

Synthesis of carbon quantum dots in a Nafion matrix: precursor effect on the ion transport properties

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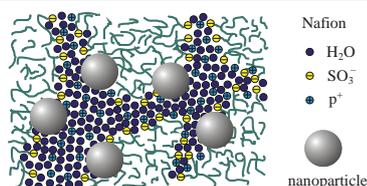
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Carbon quantum dots have been prepared in a Nafion[®] matrix via the hydrothermal treatment of organic precursors, and the swelling and ion transport properties of the prepared composite materials have been characterized.



Like inorganic fluorescent semiconductor nanoparticles, carbonaceous nanoparticles or carbon quantum dots (CQDs) exhibit tunable fluorescence allowing them to be applied in bioimaging, electro-optical and photonic materials, and energy harvesting.¹ On top of excellent optical properties, CQDs are water-soluble due to surface polar groups and biocompatible.

Many synthetic protocols to prepare CQDs with tunable optical properties have been elaborated, including chemical and laser ablation, electrochemical polymerization and microwave and solvothermal treatment.^{2,3} Attaining stable optical properties of CQDs requires their surface passivation to prevent the undesirable transformations of reactive surface groups and the agglomeration of nanoparticles, for example, by adsorption of amino-terminated polyethylene glycol or ethyleneimine copolymers.⁴ On the other hand, if CQDs are prepared directly in a nanoporous polymer matrix, the isolated nanoparticles cannot agglomerate.

In this work, we studied the preparation of CQDs inside a Nafion[®] membrane. Even though the Nafion structure details are debatable,^{5–7} it is accepted that a hydrated Nafion membrane contains uniform (3–10 nm in diameter) spherical or cylindrical hydrophilic clusters flooded with water and surrounded with a hydrophobic perfluorinated phase. The preparation of CQDs inside hydrophilic regions should afford monodisperse nanoparticles stable against aggregation. Hydrothermal treatment was used to synthesize CQDs in view of simplicity and versatility of the method.^{2,3} The precursors were chosen based on the reports showing that ascorbic acid,⁸ glucose⁹ and glucosamine hydrochloride¹⁰ are prone to the formation of carbon micro- and nanoparticles *via* hydrothermal treatment. The duration and temperature of the hydrothermal treatment[†] were based on our systematic study of the kinetics and mechanism of hydrothermal transformations of ascorbic acid.¹¹ The membranes were characterized by their

equilibrium swelling in water, through-plane proton conductivity and vanadyl (VO²⁺) permeability as described elsewhere.^{12,13} The samples coding and their preparation details are given in Table 1 along with their selected physico-chemical parameters.

The samples Ref, W, Asc and Glu were colorless, whereas the samples Asc/IPA and GluNH₂ were yellowish and brown, respectively. When the samples were illuminated with a UV lamp, the Asc/IPA and GluNH₂ ones revealed greenish fluorescence, whereas the colorless samples showed no light emission (Figure 1, Table 1).

The results could be rationalized as follows: the hydrothermal treatment of a water-swollen Nafion membrane changed its morphology (no chemical transformations occurred since the IR spectra of samples Ref and W were identical). The structure evolution during the hydration of dry Nafion membranes was discussed in detail earlier,¹⁴ and an increase in the equilibrium hydration level after hydrothermal treatment was reported.¹⁵ We also observed a noticeable extra swelling of a Nafion membrane after the hydrothermal treatment with an increase in the hydration number (the number of water molecules per sulfonic group) from 20±1 to 33±1. This range of hydration numbers corresponds to the onset of phase inversion^{14,15} and a morphology change from

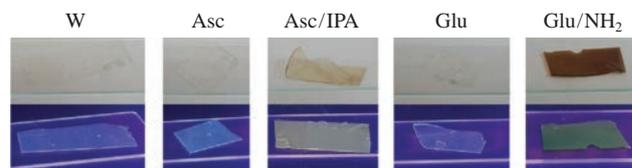


Figure 1 Optical microscopy images of Nafion 112 specimens after hydrothermal treatment: (top) in white light and (bottom) under UV irradiation at 312 nm.

[†] A commercial Nafion 112 membrane (Sigma-Aldrich) was conditioned *via* sequential boiling in distilled water (1 h), aqueous H₂O₂ (3 wt%, 1.5 h), distilled water (1 h), aqueous H₂SO₄ (0.5 M, 1.5 h) and distilled water (1 h),¹² dried and soaked with water or an organic precursor solution for 12 h. Then, the membrane was placed in a Teflon autoclave reactor filled

with water (reactor volume, 40 ml; filling degree, 90%); the reactor was closed, put in an oven pre-heated to 160 °C and kept at this temperature for 6 h. The modified specimen was rinsed with distilled water and kept in a 2.5 M aqueous solution of H₂SO₄ for at least 24 h at room temperature.

