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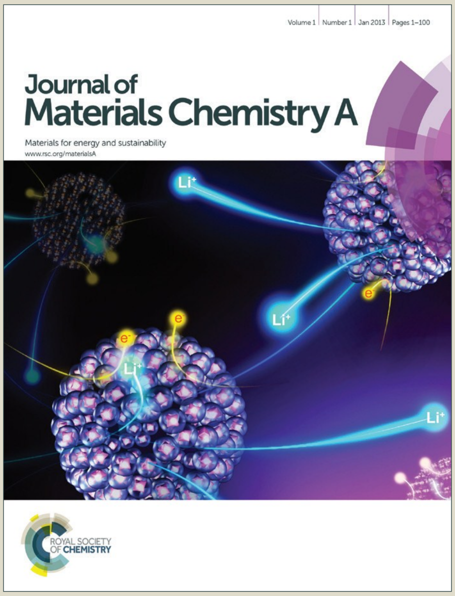

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Plug and Play Synthesis of an Organic/Inorganic Hybrid Electrode with Adjustable Porosity: Redox-Active Organosilica Confined in Mesoporous Carbon

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M. Luka,[a] S. Karreman[a] and S. Polarz*[a]

The construction of advanced materials for electrochemistry (e.g. supercapacitors) using organic, redoxactive molecules like benzoquinone is attractive due to their defined properties and high reversibility. The preparation of a unique nanohybrid electrode was achieved via a novel silsesquioxane sol-gel precursor within minutes and at low cost, basically allowing for mass-production.

Redox-active solids with accessible porosity are currently in the focus of materials research due to numerous and prevailing applications like in sensing, as corrosion inhibitors, in organic synthesis, heterogeneous catalysis and last but not least for electrochemical energy storage e.g. in the form of supercapacitors.[1, 2] Examples include nanostructured transition metal oxides like RuO_2 or MnO_2.[3] Although these oxides often have high capacities and seemingly high structural stability they nevertheless may dissolve upon electrochemical cycling. Additionally their composition is often very complex, sensitive already to small changes in crystallinity or hydratization, which leads to problems with regards to reproducibility and defined redox properties.[3] Alternatively, organic compounds like redox active polymers can be applied,[4] like polyaniline[5, 6] or polymers with redox active groups (e.g. ferrocenes, etc.)[7-10] attached to their backbone. However, redox active polymers often lack in chemical and structural stability. They may even change their conformation by changing redox states, which impedes reversibility and durability.

Nevertheless, it still appears worth exploiting organic entities known for their advantageous redox features, but one requires a matrix with higher structural and chemical stability. A powerful method to equip surfaces with organic functionalities is the generation of nanoporous, organic- inorganic hybrid materials as nicely discussed by Sanchez et al. in a recent review article.[11] For instance, one can start from mesoporous silica followed and proceed with post-functionalization of silanols (Si-OH) with organically modified sol-gel precursors, e.g. $R\text{-}Si(OEt)_3$. Few examples exist for such materials containing surface-bound, redox active entities like e.g. with ferrocenes, bipyridinium compounds or phenothiazinium derivates,[12-14] and also a hydroquinone derivate.[15] There are several problems associated with the latter approach. Only the surface of the silica is modified, often with a monolayer, which is why there one can observe only low electrochemical capacity. Furthermore, for making an electrical contact to the surface groups a material needs to be introduced into the pores.[16] Therefore, we will not go the way preparing a porous organosilica first and then infiltrating it with a conducting species. Instead a suitable silsesquioxane precursor (1) should be infiltrated into the porous electrode directly, e.g. porous carbon materials (see **scheme 1**), followed by fixation of the functional entity via sol-gel/ siloxane formation.

Furthermore, it is known that high-surface area materials with much higher density of functional organic groups can be achieved, when bis-sylilated precursors, $(EtO)_3Si\text{-}R\text{-}Si(OEt)_3$, are used for the generation of so-called PMOs (periodically ordered mesoporous organosilicas).[17, 18] Due to all of the arguments given above, we first aim at a feasible synthesis for the novel sol-gel precursor $(EtO)_3Si\text{-}R\text{-}Si(OEt)_3$ with $R \cong$ a bridging benzoquinone derivative. Benzoquinone was selected, because it certainly is the most known and best-studied redox-active organic molecule, which can be reduced and oxidized reversibly by chemical or electrochemical methods.[19]

