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Polymeric Nanoparticles

Doping of Single Polymeric Nanoparticles**

*X.-F. Zhou, W. Cheng, and Richard G. Compton**

Abstract: *The oxidative doping of single poly(N-vinylcarbazole) (PVK) nanoparticles is reported in aqueous sodium perchlorate using the nanoimpact method. Complete oxidative doping of single PVK nanoparticles with a size of approximately 120 nm is demonstrated, showing for the first time a simple strategy to synthesize and characterize doped polymeric nanoparticles at the single nanoparticle level.*

Polymeric nanoparticles (NPs) are widely used in energy storage and other applications.[1] Charge-transfer reactions using these materials involve the uptake or release of ions from the nanoparticulate polymer matrix and are generally studied by using an ensemble of nanoparticles in the form of a film or a composite which is usually supported on an electrode surface.[2] For optimal performance, it is usually desirable that the nanoparticles can become fully charged or discharged. However, the unambiguous study of such processes is challenging when using an ensemble because the charge transfer is strongly coupled to mass transport processes which typically can only be approximately quantified.

Herein, we show how the charging and doping of single polymeric nanoparticles can be studied for the first time using the newly developed nanoimpact method.[3] In this method, a suspension of nanoparticles is studied in situ using a microelectrode. The nanoparticles move randomly in solution with a Brownian motion which from time to time brings individual, single nanoparticles in contact with the electrode. If the electrode is held at a suitable potential, the nanoparticle can be oxidatively (or reductively) doped and the event detected by a "spike" in a current–time transient plot.

Hitherto, the nanoimpact method has been applied to determine the size of nanoparticles.[3b,e,4] In these experiments, charge transfer leads to dissolution of the nanoparticles. For example, silver nanoparticles are oxidized to Ag^+ ions,[3b] or indigo particles are reduced to form water-soluble leucoindigo.[3e] Alternatively, mediated electron transfer can take place on the surface of impacted nanoparticles.[5] Herein, the oxidative doping of poly(*N*-vinylcarbazole) (PVK) nanoparticles is reported in aqueous sodium perchlorate solution using the nanoimpact method. It is shown that the nanoparticles with a diameter of approximately 120 nm are oxidatively doped almost quantitatively with the uptake of one perchlorate ion per carbazole monomer unit. PVK nanoparticles are important for electroluminescent devices[6] whilst the doping of PVK films is important in battery technology.[7]

To find the approximate potentials required for nanoimpact experiments, cyclic voltammetry (CV) was used to study an ensemble of PVK NPs by modifying a macro-sized glassy carbon (GC) electrode (diameter 3 mm) with different loadings of PVK nanoparticles (from 5×10^{-11} mol up to 4×10^{-10} mol of carbazole moieties applied to the electrode; see Supporting Information for experimental details). The oxidation potential for anion doping of the PVK NPs in 1.0 M $NaClO_4$ solution was determined to be approximately +1.25 V (see Figure S1 in the Supporting Information). No peak was detected in the reverse scan or in the second cyclic voltammetry scan, indicating the oxidative doping of PVK nanoparticles is chemically irreversible and fully completed in 1.0 M $NaClO_4$. Furthermore, the number of electrons transferred per PVK monomer during the doping of PVK NPs was determined to be 2 ± 0.1 electrons. This value was calculated by integrating the area underneath the oxidative peak, namely the charge passed for oxidative doping versus the number of monomer carbazole units (Figure S2). This suggests that the oxidative doping of PVK nanoparticles requires a two-electron-transfer process, which is consistent with previous reports.[8]

Next, a clean, unmodified carbon microelectrode was placed in 1.0 M $NaClO_4$ solution and a fixed concentration of dispersed PVK nanoparticles added. The oxidative potential used for subsequent impact experiments was +1.35 V versus SCE (saturated calomel electrode), a value chosen based on our initial results to ensure that complete oxidation of PVK nanoparticles would occur (Figure S1). Under potentiostatted conditions, that is, at +1.35 V versus SCE, clear oxidative spikes from individual PVK nanoparticles were detected (Figure 1). The onset of these Faradaic spikes was found to be dependent on potential and no spike was detected at lower oxidation potentials, such as +0.4 V and +0.6 V, showing that those spikes result from the oxidative doping of PVK NPs. A control experiment was conducted at potential +1.35 V versus SCE with no PVK nanoparticles in the solution. No spikes were seen in this experiment, confirming that the individual spikes are a result of the random collisions of single PVK nanoparticles with the surface of the electrode and subsequent oxidative doping and electron transfer from the electrode.

