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ORIGINAL REPORT

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Electrodeposition of partially oxidized tetracyanoplatinate nanowires on seeds and patterns for gas sensing

Pedram Jahanian, Xuecheng Yu, Mohamed Kilani and Guangzhao Mao

Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI, USA

ABSTRACT

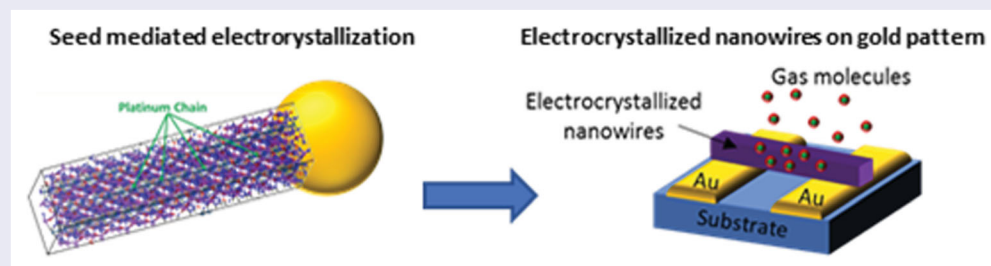
This paper describes the synthesis of a new type of nanowires, potassium tetracyanoplatinate sesquihydrate Krogmann salt or $K(def)TCP$. Seed-mediated electrocrystallization nucleates and confines the $K(def)TCP$ crystals into nanowires. Our data show that the width of $K(def)TCP$ scales proportionally with the diameter of the seed, which is consistent with the nanoconfinement effect of the seed. $K(def)TCP$ nanowires are also electrodeposited on lithographic Au patterns as interconnects and tested for impedance-based gas sensing. The results demonstrate the use of electrocrystallization to construct nanowire sensing units directly on patterned substrates to enable scaling up of nanowire sensor technology.

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KEYWORDS

Electrocrystallization; gas sensing; Krogmann salts; nanowire; seed-mediated nucleation



IMPACT STATEMENT

We show for the first time nanowires directly formed as interconnects on electronic substrates by electrocrystallization are used as sensor materials to detect gases.

1. Introduction

Nanowires are widely recognized as the next-generation building block for ultrasensitive and ultrafast chemical detection [1–4]. Nanowire sensor applications include industrial and personal safety, environmental monitoring, and antiterrorism [5–7]. Despite the research progress, very few nanowire sensors have reached the market due to their manufacturing complexity. In most cases, nanowires are synthesized in bulk, suspended in solvents, and then assembled on substrates by methods that have limited scalability [2]. In addition, there is a need for new sensing materials with better selectivity [8]. Majorities of nanowire materials are inorganic, but organic materials offer advantages in selectivity, ease of processing, and low cost. Today, the most widely explored organic materials for sensing are conducting

polymers [9,10]. In contrast, our work applies a seed-mediated electrocrystallization mechanism to synthesize small-molecule nanowire crystals. Electrocrystallization is capable of producing higher quality crystals than polymerization or chemical synthesis and has the potential to enable additive manufacturing of nanomaterials directly on electronic substrates.

Seed-mediated mechanisms have been used to synthesize nanowires [11–13]. A commonly used method is the vapour–liquid–solid (VLS) mechanism based on the eutectic reaction of a vapour source with a metallic seed particle such as the gold nanoparticle (AuNP) [14,15]. A variation of the VLS is the solution–liquid–solid (SLS) mechanism. In both cases, the metallic seed particle is in the liquid state and it catalyses nanowire growth in part by acting as a crystallization solvent [16]. We discovered

CONTACT Guangzhao Mao ✉ guangzhao.mao@wayne.edu Department of Chemical Engineering and Materials Science, Wayne State University, 5050 Anthony Wayne Drive, Detroit, MI 48202, USA

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a seed-mediated method to nucleate 1-D nanostructures of small-molecule compounds bearing morphological resemblance to those produced by VLS or SLS [17]. In our case, the small size (or highly curved nanoparticle surface) is hypothesized to directly cause the size and shape confinement of the 1-D nanostructures [18,19]. More recently, we applied the seed-mediated mechanism for the electrocrystallization of tetrathiafulvalene (TTF) charge-transfer salt nanowires [20]. TTF nanowires with diameter as small as 7 nm were synthesized by the seed-mediated mechanism. Our previous work has provided experimental evidence of the capability of nanosized electrodes in reducing crystal size of organic conductors down to the nanometer size. Here we extend this unique phenomenon towards a one-step electrochemical synthesis of nanowire sensors that enables nanowire integration into patterned circuitry. More specifically, this paper demonstrates the synthesis of a new type of nanowires made of a Krogmann salt by the seed-mediated mechanism, the electrodeposition of the Krogmann salt nanowires on lithographic patterns, and their use for gas sensing.

