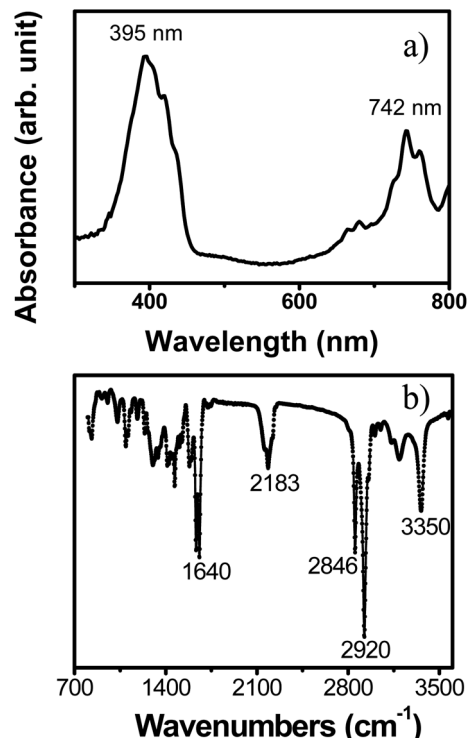
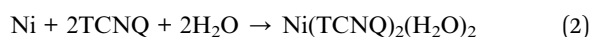


Fig. 3 (a) UV-Vis and (b) FTIR spectra of Ni(TCNQ)₂-based nanostructures, the UV-Vis was recorded at room temperature by dissolving Ni(TCNQ)₂(H₂O)₂ nanometer-sized square columns in acetonitrile, and FTIR was performed by using pressed pellets of the mixture of the nanostructures and KBr.

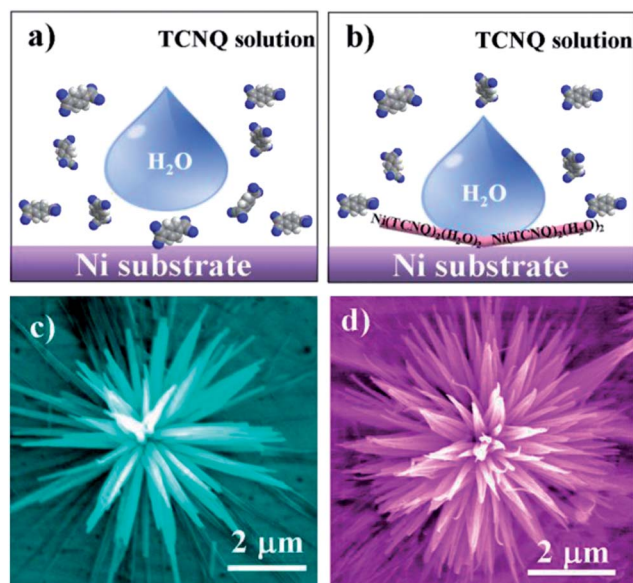
The absorption spectrum of the products is shown in Fig. 3a, wherein the peak at ~395 nm was attributed to the neutral Ni(TCNQ)_x-based material and the peak at ~742 nm was assigned to a TCNQ anion radical of the products.^{15–17} The FTIR spectrum of the square columns is shown in Fig. 3b. The band at 2183 cm⁻¹ was the typical stretching mode of C≡N bonds, which exhibited lower energies than those of a neutral TCNQ band (2224 cm⁻¹), indicating the existence of a reduced [TCNQ]⁻ radical.¹⁵ The sharp peak at 1640 cm⁻¹ confirmed the presence of TCNQ in a reduced state.⁸ Significantly, the bands at 2846, 2920, and 3350 cm⁻¹ obviously belonged to the presence of coordinated water molecules in the products of the Ni(TCNQ)_x-based material.¹⁴