The desired molecular sol-gel precursor (**1**) was obtained from the reaction of 2,3,5,6-tetrachloro-para-benzoquinone (chloranil) with 3-amino-propyltriethoxysilane; see also the experimental part given in the electronic supplementary information S-1. The success of the synthesis was proven by electron-spray ionization mass spectrometry (ESI-MS) shown in S-2. The reaction is imaginable simple and the raw product can be obtained directly in >99% yield, for what reason further purification is not necessary. Purity could be confirmed by ^1H-, ^{13}C-, ^{29}Si-NMR and elemental analysis (CHN). As a result the

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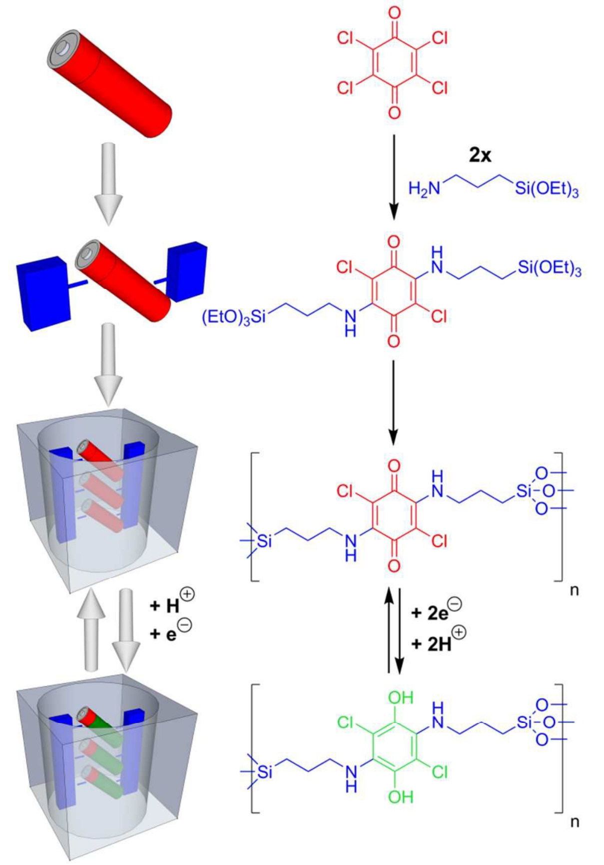
[a] *Department of Chemistry, University of Konstanz, 78457 Konstanz, Germany.*

Electronic Supplementary Information (ESI) available: (S-1): Experimental section for (1) and "Silylanil-1@mc"; (S-2-9): Additional analytical data for (1) and "Silylanil-1@mc". (S-10): Analytical data for Silylanil-1@Tropical® Coco Carb.]. See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis scheme for a new redox active organo-silica inside mesoporous carbon. It involves the synthesis of a new redoxactive precursor (1) and the subsequent incorporation into mesoporous carbon (Silylanil-1@mc).

formation of (**1**) and isolation of the product can be achieved in less than 5 min (see S-3). In order to examine the redox properties of the molecular species (**1**) cyclic voltammetry (CV) measurements are performed (for details see SI-1) and are shown in **Fig. 1**. Two redox waves with full reversibility can be observed corresponding to two single-electron steps. At the first reduction step at a potential of -1320mV (vs. ferrocene(Fc)) the radical anion is formed while the molecule is fully reduced at a potential of -1630mV (vs. Fc) accompanies by a change of color of the precursor from purple to yellow. The reduction potential is lowered in comparison to chloranil and pure p-benzoquinone, which is in agreement with the known effect of electron donating groups.[20] It should also be mentioned that the remaining chlorine and secondary amine groups may enable a subsequent functionalization of (**1**) in the future to obtain sol-gel precursors with adjustable redox transitions. In conclusion, (**1**) is a promising candidate for the preparation of redox active organosilica materials.

Next, (**1**) should be infiltrated into mesoporous carbon (MC) as a host (prepared according to literature recipes)[21]. Sucrose is used as a carbon source, which is carbonized inside mesoporous silica as a template. After dissolution of the silica under basic conditions, one obtains the MC. Some key analytical data of MC are shown in S-4.