The family of partially oxidized tetracyanoplatinates, also called the Krogmann salts, is formed by oxidation of crystalline Pt(II) complexes [21,22]. The most studied Krogmann salt, potassium tetracyanoplatinate bromide trihydrate ($K_2[Pt(CN)_4] \cdot Br_{0.3} \cdot 3H_2O$ or KCP(Br)), is an anion-deficient Krogmann salt. KCP(Br) possesses near metallic conductivity due to the short Pt–Pt separation allowing a high degree of electron delocalization along the overlapping d_z^2 orbitals [23–27]. Here we focus on the cation-deficient Krogmann salt, potassium tetracyanoplatinate sesquihydrate ($K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$ or K(def)TCP), which can be synthesized via electrocrystallization [28]. The crystal structure and conductivity of K(def)TCP are known [29,30]. The room temperature conductivity of K(def)TCP, 70–100 S/cm, while primarily depends on the Pt–Pt separation distance, is also influenced by the crystalline environment including the ligands, cations, and lattice water. This conductivity dependence on structural factors makes K(def)TCP a potentially valuable sensing material for fine tuning of its selectivity.

2. Experimental details

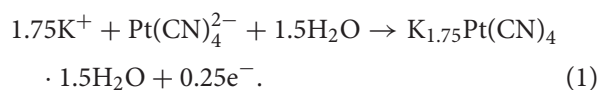
PAP 263A potentiostat (Princeton Applied Research) was used in the electrochemical deposition employing a three-electrode system. Highly oriented pyrolytic graphite (HOPG) and AuNP-decorated HOPG were used as working electrodes, a Pt wire was used as the counter electrode and an Ag wire was used as the quasi reference electrode.

The nanocrystals were characterized with a Bruker Dimension 3100 atomic force microscopy (AFM). Both tapping and contact modes were used. For the tapping mode, silicon tips with a resonance frequency of 300 kHz were used. For the contact mode, Al-coated silicon tips with a resonance frequency of 12 kHz were used. Both were from nanoScience instruments. The height, the amplitude, and phase images were recorded with a scan rate of 1 Hz. Size analysis of the nanoparticles was done with NanoScope software. Kelvin Probe Force Microscopy (KPFM) was conducted using Keysight 5500 AFM. The nanostructures deposited on the HOPG were characterized by field-emission scanning electron microscopy (FE SEM, JEOL JSM 7600F SEM). The acceleration voltage was 5 and 15 kV with a working distance of 8 mm and probe current of 6 μ A. The elemental composition data were obtained by *in situ* energy-dispersive spectroscopy (EDS) attached to the FE SEM with the EDAX Genesis v6.33 software. Impedance spectra were collected using an electrochemical impedance workstation (CH Instruments Electrochemical Workstation 600D) at 1 kHz and an oscillating voltage of 0.2 V in the three-electrode configuration.

3. Results and discussion

The seed-mediated electrocrystallization of K(def)TCP was studied using AuNPs as nucleation seeds. The electrodeposition of AuNPs on HOPG electrodes was described in our previous work [20]. We found that the AuNP morphology was primarily controlled by the $HAuCl_4$ concentration. The size of the AuNPs increases with increasing $HAuCl_4$ concentration (Figure 1(a)–(d)). The AuNP shape changes from hemi-spherical at below 1 mM $HAuCl_4$ to dendritic shape when the $HAuCl_4$ concentration is above 1 mM.

