Functional Gels

International Edition: DOI: 10.1002/anie.201507684
German Edition: DOI: 10.1002/ange.201507684

Selective Extraction and In Situ Reduction of Precious Metal Salts from Model Waste To Generate Hybrid Gels with Embedded Electrocatalytic Nanoparticles

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Abstract: *A hydrogel based on 1,3:2,4-dibenzylidenesorbitol (DBS), modified with acyl hydrazides which extracts gold/silver salts from model waste is reported, with preferential uptake of precious heavy metals over other common metals. Reduction of gold/silver salts occurs spontaneously in the gel to yield metal nanoparticles located on the gel nanofibers. High nanoparticle loadings can be achieved, endowing the gel with electrochemical activity. These hybrid gels exhibit higher conductances than gels doped with carbon nanotubes, and can be used to modify electrode surfaces, enhancing electrocatalysis. We reason this simple, industrially and environmentally relevant approach to conducting materials is of considerable significance.*

Hydrogels are attracting attention for a wide range of high-value applications.[1] Low-molecular-weight hydrogels allow molecular-scale information to be programmed-in by simple organic synthesis and then amplified into nanofibers through self-assembly.[2] Self-assembled gels combine a solid-like nanofiber matrix (typically $<1\%$) with a solvent-like gel phase ($>99\%$). The high compatibility with water means these gels have great potential as environmental remediation agents, and a number of reports have described their use as filtration media for water purification. Particular interest has been in systems where ligands displayed on the gel nanofibers form specific interactions with the pollutants, enabling selective removal.[3]

The combined hard/soft properties of hydrogels mean they have potential as interfacial materials between the soft world of biology and the hard world of electronics, and interest has been developing in using polymer hydrogels to achieve this.[4] Supramolecular gels have been less thoroughly explored.[5] Conductive gels can be approached in a number of different ways. The simplest approach to making conductive solid-like networks involves mixing conductive materials, such as carbon nanotubes, graphene, or conjugated polymers, into a gel.[6] In this approach, the gel only acts as a matrix in which the conducting units are suspended, with limited ability to organize them. A second approach assembles gels from conductive organic components that provide the conducting pathways.[7] The final approach templates the formation of conducting systems using self-assembled nanofibers, with the potential advantage of organizing highly conducting materials on the nanoscale.[8] Metal nanoparticles have potential to conduct[8a,b] and have been organized within gels.[9] Of particular interest are systems that work in water, and enable spontaneous in situ nanoparticle formation.[10]

We reasoned that a gel could both selectively remove precious heavy metals from waste water and, if followed by in situ nanoparticle formation, the resulting materials may then also have potential electronic applications. Herein, we describe our success in fusing these concepts, from waste to wealth.

We selected our recently reported hydrogelator, DBS-$CONHNH_2$, based on the industrially-relevant 1,3:2,4-dibenzylidenesorbitol,[11] which forms pH-stable hydrogels by a simple heat-cool cycle (Figure 1). We have already demonstrated the ability of this gel to bind dyes[12] and pharmaceuticals.[13] The sequestration of precious metal ions from water was initially demonstrated by testing uptake from aqueous solutions (10 mM, 2.0 mL) of gold (Au^{3+}) or silver (Ag^{+}) salts added on top of the gel (0.4 % wt/vol) and allowed to diffuse in for 48 h under ambient conditions. Analysis of the supernatant by ICP-MS and/or UV spectroscopy monitored the metal ion uptake. The maximum uptake capacity of the gel was estimated to be as high as 2000 mg g^{-1} (metal:gelator) for Au and 900 mg g^{-1} for Ag, higher than many adsorbents in the literature and competitive with some of the best.[14] The gel began to collapse at its maximum loading capacity (>2000 mg g^{-1}), which was attributed to disruption of fiber-fiber interactions caused by nanoparticle (NP) build-up on the nanofiber network (see below). The gel changed color to