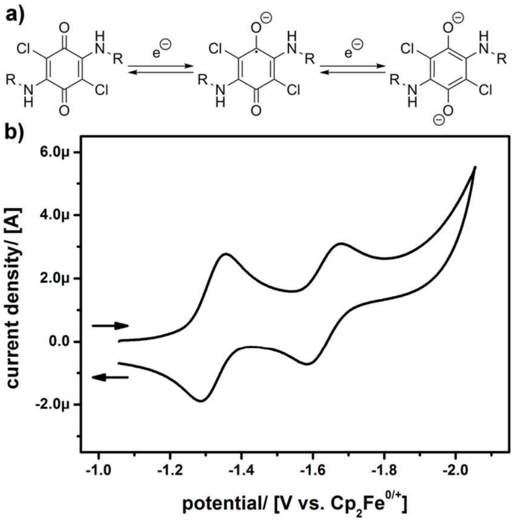


Figure 1: a) Redox reaction of Silylanil-1 including two single-electron steps ($R=CH_2CH_2CH_2Si(OEt)_3$). **b)** Cyclic voltammetry data of Silylanil-1 measured in CH_2Cl_2 at a scan rate of 100mV/s.

Because (**1**) in its pure form is solid, infiltration can either be done using a solution, or more preferably in undiluted form using a melt. Because at this point the precursor is hydrophobic in nature, it is compatible with a non-polar environment. Differential scanning calorimetry (DSC) indicates that the latter is possible. The compound has a melting point of ≈ 98°C and can be heated up reversibly to temperatures of at least 125°C without decomposition (see S-5). Next, the precursor inside the pores is hydrolyzed in an aqueous hydrochloric atmosphere at elevated temperatures. The resulting silanol groups are inducing an additional hydrophilic character in the pores. The acidic atmosphere also induces polycondensation and formation of the organosilica $(C_{12}H_{20}N_2Cl_2O_2)SiO_3$ network inside the channels of MC (see scheme 1). The resulting nanohybrid will be denoted Silylanil-1@mc hereafter. The chemical nature of Silylanil-1@mc was investigated in detail using ^{13}C solid-state NMR and FT-IR spectroscopies (see S-7). It is seen that the spectrum of the product is an exact superposition of the signals of the carbon matrix and the signals of the precursor. Thus, it is proven that the benzoquinone entity has remained intact. A further advantage of the silica formation combined with the covalent linkage to the benzoquinone unit is that any leaching of the organic constituent can be prevented as shown in S-6.

It is also very important that pore-filling can be controlled precisely. If there is too much precursor, MC might become buried in an insulating organosilica matrix, which is highly undesired. It is expected that maximum capacity can only be reached, when the pores are fully filled with the organosilica. For some applications it could also be desirable that there is still some defined porosity remaining, represented by only partially filled pores. The amount of precursor (**1**) (defined as its relative amount in the composite Q(1)) was successively increased, and the remaining pore-volume was checked using

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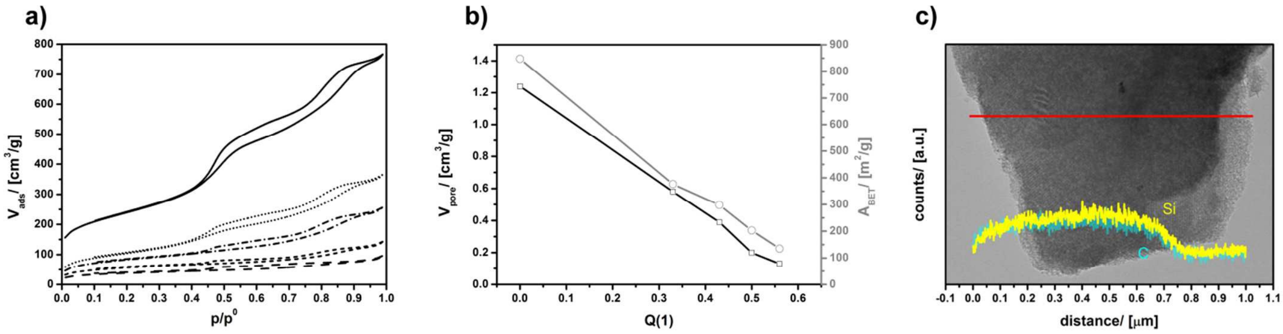

Figure 2: (a) N_2-physisorption data of materials with different mass ratios of (1):m_{ges} = Q(1): Q(1) = 0 (continuous line), = 0.33 (dotted line), = 0.43 (dashed/dotted line), = 0.50 (shortly dashed line) and = 0.55 (dashed line). (b) V_{pore} and A_{BET} in dependence of Q(1). (c) HR-TEM EDX-Linescan data of Silylanil-1@mc.