Electrocrystallization of K(def)TCP was carried out on the anode HOPG upon a potential pulse of 1.5 V (vs. standard calomel electrode (SCE)) for 0.1 s in 0.07 M of $K_2Pt(CN)_4$ in deionized water to partially oxidize Pt^{2+} to $Pt^{2.25+}$ [28]:



The $Pt^0/Pt(CN)_4^{2-}$ oxidation potential is 0.59 V (vs. SCE). H_2 was produced at the platinum wire cathode. A silver wire was used as the pseudo-reference electrode. In the absence of the AuNPs, elongated thin plate-like crystals with a size range of 0.6–5 μ m in length and 0.1–0.5 μ m in width were synthesized (Figure 1(e)). The average aspect ratio of the K(def)TCP microcrystals is 3.2 ± 0.9 , in the range of reported bulk values [30,31].

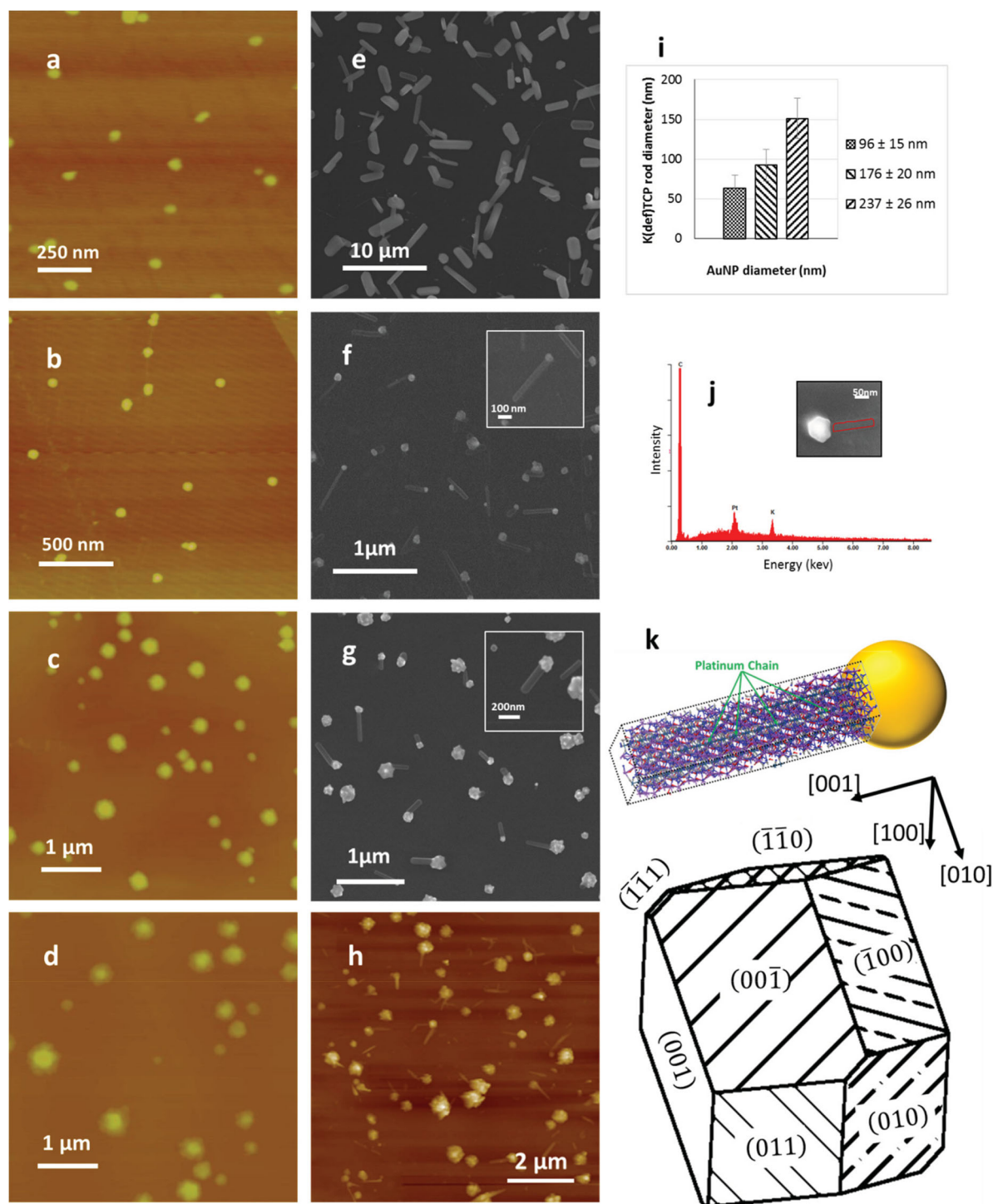


Figure 1. AFM height images of electrodeposited AuNPs on HOPG in different HAuCl_4 concentrations: (a) 0.01 mM, (b) 0.1 mM, (c) 1 mM, and (d) 5 mM. The applied overpotential was -0.5 V and deposition time was 0.01 s. FE SEM images of K(def)TCP crystals electrochemically deposited on (e) bare HOPG and (f–g) AuNP-decorated HOPG. In (f), the AuNP particles were deposited at 0.1 mM HAuCl_4 . In (g) the AuNP particles were deposited at 1 mM HAuCl_4 . (h) *In situ* AFM image of K(def)TCP nucleation on AuNPs (made at 5 mM HAuCl_4). (i) Average AuNP diameter vs. average K(def)TCP width. (j) EDS spectrum of K(def)TCP attached to the AuNP. (k) The unit cell of K(def)TCP crystal structure showing the Pt chain extending along the [001] direction and the simulated crystal morphology using the Wulff theorem.

The K(def)TCP crystals grown on the AuNP-decorated HOPG anode are shown in Figure 1(f)–(h) as a function of the AuNP particle size. The FE SEM images

clearly show the preferential nucleation of K(def)TCP on the AuNPs. Roughly 75% of the K(def)TCP crystals are directly attached to the AuNPs. The electrocrystallization

process was also studied by real-time AFM. Figure 1(h) shows an AFM image of K(def)TCP being nucleated on the AuNP-decorated HOPG electrode in the aqueous solution of 0.07 M $K_2[Pt(CN)_4]$. Using AFM sectional height analysis, we determined the AuNP height and diameter to be 82 ± 23 nm and 336 ± 35 nm, respectively, while the average K(def)TCP nanocrystal height, width, and length to be 39 ± 4 nm, 80 ± 15 nm, and 370 ± 51 nm, respectively. The lateral sizes were determined by the lateral distances at the half maximum height of the object in order to