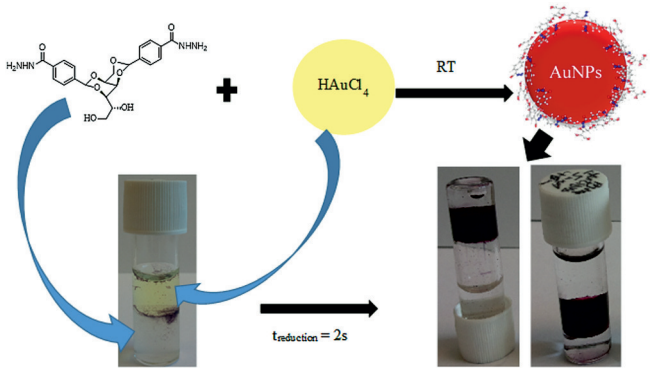

Figure 1. Structure of DBS-$CONHNH_2$ and schematic of gold salt adsorption and in-situ reduction, along with representative photographs of the gels.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507684.

ruby red or yellow as Au^{3+} or Ag^{+} diffused into it (Figure 1), characteristic of the metal NPs capped with hydrazides,[15] suggesting the gel fibers reduce and cap metal NPs in situ within the network.[15] As such, this is a rare example of a gel in which NP formation occurs spontaneously, nucleated by the nanofibers, without external reductant. The Au^{3+} ions changed color within 2 s while Ag^{+} required about 30 min. This could be attributed to their reduction potentials: for Au^{3+} ($Au^{3+} + 3e^{-} \rightarrow Au^{0}$, 1.50 V vs. SHE) and Ag^{+} ($Ag^{+} + e^{-} \rightarrow Ag^{0}$, 0.80 V vs. SHE). Furthermore, the gel even responded to ultra-trace levels (< 5 nM) of Au^{3+} or Ag^{+} in water, giving it potential as a colorimetric sensor for Au^{3+} or Ag^{+} in aqueous waste.

A key review explores green approaches for recovery and re-use of precious metals,[16] and highlights the extraction of such metals from waste electronic and electrical equipment (WEEE). For example, as much as 30 % of total metal content in mobile phones is Au/Ag (other metals include Fe, Cu, Ni, Zn, and Pb).[17] There is also increasing interest in mining small-scale precious metal deposits using leaching,[18] as well as extracting precious metals from non-traditional sources such as sewage sludge.[19] We therefore decided to test the feasibility of using our gel as a low-energy, high selectivity leaching extraction method from mixtures containing Ni and Cu, metals that occur in nature alongside the platinum group elements, and earth-abundant Zn and Fe. An aqueous solution containing Ni^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Pt^{2+}, Pd^{2+}, Au^{3+}, and Ag^{+} (all chlorides, except $AgNO_3$, all 100 mg L^{-1}, 5 mL, 1.64–3.94 μmol) as a model leaching solution was allowed to diffuse into the gel (mass of gelator, 4 mg, 8.4 μmol) for about 48 h under ambient conditions (Figure 2). Dilute HNO_3 (0.1 M) was added to the mixture of metal ions to ensure solubility. The supernatant was analyzed by ICP-MS for residual metals. The gel exhibited higher affinity towards precious metals. The metal ions best extracted were those with the highest reduction potentials (Figure 2), suggesting selectivity is a consequence of the ability of the hydrazide groups to reduce precious metals in situ (see below). Clearly Pd and Pt within gels could also be of use in chemical catalysis, but we focus here on the precious metals Au and Ag. Obviously, it is important to test such systems on real waste, rather than model waste,[16] but this was beyond the scope of our preliminary studies and will be the focus of future work.