Table 1 Coding, preparation conditions and physico-chemical properties of membranes.^a

Sample	Pre-treatment ^b	<i>d</i> /μm	<i>w</i> (wt%)	<i>σ</i> /S cm ⁻¹	<i>P</i> /10 ⁵ cm ² min ⁻¹
Ref	Reference ^c	60	25	0.07±0.01	4.5
W	Water	81	35	0.5±0.1	5.2
Asc	10 wt% aqueous solution of ascorbic acid	79	27	0.17±0.04	4.1
Asc/IPA	8.4 wt% solution of ascorbic acid in water–isopropanol (7:3, v/v)	76	23	0.26±0.06	4.5
Glu	10 wt% aqueous solution of glucose	80	32	0.36±0.08	4.9
GluNH ₂	5 wt% aqueous solution of glucosamine hydrochloride	74	33	0.33±0.07	4.7

^a*d* is the membrane thickness, accuracy ±2 μm; *w* is the equilibrium water content, accuracy ±1 wt%; *σ* is the proton conductivity; *P* is the permeability towards VO²⁺ ions, accuracy ±0.1×10⁻⁵ cm² min⁻¹. The measurements were performed at least in triplicate, and the results were averaged. ^bThe composition of the solution soaked prior to hydrothermal treatment is given. ^cThe sample was not treated under hydrothermal conditions.

percolated pores to fused polymer particles. Such a structure change coincides with the significantly increased proton conductivity of the membrane (from 0.07 to 0.5 S cm⁻¹, cf. Table 1), which can be attributed to the improved percolation of conductive paths.

Further, we attempted to prepare CQDs *via* the hydrothermal treatment of a Nafion membrane in the presence of ascorbic acid, glucose and glucosamine organic precursors. To the best of our knowledge, such an approach has been discussed in the only publication¹⁶ reporting the hydrothermal modification of a Nafion 117 film in 5 wt% glucose solution. However, our attempts to reproduce the experiment failed: the produced specimens were too fragile, and they could not be transferred from the reactor. Therefore, we performed the hydrothermal treatment of Nafion in aqueous medium, and a precursor was introduced into the membrane at the pre-treatment soaking stage.

Two of the modified membranes (Asc and Glu samples) were colorless, and they exhibited no fluorescence due to the absence of CQDs from the samples. The inability to produce CQDs inside the Nafion matrix could be due to the inefficient sorption of the precursor (ascorbic acid or glucose) from the soaked solution: the size of the precursor molecule was comparable to the size of pores (channels) in the membrane, and there was no additional driving force of the neutral or acidic precursor sorption.

We attempted to enhance the sorption either using a water–isopropanol (3:7) mixture instead of water as the solvent of a soaking solution (to increase the equilibrium swelling of the membrane *via* the extension of pores) or using a basic precursor which could bind with the membrane sulfonate groups *via* Coulomb interactions. Indeed, in both cases (samples Asc/IPA and GluNH₂), the membranes were colored after the modification and exhibited greenish fluorescence under UV irradiation, suggesting the presence of a considerable amount of CQDs in the specimens.

The presence of an organic precursor in the soaked solution had almost no effect on the modified membrane thickness (74–80 μm), yet the equilibrium water content was substantially different, spanning the entire range between that of the Ref and W samples (23–33 wt%, cf. Table 1). Hence, the increase in the membrane thickness was mainly due to the hydrothermal treatment, and the water uptake was affected by the chemical structure of the CQD precursor.

The through-plane proton conductivity of the modified membranes (0.17–0.36 S cm⁻¹) was in line with the equilibrium water uptake: being in between that for Ref (0.07 S cm⁻¹) and W (0.5 S cm⁻¹) samples, the proton conductivity was considerably higher for the samples with the highest equilibrium swelling (Glu and GluNH₂ vs. Asc and Asc/IPA). Quite unexpectedly, those properties were not directly related to the presence of CQDs in the membrane.

We did not find any systematic variation in the permeability of a larger cation (vanadyl VO²⁺) through a membrane depending on the modification conditions (see Table 1). This is surprising since the increase in proton conductivity due to the modification was up to 7 times (from 0.07 to 0.5 S cm⁻¹ for Ref and W samples, respectively); this fact deserves more detailed investigation. At this stage, two explanations may be suggested. First, according to the common Nafion structure models, the membrane pores are only partially accessible for ion transport. The hydrothermal modification apparently increases the fraction of accessible pores thus facilitating the transport of protons (due to the enhanced free volume fraction or the channels connectivity), while the transport of larger vanadyl ions can remain restricted by the pore size thus being less sensitive to an increase in the porosity. Moreover, the proton conductivity of Nafion has a significant contribution of the Grotthuss mechanism based on only reorganization of covalent and hydrogen bonds in the water network, whereas vanadyl permeability requires true physical mass transfer of the ions.^{5,6}

The hydrothermal modification of a Nafion membrane impregnated with an organic precursor is a complex phenomenon with several processes occurring simultaneously: a change¹⁴ in the membrane morphology, the carbonization of the precursor^{8–10} and its diffusion outside the membrane. Moreover, Nafion exhibits special catalytic properties and, in certain cases, it can change the pathway of hydrothermal carbonization.¹⁶ Thus, the elucidation of the effect of a Nafion matrix on the hydrothermal synthesis of CQDs requires more systematic experiments including quantitative analysis of spectral properties and permeability of composite Nafion membranes as a function of the precursor concentration and treatment duration.

In summary, we prepared CQDs inside a nanoporous Nafion membrane *via* the hydrothermal decomposition of organic precursors. The hydrothermal treatment of a Nafion membrane induces its swelling and significantly enhances the proton conductivity. The incorporation of CQDs reduces the proton conductivity of the membrane, yet keeping it above that of the pristine membrane. Vanadyl permeability through the membrane is marginally affected by the hydrothermal treatment and incorporation of CQDs.

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