minimize AFM tip convolution [32]. The AFM-determined size of the K(def)TCP crystals is smaller than the FE SEM size because AFM captures the beginning stage of K(def)TCP crystallization in solution. Figure 1(i) plots the size histogram of the AuNP diameter and the attached K(def)TCP width. While there is no significant change in the crystal aspect ratio (2.9–4.2), the size of the K(def)TCP crystals is significantly reduced by its nucleation on the AuNPs. The average K(def)TCP width is 151 ± 25 nm when the AuNP diameter is 237 ± 26 nm. The average K(def)TCP width is 92 ± 20 nm when the AuNP diameter is 176 ± 20 nm. The K(def)TCP width is 63 ± 16 nm when the AuNP diameter is 96 ± 15 nm. The dimensional correlation between the AuNP and the attached K(def)TCP can be seen in the inset images of Figure 1(f)–(g). We also determined that a majority ($\sim 67\%$) of K(def)TCP nanocrystals are oriented with their rod axis perpendicular to the seed/crystal interface. This suggests a preferential molecular attachment or nucleation direction of the crystal on the AuNP seed. The chemical composition of the K(def)TCP crystals grown on the AuNPs was studied by EDS attached to the FE SEM. Both K and Pt were detected on K(def)TCP (Figure 1(j)). The measured K/Pt molar ratio, 1.84, is close to the theoretical value of K(def)TCP. The crystal structure of K(def)TCP was determined using single crystal neutron diffraction [29,30]. K(def)TCP exhibits a triclinic crystal structure with the following unit cell lattice parameters: $a = 10.36$ Å, $b = 11.83$ Å, $c = 9.30$ Å, $\alpha = 102.4^\circ$, $\beta = 106.4^\circ$, $\gamma = 114.7^\circ$, and $V_C = 918.3$ Å³. Figure 1(k) illustrates the orientation of K(def)TCP nucleated on the AuNP seed with its long axis (the c axis) in the radial direction perpendicular to the seed/crystal interface. The Pt–Pt chain extends along this axis. Crystal morphology simulations were conducted using the Morphology tool in the Materials Studio software based on the Wulff theorem of the X-ray powder diffraction data [33]. Figure 1(k) shows the simulated morphology of the K(def)TCP crystal and various prominent crystal faces. The percentage of various faces is listed in Table 1. The relatively large Pt–Pt separation distance lowers the surface energy of the (001) face making it a prominent face

Table 1. The percentage of prominent crystal faces according to the Wulff construction.