To gain insight into the NPs in the gel, we used spectroscopic methods. The composite hydrogel-AuNP or AgNP systems display strong absorption bands in the visible region at approximately $\lambda_{max} = 525$ nm (AuNPs) or $\lambda_{max} = 420$ nm (AgNPs), corresponding to the SPR bands of the metal nanoparticles. FT-IR spectroscopy indicated the bands for C–N, C=O, N–H (bends), N–H, and OH (stretches) at 1333, 1600, 1644, 3178, and 3315 cm^{-1} shifted by 9, 15, 46, 48, and 90 cm^{-1}, respectively, when Au^{3+} or Ag^{+} ions were adsorbed. It can therefore be inferred that the metals interact directly with the gel nanofibers. Using XPS, the C1s and O1s peaks were shifted in the presence of Au. Most significantly, however, the N1s peak was broadened, potentially indicative of strong interactions between N and Au, giving a variety of environments. The Au4f binding energies (BEs) were 84 and 88 eV, corresponding to $4f_{7/2}$ and $4f_{5/2}$ in the Au^{0} oxidation state with a spin–orbit splitting (SOS) of 4 eV; no peaks corresponding to Au^{3+} were observed, supporting complete Au^{0} nanoparticle formation. In the presence of Ag, there were also changes to C1s and O1s, in particular the O1s peak corresponding to C=O. There was a very significant change to N1s (but no broadening), supporting N–Ag interactions. The Ag3d peaks at BEs of 368.2 and 374.4 eV correspond to Ag^{0}, suggesting reduction of Ag^{+} to Ag^{0}. No Ag^{+} was observed.

Transmission electron microscopy (TEM; Figure 3) indicated NP diameters of approximately 5.0 and 10.0 nm for AuNPs and AgNPs, respectively (see the Supporting Information). For Au, the NPs were found mainly (> 90 %) on the gel fibers rather than in solvent pockets within the gel-network. The imaging was done both on unstained and stained xerogels, to improve the contrast on the nanofibers, but some NPs appeared to be washed off after staining. For AgNPs, almost all (> 99 %) were imaged on the network. NP organization has been previously reported as a consequence of ligand–metal interactions.[9,20] We propose that localization of NPs on nanofibers is due to interactions between the hydrazide-functionalized gel fibers and metal ions, leading to their reduction on the periphery of the nanofibers.

We determined the impact of NPs on gel thermal stability (T_{gel}) using simple reproducible tube-inversion methodology. There was no obvious change in the NP color on heating the gel-NP hybrid. Moreover, the T_{gel} increased from approximately 65 °C to 87 °C on increasing the concentration of Au^{3+} (Supporting Information). Such an improvement has previ-

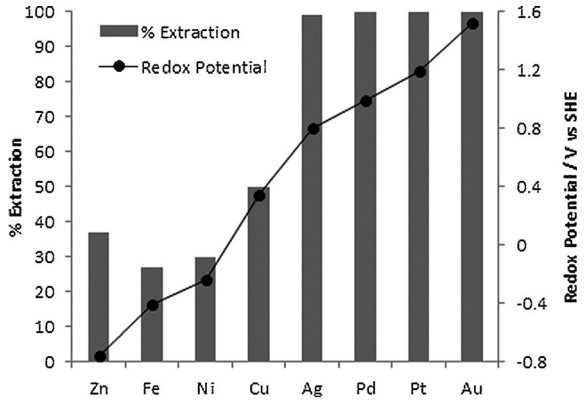

Figure 2. Percentage metal ion recovery from mixed aqueous solutions by DBS-$CONHNH_2$ hydrogel (left axis) and redox potentials of the metals (right axis).

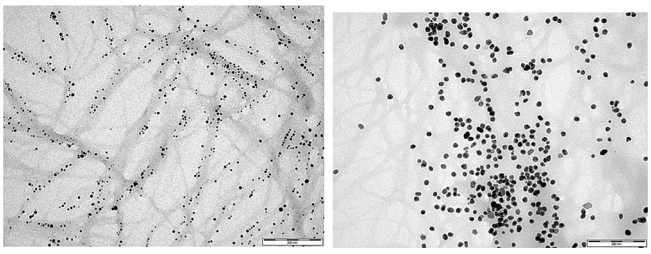

Figure 3. Transmission electron microscopy (TEM) images of gold (left) and silver (right) nanoparticles as formed in situ within the DBS-$CONHNH_2$ hydrogel. Scale bars = 200 nm.

ously been reported by Bhattacharya et al.,[21] and it was suggested that AuNPs may help crosslink the gel fibers. Clearly the nanofibers prevent uncontrolled aggregation of Au^0 or Ag^0 during spontaneous in situ reduction. We further probed the stability of these hybrid materials to external influences using UV/Vis spectroscopy to monitor the NP SPR band. The ambient pH was adjusted between pH 2 and 12 with 0.1 M HCl and 0.1 M NaOH, but the SPR bands of the NPs in the hydrogel remained constant, suggesting a high degree of pH-tolerance of both gel fibers and metal NPs. The AuNPs and AgNPs also remained stable under ambient conditions over a period of 90 days.