The Ni2p_{3/2} and Ni2p_{1/2} signals from XPS characterization suggested that Ni elements in the products were essentially Ni²⁺.¹³ Moreover, the N1s orbital appeared as a single feature at 398.7 eV, indicating one type of TCNQ in the final products.^{18,19} TGA data of the products suggested that the compound lost its ~7% mass at temperatures below 225 °C, which corresponded to the molecular weight of two water molecules. When the temperature was over 225 °C, a large mass loss occurred due to the decomposition of the products *via* the loss of TCNQ.^{16,20} All experimental evidence strongly supported the conclusion that the synthesized products were Ni[TCNQ]₂(H₂O)₂. Therefore, the synthesis of the products could be depicted by eqn (2):

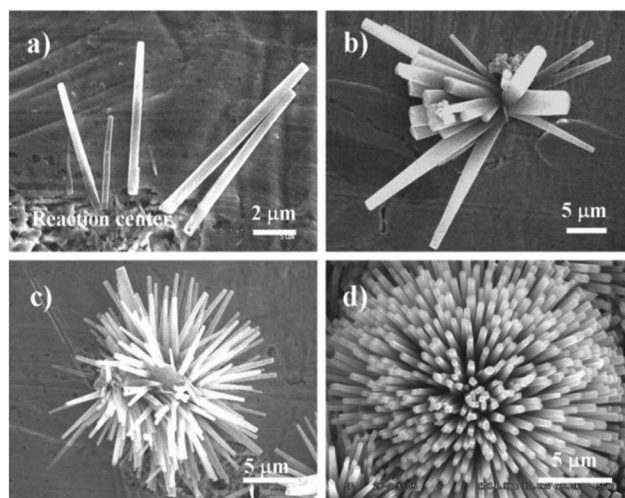


1 Considering the key role of water in the growth of Ni
 [TCNQ]₂(H₂O)₂, the morphology of the final products can be
 5 potentially tuned by water. Because the solubility of TCNQ in
 water is rather low, when one droplet of water was added into
 the TCNQ solution, it would sink down to the nickel substrate
 quickly (Fig. 4a) and give rise to the reaction. The generated
 products were supposed to be firstly formed at the three phase
 10 interfaces (water/TCNQ/Ni), *i.e.*, at the bottom of the water drop
 (Fig. 4b). Indeed, Ni[TCNQ]₂(H₂O)₂ was found on Ni substrates
 as soon as the water drops contacted the substrate (removed the
 substrate quickly from the solution and checked the surface by
 SEM). With the reaction on going, the growth of Ni
 15 [TCNQ]₂(H₂O)₂ continued by consuming the water droplet.
 Because water was the core for the growth of the nanostructures
 layer-by-layer, finally flower-like structures evolved (Fig. 4c).
 As shown in Fig. 4d, very beautiful flower-shaped nanostructures
 of Ni[TCNQ]₂(H₂O)₂ were found after the complete consump-
 20 tion of the water drop (Fig. 4d). The results confirmed (i) the
 indispensable role of water in the growth of Ni[TCNQ]₂(H₂O)₂
 and (ii) the ability of water to tune the reaction process and the
 morphologies of the final products.

It was noticed that the structures of Fig. 2 and 4 were different
 25 which was probably due to the difference in the growth velocity of
 the products. It is understandable that, as discussed above, there
 were two opposite competitive processes in the solution, (i) the
 generation of Ni[TCNQ]₂(H₂O)₂ for the crystallization of the
 nanostructures and (ii) the dissolution of Ni[TCNQ]₂(H₂O)₂
 30 in solution, which hindered the formation of the nanostructures.
 Therefore, the final structures were a balance of the two processes,
 which could be tuned easily by the reaction parameters, *e.g.*,