Face {h k l}	%
{0 0 1}	24.45
{1 0 $\bar{1}$ }	20.67
{0 1 0}	15.86
{1 0 0}	13.58
{1 1 0}	12.60
{0 1 1}	11.97
{1 1 $\bar{1}$ }	0.87

in the overall morphology. The electrochemically grown K(def)TCP on the other hand does not prominently exhibit the (001) face due to the 1-D growth kinetics along the conductive c axis.

KPFM was used to study the electrical behaviour of the K(def)TCP nanowires in the presence of water vapour [34]. Figure 2(a) shows the capacitance gradient on the K(def)TCP nanocrystals to be uniform regardless of their size and shape. The uniform potential indicates uniform chemical composition of the crystals. Figure 2(b) shows the average contact potential difference change of K(def)TCP when exposed to water vapour. The data show that K(def)TCP surface potential increases upon exposure to water vapour and that the effect is reversible after purging with N_2 . An increase in surface potential corresponds to a decrease in the work function of the sample in the case of a conductive sample here. The same trend was observed for different sizes of K(def)TCP with a length range of 100–2000 nm (Figure 2(c)). The KPFM measurements show that individual K(def)TCP nanowires change their capacitance when exposed to water vapour.

The same electrochemistry as described by Equation (1) was used to synthesize K(def)TCP nanowires on metallic lithographic patterns with the metal lines acting as the electrodes. We show that electrocrystallization of K(def)TCP is used to make interconnects between electrical contacts in chips for gas sensing. K(def)TCP interconnects were synthesized on Cr/Au patterns by electrochemical oxidation of $K_2Pt(CN)_4$ using 0.3 M $K_2Pt(CN)_4$, 1.5 V applied overpotential, and 300 s reaction time. The Cr/Au pattern was deposited by standard photolithography [35]. Figure 3(a) shows the Cr/Au comb-like interdigitated pattern with spacing of 5, 10, and 20 μ m printed on a glass plate. Figure 3(b) shows an SEM image of K(def)TCP nanowires electrochemically deposited across the Cr/Au lines as interconnects for impedance measurements in the presence of various vapours. Chemical sensing measurements on the chip were conducted using an electrochemical impedance workstation in a home-built vapour chamber. Two gas lines were used. One line contains the target gas and a