We then wanted to study the electronic properties of these gels, reasoning that since the AuNPs form on the DBS gel fibers, our material would maintain NP stability and integrity during electrochemical applications. In their own right, supramolecular gels are relatively weak and difficult to handle/manipulate. To create a gel which could be incorporated into devices, we mixed self-assembling DBS-$CONHNH_2$ with agarose polymer hydrogel to create a hybrid hydrogel (dual-network gel), an effective strategy for making self-assembled gels more robust.[22] A simple heat–cool cycle led to the formation of the hybrid hydrogel; NP formation was wholly analogous to that observed in DBS-$CONHNH_2$ alone.

To probe the electronic performance of these hybrid materials, we initially measured conductance. The hydrogels were made in a mould and extruded, providing hydrogels with reproducible dimensions. These gel blocks were suspended in solutions of Au^{3+} or Ag^+, and metal ion incorporation and in situ reduction occurred to yield NPs. We constructed graphite block electrodes glued to a glass slab, separated by a fixed distances, such that they could accommodate various gel block sizes (Ø = 0.5 cm–1.0 cm). After careful calibration, a block of the gel was inserted into the space between the two graphite rods, and we then determined conductances of nanogel-AuNP, nanogel-AgNP, nanogel alone (negative control), and nanogel doped with single-walled carbon nanotubes (SWNTs; positive control). Both nanoparticles and SWNTs enhance conductance (Figure 4). Given that TEM showed the NPs within DBS-$CONHNH_2$ gels to be 5–10 nm and located on gel fibers rather than in solvent pockets, we assume that they will not diffuse through the gel. Rather, we interpret the enhanced conductivity of gel-AuNPs as arising from a conductance mechanism similar to that in metalloproteins containing electron-transfer chains of redox-active iron–sulfur, heme, or Cu centers where electrons are envisaged to tunnel through the protein polymer matrix.[23] The blocks of nanogel-nanoparticle composites were also air-dried for about 3 h until 30% of the water was lost. Conductance increased significantly, more so for the systems incorporating nanoparticles than those with SWNTs (Figure 4). Although there are many nanofibers in the wet hydrogel, they are highly solvated and therefore have relatively few contacts, limiting conductivity. We propose that drying increases network connectivity, decreasing the distance between NPs and increasing conductance. This effect will be less important for SWNTs than for nanoparticles because SWNTs already have extended conduction pathways, whereas electron "hopping" mechanisms between metal sites are known to be highly dependent on separation distances.[23]

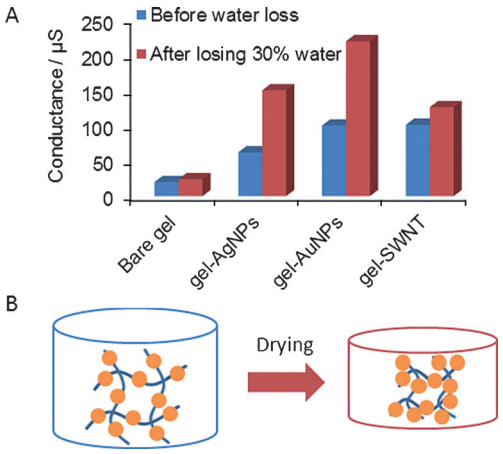

Figure 4. A) Conductances of hybrid hydrogels incorporating AuNPs and AgNPs compared against native hybrid hydrogel and hybrid hydrogel incorporating SWNTs. Gel blocks were 0.80 cm in diameter and after removal of 30% of water by drying ca. 0.68 cm. B) Cartoon of effect of gel drying on close-packing of gel morphology and embedded nanoparticles.