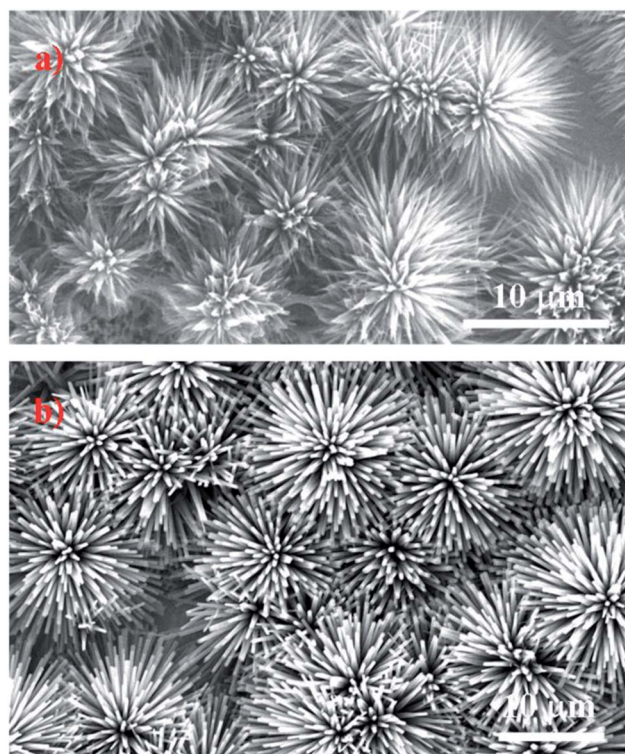


35 Fig. 4 The generation of Ni(TCNQ)₂(H₂O)₂ nanostructures with the
 addition of water droplets. (a) When one water drop was added into
 the TCNQ solution, it would sink down to the nickel substrate
 40 quickly. (b) The generated products were firstly formed at the bottom
 of the water drop. (c and d) The growth of Ni(TCNQ)₂(H₂O)₂ continued
 by the consumption of the water drop, finally evolved into flower-like
 45 structures.



50 Fig. 5 The controllable synthesis of nanometer sized square columns
 of Ni[TCNQ]₂(H₂O)₂ by controlling the concentration of TCNQ (>10 mM).
 (a) to (d) depict the growth processes of the square column flowers.

TCNQ concentrations. It is suggested that a high concentration of
 55 TCNQ is beneficial for a high yield of products and the crystalliza-
 tion of the products for square columns. Indeed, when the
 concentration of TCNQ was over 10 mM, the generated Ni
 [TCNQ]₂(H₂O)₂ were nanometer sized square columns (Fig. 5).
 The results open the door for tuning the reaction and the product
 morphology of TCNQ-based structures.



60 Fig. 6 Patterning of nanostructured Ni[TCNQ]₂(H₂O)₂ flowers on
 nickel substrates by water drops, (a and b) two kinds of beautiful
 nanostructured flowers were generated by tuning the TCNQ
 65 concentration, (a) TCNQ <5 mM and (b) TCNQ >10 mM.

Depending on the facile tuning of the reaction process or product morphologies by the TCNQ concentration and water drops, it is approachable to pattern Ni[TCNQ]₂(H₂O)₂ nanostructures. Interestingly, it can be realized conveniently by dropping a series of water drops successively on nickel substrates. Two kinds of beautiful patterns of nanoflowers were obtained as shown in Fig. 6b (<5 mM) and Fig. 6c (>10 mM). Both patterns can be patterned in a large area facilely, indicating their potential application based MTCNQ nanostructures in a large area and their further application in devices,^{10,11} e.g., for water and moisture monitoring and detection as well as for the nanobio-detection.

Finally, it is very interesting to mention that thin films of the Ni[TCNQ]₂(H₂O)₂ nanostructures exhibited good semiconducting properties. The current increased with increasing temperature, indicating the possible hopping mechanism of charge transport through the nanostructures. The good semiconducting properties will be attractive for the application of the material in novel semiconducting devices, such as field-effect transistors, etc.^{21,22} More experiments on constructing electronic devices based on Ni[TCNQ]₂(H₂O)₂, especially those with single crystalline nanostructures²³ are underway.

Conclusions

In summary, in this communication a facile and efficient way for synthesizing well-ordered Ni[TCNQ]₂(H₂O)₂ nanostructures is introduced. By finely tuning the amount of water added into the TCNQ solution, well-ordered and large-scale patterns of Ni[TCNQ]₂(H₂O)₂ were successfully obtained in a controllable manner. This method is believed to be applicable to various MTCNQ nanostructures. It will not only facilitate the potential applications of MTCNQ in nanoscale opto-electronic devices, but also enrich the chemistry of TCNQ.