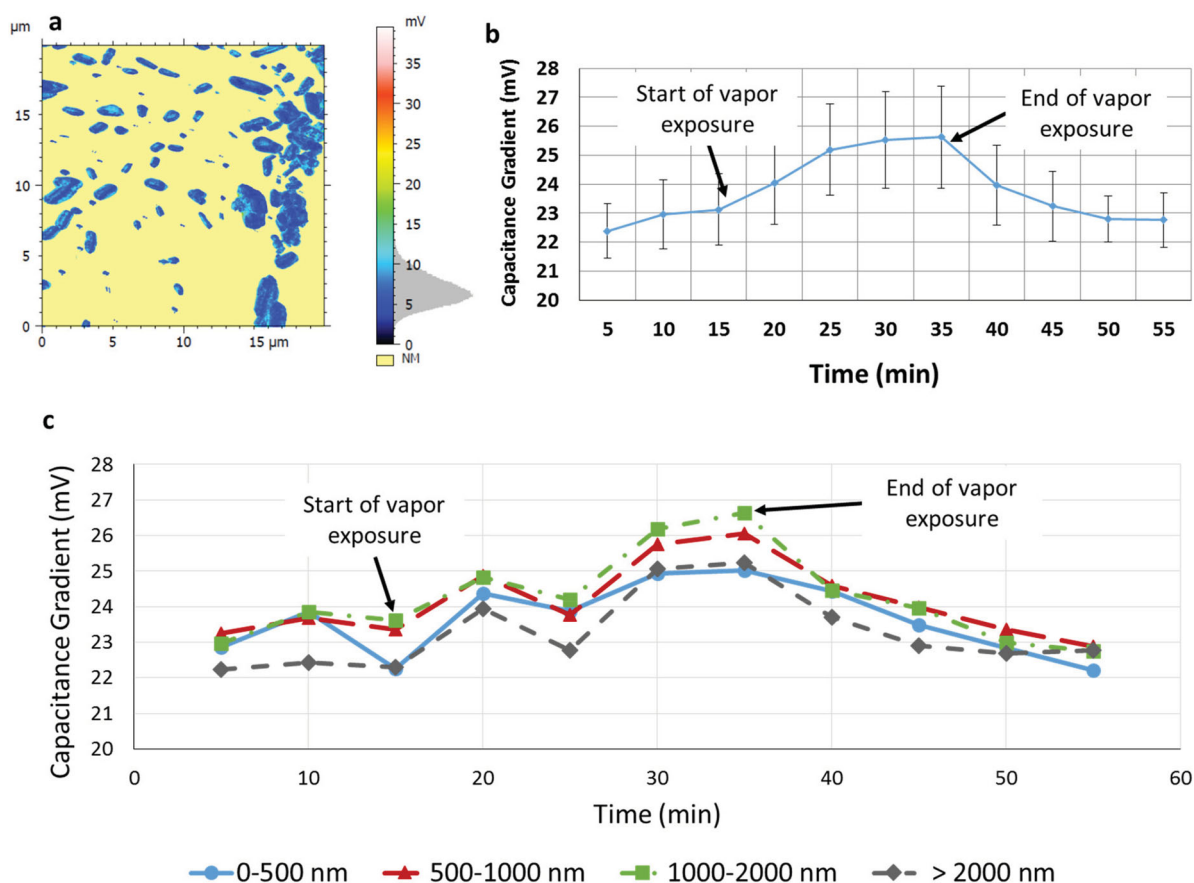


Figure 2. (a) Capacitance KPFM image of K(def)TCP nanowires. (b) Surface potential change of K(def)TCP when exposed to the water vapour (data averaged over multiple data sets). (c) Surface potential changes of K(def)TCP of different sizes when exposed to the water vapour. The arrows point to the beginning and end of water vapour exposure.

bubbler while the second line contains N_2 to dilute the target gas concentration. The concentration and flow rate of the target gas are controlled by two mass flow controllers (Fluke GFC17). The target gas was then introduced to the gas chamber containing the sensor chip. The chamber was purged with N_2 prior to the introduction of each vapour. The change in impedance with time was measured with zero bias and an oscillating voltage of amplitude 0.2 V at 1 kHz. Figure 3(c) shows the impedance change as a function of exposure time for different vapours. The K(def)TCP resistance measured in N_2 is in the range of $5 \times 10^6 \Omega$, which yields a conductivity value of 100 S/cm. The K(def)TCP sensor shows higher sensitivity to polar solvents while little or no impedance change when they are exposed to non-polar solvents. In the presence of water and alcohols, the impedance of the nanowire assembly decreases. The reproducibility of the K(def)TCP sensor was assessed by repeated measurements in water vapour (Figure 3(d)). The sensitivity of the sensor maintained constant for 10 cycles with a relative standard deviation of 0.034%. This also indicates that water molecules are physisorbed on the

sensor surface and they can be readily desorbed during N_2 purging. When stored in typical laboratory atmosphere at 23°C for more than one week, the response current of the K(def)TCP sensor remained unchanged. To demonstrate the sensitivity of K(def)TCP conductivity, water vapour concentration was varied in the range of 0.002–0.011 v/v by controlling the volumetric flow rates of saturated water vapour and N_2 . Figure 3(e) shows the impedance change decreasing with decreasing water concentration. It is worth noting that though other more established nanomaterials, such as carbon nanotubes (CNTs), metal oxides, and conductive polymers, have in some cases shown better sensor performance, for example, a CNT sensor was able to detect 50 ppb of ammonia in a few minutes [36], this is a first study of a new nanomaterial, K(def)TCP, with the potential to enable nanosensor scale up. Nanosensor scale up remains a major barrier against successful nanosensor commercialization.