As well as determining bulk conductance, we made a preliminary exploration of the potential of these materials for electrode modification. In fuel cell applications, carbon electrodes have been used as cathodes for O_2 reduction.[24] However, such electrodes are poor electrocatalysts. Thus, deposition of nanoparticles has been used to activate the carbon.[25] Even though electrochemical deposition and adsorption are commonly employed for depositing gold nanoparticles onto electrodes, limitations such as (i) formation of bulk gold and (ii) leaching of nanoparticles into electrolyte remain. We reasoned that our hybrid gels could effectively wire NPs onto the electrode through their inherent nanofibrillar networks, whilst maintaining NP stability and integrity during use. Our gel networks transform planar carbon supports into porous, solvated, 3D electrochemically-active surfaces, overcoming traditional issues with solvent access. Reports of this approach are scarce except for some polymer gels.[26]

We generated our AuNP hybrid nanogel as described above, and removed any traces of unreacted Au^{3+} by submerging in deionized water (200 mL) for 2 h and replacing the water until leaching was no longer observed. It is essential that free Au^{3+} ions are completely removed prior to electrocatalysis, or they will diffuse into the electrolyte or electroplate onto the electrode surface. No leaching of AuNPs was observed, confirming their trapping within the gel. The gel-catalyzed O_2 reduction was investigated using cyclic voltammetry, scanning in air between −0.25 V and 0.15 V at 20 mV s^{-1} for 5 cycles. The bare carbon rod showed a typical non-Faradaic, capacitive current response (Figure 5, red line). The electrode modified with just hybrid hydrogel produced a different CV (Figure 5, green line), with clear oxidative (positive) current at potentials more positive than +0.2 V versus SCE (equivalent to +0.42 V vs. SHE). We attribute this oxidation to the gelator since the observed CV is similar

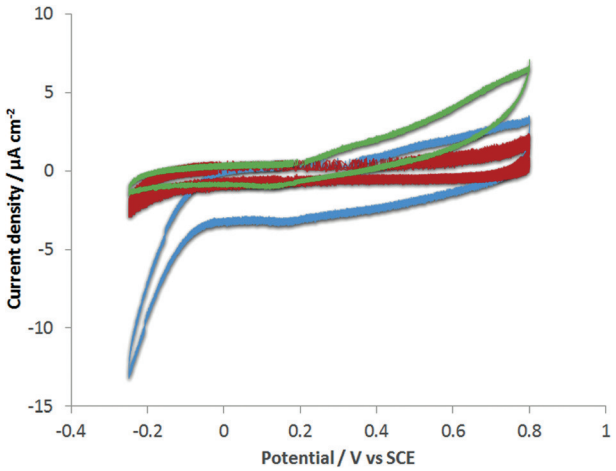

Figure 5. Cyclic voltammetry of bare carbon rod electrode (red) and carbon rod electrodes modified with hybrid hydrogel both in the absence (green) and presence (blue) of AuNPs illustrating the relative currents associated with oxygen reduction.

to that of native DBS gel.[27] This helps explain the correlation between % metal uptake and redox potential (Figure 2): the gel can only reduce metal ions with a midpoint redox potential $>+0.42$ V versus SHE. When the hybrid hydrogel loaded with AuNPs was used (Figure 5, blue line) a large reductive current was observed at potentials more negative than -0.2 V versus SCE. This was attributed to Au-catalyzed O_2 reduction. Therefore, the NPs embedded in this gel enable communication with a carbon electrode.

We report a simple, pH-stable hydrogel which extracts precious metal ions with a degree of selectivity from metal-ion mixtures typical of leaching solutions. These ions are reduced in situ to form Au or Ag nanoparticles with a degree of organization on the gel nanofibers. These hybrid materials are conductive as a result of the embedded nanoparticles, and can operate as modified electrodes. They therefore have potential high value applications in nanoelectronics. Conductive nanostructured nanocomposites may be useful to bridge the soft matter world of biology and the hard matter world of electronics. In summary, this system demonstrates how, in principle, we can simply and in one step, convert waste to wealth.