A total of 249 spikes were detected from 131 chronoamperograms, each of 5 seconds duration, recorded at +1.35 V,

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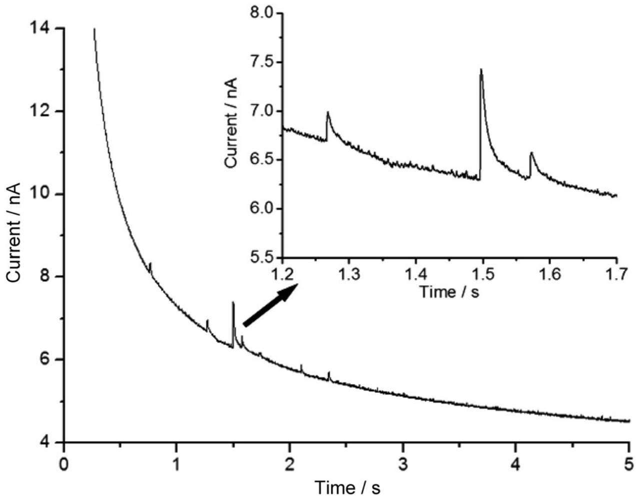


Figure 1. Typical chronoamperometric profiles showing oxidative Faradaic spikes of PVK NPs in 1.0 M $NaClO_4$ at +1.35 V versus SCE. Inset: detailed impact spikes.

corresponding to the oxidative doping of 249 individual PVK NPs. The charge of the electrons during doping of single nanoparticles was then calculated by integrating the area underneath the individual spikes (Figure S3). This is the first time oxidative doping of single polymeric nanoparticles has been detected or measured.

To characterize the yield of oxidative doping of single polymeric nanoparticles, the modal size D_{np} (size distribution) of the same batch of PVK NPs was estimated to be 121 nm through dynamic light scattering (DLS) experiments (Figure S3). If the charge is passed as a result of complete doping of single nanoparticles, then the theoretical charge (Q) of electron transfer from the complete doping of single polymeric nanoparticles, assuming that the PVK nanoparticles are spherical, can be determined by Equation (1):

$$Q = \frac{D_{np}^3 nF\pi\rho}{6M} \tag{1}$$

where D_{np} is the diameter of PVK nanoparticles, M is the molar mass of each PVK monomeric unit, ρ is the density of PVK, and F is the Faraday constant. The parameter n is the number of electrons transferred per PVK monomer during nanoparticle oxidation. The value of n ($n=2$) was obtained from Figure S4 (see above). Finally, comparing the modal charge Qy (where $Qy = 1.23\times10^{-12}$ C) resulting from the oxidative doping of 249 single polymeric nanoparticles from the experimental nanoimpact method with the theoretical estimated maximum charge Q ($Q = 1.09\times10^{-12}$ C) of single polymeric nanoparticles, indicates that there is effectively complete oxidative doping ($110\pm20\%$) of single polymeric PVK NPs. The slightly larger estimated charge may be attributed to the aggregation/agglomeration of polymeric nanoparticles at a high concentration in sodium perchlorate solution during the course of the nanoimpact experiments.

In addition, there was good agreement between the distribution of charge from the oxidative doping by the nanoimpact method, as analyzed from the above equation for all 249 single polymeric PVK NPs, and the theoretical estimation (Figure 2). The similar normal distribution (see the Supporting Information for details) further indicates complete oxidative doping of individual polymeric PVK nanoparticles even if there is size distribution of the analyzed individual nanoparticles. First, the results show the almost complete oxidative doping of single polymeric PVK nanoparticles and that a quantitative analysis of doping yield of single polymeric NPs is viable using the nanoimpact method. Second, the results show that the PVK nanoparticles are quantitatively oxidized with the uptake of one perchlorate ion per carbazole monomer unit, as illustrated in Scheme 1, based on the expected electro-oxidation of PVK.[8]