The mechanism for conductance-based nanowire gas sensing is usually attributed to the change in carrier concentration due to gas molecule adsorption on the

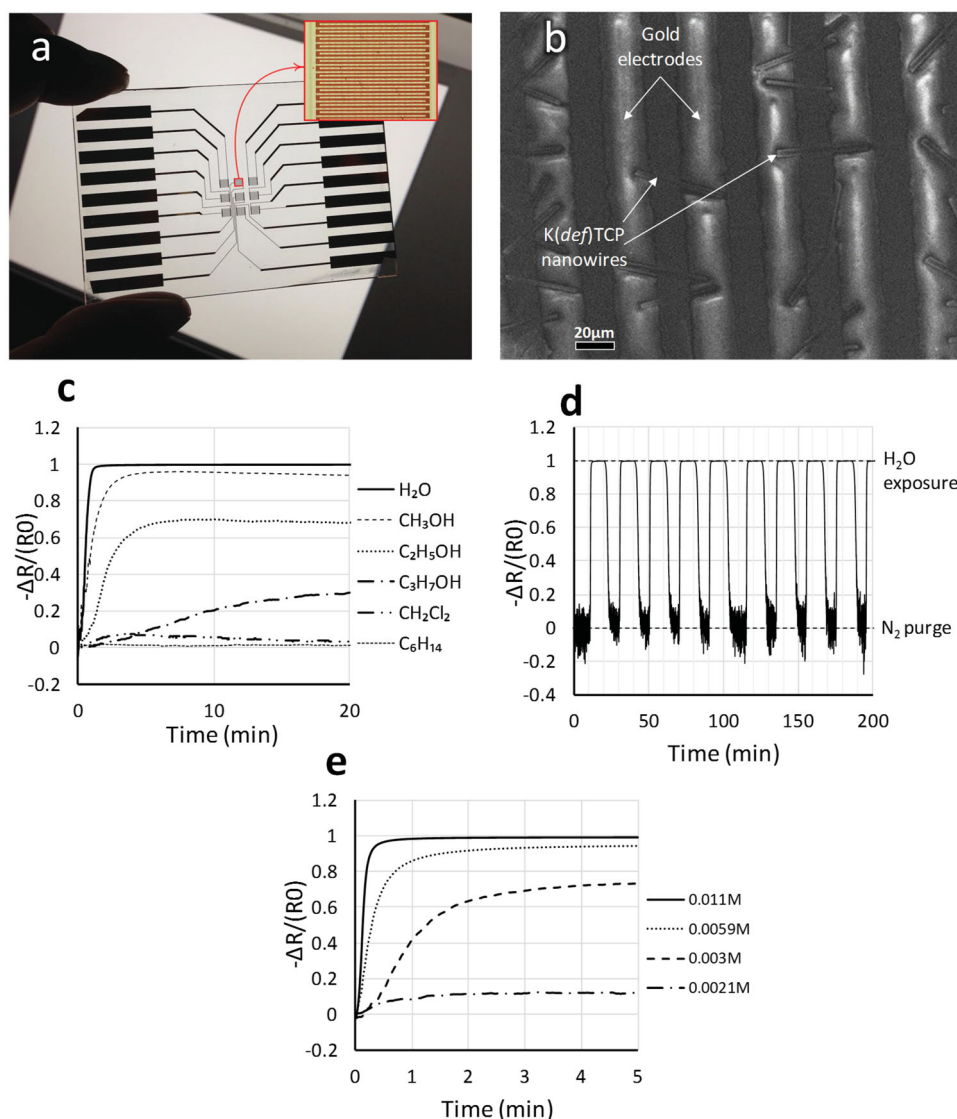


Figure 3. (a) A photo of the comb-like interdigitated lithographical pattern of Cr/Au printed on a glass plate. (b) An SEM photo of K(def)TCP nanowires electrochemically grown on the Cr/Au lithographical pattern as interconnects. (c) Impedance changes of the K(def)TCP sensor when exposed to different vapours. (d) Impedance changes of the K(def)TCP sensor to repeated exposure to water vapour. (e) Impedance changes of the K(def)TCP sensor to different water vapour concentrations.