Acknowledgements

This work was supported by a Wild Fund Scholarship to B.O.O. and White Rose funding for S.K.S. We thank Darren Philip (BDC, University of York) for running ICP-MS samples and Meg Stark (Biology Technology Facility, University of York) for SEM/TEM. XPS spectra were measured by Kellye Curtis at Leeds EPSRC Nanoscience and Nanotechnology Facility (LENNF).

Keywords: electrochemistry · hydrogels · nanoparticles · self-assembly

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 183–187
Angew. Chem. **2016**, *128*, 191–195

[1] a) A. R. Hirst, B. Escuder, J. F. Miravet, D. K. Smith, *Angew. Chem. Int. Ed.* **2008**, *47*, 8002–8018; *Angew. Chem.* **2008**, *120*, 8122–8139; b) S. Banerjee, R. K. Das, U. Maitra, *J. Mater. Chem.* **2009**, *19*, 6649–6687; c) A. Dawn, T. Shiraki, S. Haraguchi, S.-i. Tamaru, S. Shinkai, *Chem. Asian J.* **2011**, *6*, 266–282.

[2] a) P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133–3160; b) J. W. Steed, *Chem. Commun.* **2011**, *47*, 1379–1383; c) R. G. Weiss, *J. Am. Chem. Soc.* **2014**, *136*, 7519–7530.

[3] a) S. Ray, A. K. Das, A. Banerjee, *Chem. Mater.* **2007**, *19*, 1633–1639; b) S. Debnath, A. Shome, S. Dutta, P. K. Das, *Chem. Eur. J.* **2008**, *14*, 6870–6881; c) B. Adhikari, G. Palui, A. Banerjee, *Soft Matter* **2009**, *5*, 3452–3460; d) S. Dutta, D. Das, A. Dasgupta, P. K. Das, *Chem. Eur. J.* **2010**, *16*, 1493–1505; e) F. Rodríguez-Llansola, B. Escuder, J. F. Miravet, D. Hermida-Merino, I. W. Hamley, C. J. Cardin, W. Hayes, *Chem. Commun.* **2010**, *46*, 7960–7962; f) K. N. King, A. J. McNeil, *Chem. Commun.* **2010**, *46*, 3511–3513; g) D. M. Wood, B. W. Greenland, A. L. Acton, F. Rodríguez-Llansola, C. A. Murray, C. J. Cardin, J. F. Miravet, B. Escuder, I. W. Hamley, W. Hayes, *Chem. Eur. J.* **2012**, *18*, 2692–2699; h) P. J. Knerr, M. C. Branco, R. Nagarkar, D. J. Pochan, J. P. Schneider, *J. Mater. Chem.* **2012**, *22*, 1352–1357; i) P. K. Sukul, S. Malik, *RSC Adv.* **2013**, *3*, 1902–1915; j) K. K. Carter, H. B. Rycenga, A. J. McNeil, *Langmuir* **2014**, *30*, 3522–3527; k) S. Sengupta, R. Mondal, *J. Mater. Chem.* **2014**, *2*, 16373–16377.

[4] a) R. A. Green, S. Baek, L. A. Poole-Warren, P. J. Martens, *Sci. Technol. Adv. Mater.* **2010**, *11*, 014107; b) Y. Zhao, B. Liu, L. Pan, G. Yu, *Energy Environ. Sci.* **2013**, *6*, 2856–2870; c) *Biointerfaces: Where Material Meets Biology* (Eds.: D. W. Huntmacher, W. Chrzanowski), RSC, Cambridge, **2015**.

[5] a) D. B. Amabilino, J. Puigmartí-Luis, *Soft Matter* **2010**, *6*, 1605–1612; b) D. Das, T. Kar, P. K. Das, *Soft Matter* **2012**, *8*, 2348–2365; c) J. Puigmartí-Luis, D. B. Amabilino, in *Functional Molecular Gels* (Eds.: B. Escuder, J. F. Miravet), RSC, Cambridge, **2014**, pp. 195–254.