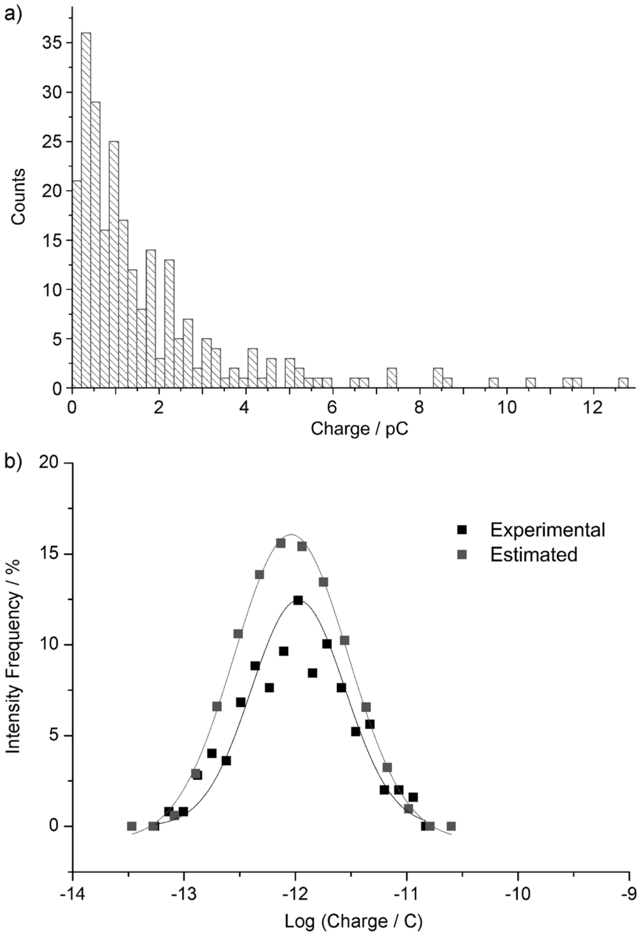
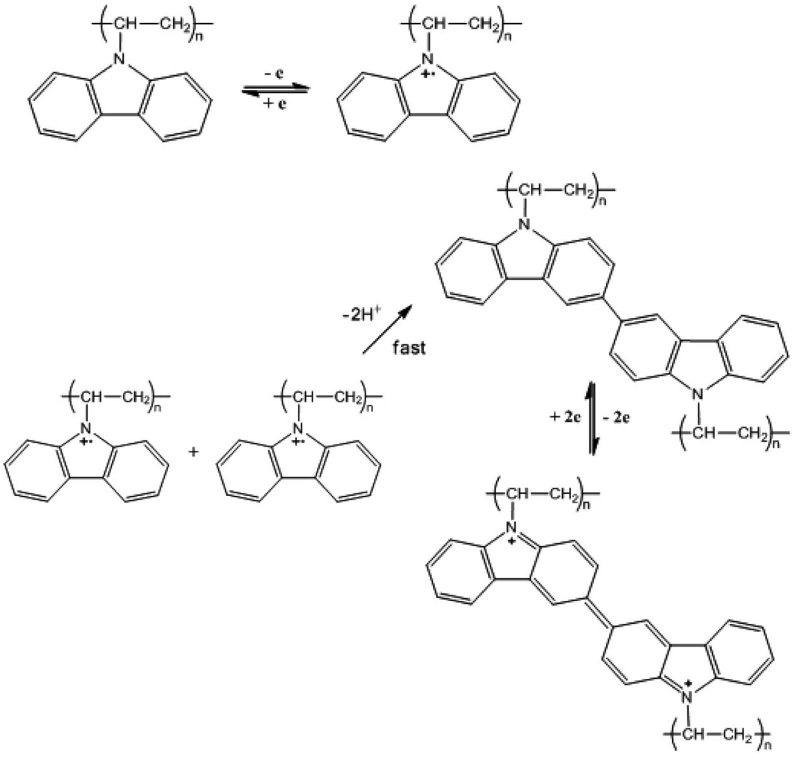


Figure 2. a) Distribution of charge from oxidative doping of single PVK NPs by analysis of the 249 oxidation spikes from nanoimpact experiments. b) Charge distribution of single PVK NPs derived from charge per spike from nanoimpact experiments (black) and the theoretical values (grey) estimated using Equation (1) from DLS data (see Supporting Information).

To our knowledge, no studies have been reported to demonstrate doping of single individual polymeric nanoparticles. In this Communication, we have shown the nanoimpact method for doping single polymeric nanoparticles and further demonstrated how to characterize the doping yield from doped single nanoparticles. We believe that this strategy



Scheme 1. Proposed mechanism for PVK nanoparticle oxidation based on Ref. [8].

will have major applications in both the synthesis and characterization of doped polymeric nanoparticles for new materials and energy applications. This method additionally provides unique characterization of polymeric single nanoparticles, such as dopant effect and doping yield, which are difficult to characterize by other spectroscopic and electron microscopy methods.

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