nanowire surface. Water molecules donate electrons to cause the increase in conductivity of n-type ceramics and decrease in conductivity of p-type ceramics [37,38]. For intrinsic 1-D conductors such as K(def)TCP, the increase in electronic conductivity can be attributed to the general mechanism of surface electron accumulation resulting from the preferential alignment of the water dipoles [37]. Our data show an increase in sensitivity with the dipole moment in analyte molecules, which supports this generic electronic resistive sensing mechanism. Our data show that K(def)TCP sensor becomes saturated when the concentration exceeds 0.01 M (Figure 3(e)), which is different from the linear to exponential response based on the above surface electronic mechanism [39]

or the empirical power-law response of semiconducting oxides to gas partial pressure [40]. We suggest a possible molecular mechanism for this apparent surface-limiting response. Figure 4(a) shows the surface view of a crystal cleaved along the (100) face, which is rich in water molecules. The conductivity of K(def)TCP primarily depends on the Pt–Pt separation distance [29,30]. The planar $[\text{Pt}(\text{CN})_4]^{-1.75}$ group stacks along the *c* axis and is stabilized by the ionic bond between K^+ and CN^{-1} and the H-bond between CN^{-1} and H_2O . The zigzag distribution of the H-bond between CN^{-1} and H_2O causes the zigzag Pt chain configuration (Figure 4(b)). The H-bond changes the $[\text{Pt}(\text{CN})_4]^{-1.75}$ torsion angle, which further increases the Pt–Pt separation distance. We therefore

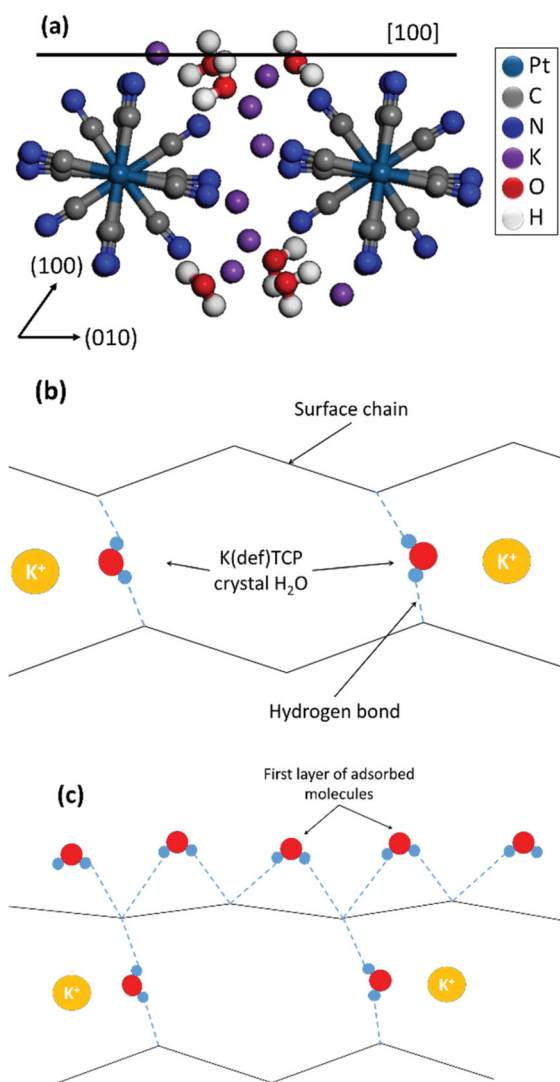


Figure 4. Illustration of the K(def)TCP crystal surface structure (a) and the change in Pt–Pt distortion due to interactions with water molecules adsorbed at the crystal surface (b–c).

hypothesize that adsorbed water molecules compete with lattice water for H bonding with CN^{-1} and K^{+} and this results in a subtle change in the attractive force among Pt chains near the surface to reduce the distortion of the Pt chain and Pt–Pt separation distance (Figure 4(c)). This results in an overall increase in the K(def)TCP nanowire conductivity. Since this effect is only restricted to the adsorbed surface water layer, the outer water layers will have a much weaker interaction with the crystal surface structure and hence the surface-limiting response in the impedance change.

4. Summary and conclusions

In summary, we described the first Krogmann salt nanosensor in which an organic conductor, K(def)TCP,

was directly deposited on the microelectrode substrate using electrocrystallization from an aqueous solution. We have demonstrated a strategy of seed-mediated growth of organic nanowires using nanoparticles as nucleation seeds. The concept can be applied to deposit other types of nanocrystals on lithographical patterns, potentially utilizing the geometry of the pattern itself to direct nanowire deposition. Our ultimate goal is to apply this methodology for integration and manufacturing of nanowire gas sensors.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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