[6] a) S. Srinivasan, S. S. Babu, V. K. Praveen, A. Ajayaghosh, *Angew. Chem. Int. Ed.* **2008**, *47*, 5746–5749; *Angew. Chem.* **2008**, *120*, 5830–5833; b) S. K. Samanta, A. Pal, S. Bhattacharya, C. N. R. Rao, *J. Mater. Chem.* **2010**, *20*, 6881–6890; c) S. K. Samanta, K. S. Subrahmanyam, S. Bhattacharya, C. N. R. Rao, *Chem. Eur. J.* **2012**, *18*, 2890–2901; d) S. Roy, A. Baral, A. Banerjee, *Chem. Eur. J.* **2013**, *19*, 14950–14957; e) P. Chakraborty, P. Bairi, S. Mondal, A. K. Nandi, *J. Phys. Chem. B* **2014**, *118*, 13969–13980; f) R. Y. Kuwahara, H. Yamagishi, K. Hashimoto, S. Tamesue, T. Yamachi, N. Tsubokawa, *Polymer* **2015**, *61*, 99–107.

[7] For reviews see: a) S. S. Babu, S. Prasanthkumar, A. Ajayaghosh, *Angew. Chem. Int. Ed.* **2012**, *51*, 1766–1776; *Angew. Chem.* **2012**, *124*, 1800–1810; b) S. S. Babu, V. K. Praveen, A. Ajayaghosh, *Chem. Rev.* **2014**, *114*, 1973–2129.

[8] a) J. Puigmartí-Luis, A. Pérez del Pino, E. Laukhina, J. Esquena, V. Laukhin, C. Rovira, J. Vidal-Gancedo, A. G. Kaneras, R. J. Nichols, M. Brust, D. B. Amabilino, *Angew. Chem. Int. Ed.* **2008**, *47*, 1861–1865; *Angew. Chem.* **2008**, *120*, 1887–1891; b) E. Taboada, L. N. Feldborg, A. Pérez del Pino, A. Roig, D. B. Amabilino, J. Puigmartí-Luis, *Soft Matter* **2011**, *7*, 2755–2761; c) D. Canevet, A. Perez del Pino, D. B. Amabilino, M. Salle, *Nanoscale* **2011**, *3*, 2898–2902; d) S. Roy, A. Banerjee, *RSC Adv.* **2012**, *2*, 2105–2111; e) B. Lv, X. Shi, X. Ma, Z. Zhang, K. Wang, *New J. Chem.* **2015**, *39*, 349–354.

[9] a) M. Kimura, S. Kobayashi, T. Kuroda, K. Hanabusa, H. Shirai, *Adv. Mater.* **2004**, *16*, 335–338; b) L.-s. Li, S. I. Stupp, *Angew. Chem. Int. Ed.* **2005**, *44*, 1833–1836; *Angew. Chem.* **2005**, *117*, 1867–1870; c) J. van Herrikhuyzen, S. J. George, M. R. J. Vos,

N. A. J. M. Sommerdijk, A. Ajayaghosh, S. C. J. Meskers, A. P. H. J. Schenning, *Angew. Chem. Int. Ed.* **2007**, *46*, 1825 – 1828; *Angew. Chem.* **2007**, *119*, 1857 – 1860; d) V. R. R. Kumar, V. Sajini, T. S. Sreeprasad, V. K. Praveen, A. Ajayaghosh, T. Pradeep, *Chem. Asian J.* **2009**, *4*, 840 – 848; e) I. A. Coates, D. K. Smith, *J. Mater. Chem.* **2010**, *20*, 6696 – 6702.

[10] a) P. K. Vemula, G. John, *Chem. Commun.* **2006**, 2218 – 2220; b) P. K. Vemula, U. Aslam, V. A. Mallia, G. John, *Chem. Mater.* **2007**, *19*, 138 – 140; c) R. N. Mitra, P. K. Das, *J. Phys. Chem. C* **2008**, *112*, 8159 – 8166; d) S. Dutta, A. Shome, T. Kar, P. K. Das, *Langmuir* **2011**, *27*, 5000 – 5008; e) J.-S. Shen, Y.-L. Chen, J.-L. Huang, J.-D. Chen, C. Zhao, Y.-Q. Zheng, T. Yu, Y. Yang, H.-W. Zhang, *Soft Matter* **2013**, *9*, 2017 – 2023.