N_2 physisorption analysis shown in **Fig. 2**. Starting from the empty MC the adsorbed volume decreases the more precursor has been infiltrated. It can be seen that there is an almost linear decrease of pore-volume V_{pore} and surface area A_{BET} the more the pores are filled (see also S-8). The pore diameter is also decreased indicating a layer-by-layer infiltration of the precursor. It was checked using transmission electron microscopy (TEM; see also S-7v) combined with energy-dispersive X-ray spectroscopy (EDX) line scans (see Fig. 2c) that there is no organosilica outside the MC pores, and that Si and C are homogeneously distributed.

A question of imminent importance is, if the benzoquinone groups are still redox-active, and that despite the insulating character of the organosilica they can be addressed electrochemically via the MC. The electrochemical behavior of Silylanil-1@mc has thus been studied using cyclic voltammetry (vs. a Ag/AgCl (3M NaCl) reference electrode) (**Fig. 3)** and is compared to empty MC. Pure MC shows a typical curve for a material developing double layer capacitance only. As expected there is a pronounced effect due to the presence of the redox active organosilica in Silylanil-1@mc. Capacities (area of the CV curves) are magnitudes larger and one can clearly identify redox transitions at -0.28V and -0.46V (shoulder) analogous to the precursor (1). Silylanil-1@mc reaches a capacity of 170F/$g_{organosilica}$ at a scan rate of 5mV/s. The theoretical limit considering exclusively the charges released by the quinones redox reaction and a composite ratio of Q(1)=0.5 is a capacitance of 260F/g. Charge and discharge curves were also acquired and are shown in S-9, and also the internal resistance (ESR) was measured (see S-10). In addition to cyclic voltammetry measurements performed at different scan rates, it can be seen that the redox reactions of the benzoquinone molecules bound to the carbon surface is occurring fast.

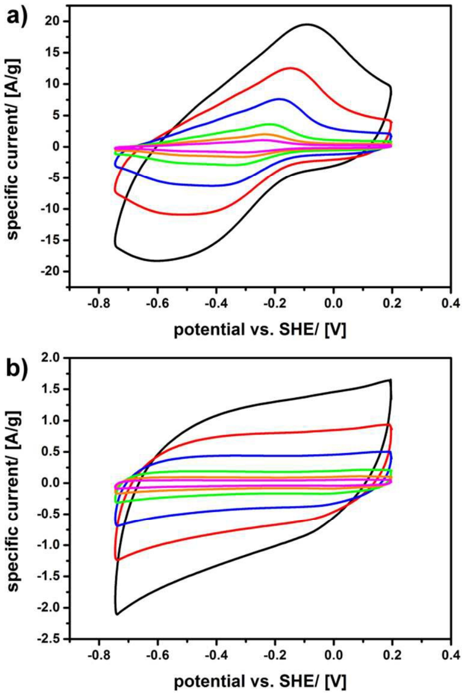

Figure 3: Cyclic voltammetry data of Silylanil-1@mc (a) and MC (b) with scan rates of: black: 200mV/s; red: 100mV/s; blue: 50mV/s; green: 20mV/s; orange: 10mV/s; magenta: 5mV/s.

Whereas the reported capacities are currently inferior to highest values reported in the literature for competitive systems like metal oxides[21] and materials optimization will be necessary in the future, the current approach features numerous advantages.

The materials presented here can be provided very fast and only highly available compounds are used. Our approach can be transferred to any porous electrode. For instance, instead of the ordered mesoporous carbon materials discussed above, one can also use commercially available porous carbon materials like “Tropical® Coco Carb” as shown for proof of concept in S-11. As a result, the costs for the generation of our supercapacitor material can be as low as ≈ 0.25€ per gram.

Conclusions

We could show in the current paper that well established redox-active, low-molecular weight compounds known from organic chemistry like benzoquinone can be made accessible for applications e.g. as a supercapacitor using organosilane chemistry. We prepared a new, redox-active, bis-silylated sol-gel precursor, which can be immobilized and converted into a stable organosilica network in any porous electrode. The material has been characterized in detail and in particular its electrochemical properties were reported. We showed that the target materials are imaginable cheap and can be prepared most easily - the precursor itself even within minutes! Therefore our results open the way towards a direct technological implementation and a potential mass-production in industrial context.

Notes and references

AUTHOR INFORMATION
Corresponding Author
*Email: Sebastian.Polarz@uni-konstanz.de

Notes
The authors declare no competing financial interest.

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A hybrid, supercapacitor electrode with adjustable porosity was obtained via preparation of a redox-active organosilica in mesoporous carbon hosts.