Acknowledgements

The authors acknowledge financial support from National Natural Science Foundation of China (51033006), and are grateful to Dr Qing Meng (ICCAS), Dr Tao Li (Copenhagen University) and Dr Evans David (Beijing University of Chemical Technology) for English polishing.

Notes and references

- 1 D. S. Acker, R. J. Harder, W. R. Hertler, W. Mahler, L. R. Melby, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, 1960, **82**, 6408.

- 2 R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, 1976, **98**, 3916.
- 3 R. S. Potember, T. O. Poehler and D. O. Cowan, *Appl. Phys. Lett.*, 1979, **34**, 405.
- 4 R. S. Potember, T. O. Poehler, A. Rappa, D. O. Cowan and A. N. Bloch, *J. Am. Chem. Soc.*, 1980, **102**, 3659.
- 5 K. Xiao, I. N. Ivanov, A. A. Puzetzy, Z. Q. Liu and D. B. Geohegan, *Adv. Mater.*, 2006, **18**, 2184.
- 6 K. Xiao, J. Tao, Z. Pan, A. A. Puzetzy, I. N. Ivanov, S. J. Pennycook and D. B. Geohegan, *Angew. Chem., Int. Ed.*, 2007, **46**, 2650.
- 7 K. Xiao, M. Yoon, A. J. Rondinone, E. A. Payzant and D. B. Geohegan, *J. Am. Chem. Soc.*, 2012, **134**, 14353.
- 8 Y. Liu, Z. Ji, Q. Tang, L. Jiang, H. Li, M. He, W. Hu, D. Zhang, L. Jiang, X. Wang, C. Wang, Y. Liu and D. Zhu, *Adv. Mater.*, 2005, **17**, 2953.
- 9 Y. Liu, H. Li, D. Tu, Z. Ji, C. Wang, Q. Tang, M. Liu, W. Hu, Y. Liu and D. Zhu, *J. Am. Chem. Soc.*, 2006, **128**, 12917.
- 10 Y. Liu, L. Jiang, H. Dong, Z. Tang and W. Hu, *Small*, 2011, **7**, 1412.
- 11 Y. Liu, L. Jiang, H. Dong, Z. Tang and W. Hu, *Small*, 2012, **8**, 557.
- 12 A. R. Siedle, G. A. Candela and T. F. Finnegan, *Inorg. Chim. Acta*, 1979, **35**, 125.
- 13 R. A. Heintz, H. Zhao, X. Ouyang, G. Grandinetti, J. Cowen and K. R. Dunbar, *Inorg. Chem.*, 1999, **38**, 144.
- 14 Z. Ji, H. Dong, M. Liu and W. Hu, *Nano Res.*, 2009, **2**(11), 857.
- 15 L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler and R. E. Benson, *J. Am. Chem. Soc.*, 1962, **84**, 3374.
- 16 D. L. Jeanmaire and P. van Duyne, *J. Am. Chem. Soc.*, 1976, **98**, 4029.
- 17 S. Liu, Y. Liu, P. Wu and D. Zhu, *Chem. Mater.*, 1996, **8**, 2779.
- 18 C. M. Bolinger, J. Darkwa, G. Gammie, S. D. Gammon, J. W. Lyding, T. B. Rauchfuss and S. R. Wilson, *Organometallics*, 1986, **5**, 2386.
- 19 A. S. N. Murthy and G. R. L. Anita, *Anal. Chim. Acta*, 1994, **289**, 43.
- 20 R. Clerac, S. O'Kane, J. Cowen, X. Ouyang, R. Heintz, H. Zhao, M. J. Bazile, Jr and K. R. Dunbar, *Chem. Mater.*, 2003, **15**, 1840.
- 21 C. Wang, H. Dong, W. Hu, Y. Liu and D. Zhu, *Chem. Rev.*, 2012, **112**, 2208.
- 22 Y. Wen, Y. Liu, Y. Guo, G. Yu and W. Hu, *Chem. Rev.*, 2011, **111**, 3358.
- 23 R. Li, W. Hu, Y. Liu and D. Zhu, *Acc. Chem. Res.*, 2010, **43**, 529.