[11] B. O. Okesola, V. M. P. Vieira, D. J. Cornwell, N. K. Whitelaw, D. K. Smith, *Soft Matter* **2015**, *11*, 4768 – 4787.

[12] B. O. Okesola, D. K. Smith, *Chem. Commun.* **2013**, *49*, 11164 – 11166.

[13] E. J. Howe, B. O. Okesola, D. K. Smith, *Chem. Commun.* **2015**, *51*, 7451 – 7454.

[14] A. Muñoz García, A. J. Hunt, V. L. Budarin, H. L. Parker, P. S. Shuttleworth, G. J. Ellis, J. H. Clark, *Green Chem.* **2015**, *17*, 2146 – 2149.

[15] a) Y. Sun, Y. Yao, C.-G. Yan, Y. Han, M. Shen, *ACS Nano* **2010**, *4*, 2129 – 2141; b) D. J. Vyas, B. A. Makwana, H. S. Gupte, K. D. Bhatt, V. K. Jain, *J. Nanosci. Nanotechnol.* **2012**, *12*, 3781 – 3787; c) S. Malathi, T. Ezhilarasu, T. Abiraman, S. Balasubramanian, *Carbohydr. Polym.* **2014**, *111*, 734 – 743.

[16] J. R. Dodson, H. L. Parker, A. Muñoz-Garcia, A. Hicken, K. Asemave, T. J. Farmer, H. He, J. H. Clark, A. J. Hunt, *Green Chem.* **2015**, *17*, 1951 – 1965.

[17] Y. J. Park, D. J. Fray, *J. Hazard. Mater.* **2009**, *164*, 1152 – 1158.

[18] C. N. Mpinga, J. J. Eksteen, C. Aldrich, L. Dyer, *Min. Eng.* **2015**, *78*, 93 – 113.

[19] P. Westerhoff, S. Lee, Y. Yang, G. W. Gordon, K. Hristovski, R. U. Halden, P. Herckes, *Environ. Sci. Technol.* **2015**, *49*, 9479 – 9488.

[20] T. Kar, P. K. Das, in *Functional Molecular Gels* (Eds.: B. Escuder, J. F. Miravet), RSC, Cambridge, **2014**, pp. 255 – 303.

[21] S. Bhattacharya, A. Srivastava, A. Pal, *Angew. Chem. Int. Ed.* **2006**, *45*, 2934 – 2937; *Angew. Chem.* **2006**, *118*, 3000 – 3003.

[22] For a review: a) D. J. Cornwell, D. K. Smith, *Mater. Horiz.* **2015**, *2*, 279 – 293; For examples: b) J. Wang, Z. Wang, J. Gao, L. Wang, Z. Yang, D. Kong, Z. Yang, *J. Mater. Chem.* **2009**, *19*, 7892 – 7896; c) D. J. Cornwell, B. O. Okesola, D. K. Smith, *Soft Matter* **2013**, *9*, 8730 – 8736.

[23] C. C. Page, C. C. Moser, X. Chen, P. L. Dutton, *Nature* **1999**, *402*, 47 – 52.

[24] G.-P. Hao, F. Hippauf, M. Oschatz, F. M. Wisser, A. Leifert, W. Nickel, N. Mohamed-Noriega, Z. Zheng, S. Kaskel, *ACS Nano* **2014**, *8*, 7138 – 7146.

[25] N. J. Ronkainen, H. B. Halsall, W. R. Heineman, *Chem. Soc. Rev.* **2010**, *39*, 1747 – 1763.

[26] For a review see: U. A. Argueta-Robles, A. J. Woolley, L. A. Poole-Warren, N. H. Lovell, R. A. Green, *Front. Neuroeng.* **2014**, *7*, 15.

[27] T. M. Nahir, Y.-J. Qiu, J. L. Williams, *Electroanalysis* **1994**, *6*, 972 – 975.

Received: August 17, 2015
Revised: October 13, 2015
Published online: November 9, 2015

