



Redox-active silica nanoparticles. Part 7. Redox behavior of core/shell structured viologen modified silica particles immobilized at paraffin impregnated graphite electrodes [☆]



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ABSTRACT

The redox behavior of viologen modified spherical and nonporous Stöber silica particles with diameters of 125 nm immobilized at paraffin impregnated graphite electrodes in 0.1 M KCl/H₂O is described. A permanent particle coverage was obtained by mechanical attachment to the graphite electrodes. The particles preferentially form clusters on the electrode surface as indicated by SEM. The presence of the viologen salt was shown by EDS of a modified electrode. Cyclic and differential pulse voltammetry were used to study the redox behavior in the immobilized state. Cyclic voltammograms of the modified particles exhibit two chemically reversible reduction waves corresponding to the first and second single electron reduction of the viologen dication. The mid-point potentials of the viologen units in the immobilized state are close to those of the reference compound methyl viologen. However, values of the semi-quinone formation constant K_{sem} of the modified silica material are increased compared to those of dissolved methyl viologen. This indicates a stabilizing effect of the solid supporting matrix/electrode with respect to disproportionation of the anchored viologen mono radical cations compared to methyl viologen.

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1. Introduction

The use of modified nano- or micro-particles as catalysts [2,3], biochemical sensors [4] or in electrochemical [5] applications has reached great attention. It combines the advantages of molecular control and simple separation based on the solid support. A broad spectrum of electrochemical applications has been reported: for example, modified Pt nanoparticles were used as catalysts for the oxygen reduction reaction [6] or in an electrochemical DNA sensor [7]. Carbon nanotubes modified with gold particles were utilized for the electrochemical detection of arsenic (III) species [8]. The application of modified particle based systems as solid electrolytes [9] and as solid-supported bases for Kolbe type electrosynthesis [10] was described as well.

Core/shell particles with an electrochemically inert solid core and an electrochemically addressable shell, e.g. materials based on silica [1,11–14] are specific examples of redox-active submicrometric structures. Here, a direct contact between the redox-active unit located in the shell and an electrode becomes possible. Ferrocene [11–14], a Noyori-type catalyst [11] and a viologen derivative

[1] were immobilized on Stöber silica particles and their electrochemical behavior was studied in non-aqueous electrolytes.

If the electrochemical characterization of such particulate materials is hampered by weak electrode-particle interactions, adsorption of the modified particles can be improved by chemical modification of the electrode [1,15].

A different approach for the characterization of the electrochemical behavior of redox-active particles is given by the use of paraffin impregnated graphite electrodes (PIGEs) [16], which provide a fast and simple access to immobilization, based on mechanical attachment. No pre-treatment of the electrode is necessary and, after immobilization, the modified PIGEs can easily be transferred into the electrolyte. For example, PIGEs have been used to study the electrochemical behavior of prussian blue [17] or of lutetium bisphthalocyanine [18] particles in aqueous electrolytes.

Here we report on the electrochemical behavior of core/shell structured viologen modified Stöber silica particles **vio@S125** with diameters of about 125 nm [1] mechanically attached to such PIGEs in aqueous solutions.

The synthesis and the spectroscopic characterization of material **vio@S125** (Fig. 1) were reported recently [1]. The base material consists of rehydroxylated, nonporous, spherical Stöber silica particles with low polydispersity ($d = 125 \pm 14$ nm). The viologen units were anchored through a condensation reaction between an alkoxysilane modified viologen derivative and surface located Si–OH

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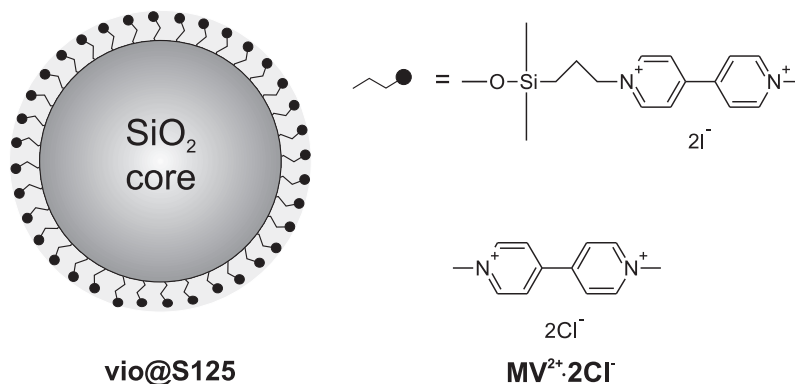


Fig. 1. Schematic view of the core/shell structured silica material **vio@S125** with $d = 125$ nm and reference compound methyl viologen $MV^{2+} \cdot 2Cl^-$.

groups of the rehydroxylated material. The specific surface concentration of the material was estimated to 48–100 $\mu\text{mol/g}$.

The electrochemical behavior studied by cyclic and differential pulse voltammetry of **vio@S125** at Pt and with potassium mercapto propionate modified gold electrodes in non-aqueous solvents was described [1]. Cyclic voltammetric experiments of **vio@S125** adsorbed onto a Pt electrode in acetonitrile reveals voltammograms with two weak signals of slight reversibility corresponding to the first and second reduction of the viologen unit. In contrast, the i - E curves of **vio@S125** adsorbed at chemically modified gold electrodes show two pronounced and separate reduction waves which are, however, chemically totally irreversible. Consequently, only values for the peak potentials of the reductions (E_p^{red}) are accessible and it is not possible to determine the exact formal (E^0) or mid-point potentials (\bar{E}), respectively, of both electron transfer steps. The semi-quinone formation constant K_{sem} was estimated only under the assumption that $\Delta E^0 = \Delta E_p^{\text{red}}$ [19]. In addition, the preparation of the modified gold electrodes is complex and time consuming.

At both electrode materials, the values of the reduction potentials E_p^{red} are in good agreement with those of the free modifier in the same electrolyte. Furthermore, values of K_{sem} are large and comparable with those of other free viologens [19,20].

2. Experimental part

2.1. Materials and methods

All chemicals and solvents were purchased from Sigma–Aldrich, Alfa-Aesar or Fluka and used as received if not otherwise noted. Methyl viologen hydrate was dried under reduced pressure at elevated temperatures. The synthesis and characterization of material **vio@S125** was described earlier [1].

2.2. Surface characterization

Scanning electron micrographs and EDS spectra were recorded with a Zeiss FE SEM Ultra Plus microscope equipped with an integrated EDAX Trident analyzer (SD detector; resolution: 127 eV). For experiments with the paraffin impregnated electrodes, the graphite rods were fixed with carbon tape on Al holders. The modified electrodes were washed with water and dried in an Argon stream before measurement.

2.3. Electrochemical experiments

All electrochemical experiments were performed with a BAS100B Electrochemical Workstation (BASi, West Lafayette, IN/

USA). All CV and DPV measurements were carried out in a gas-tight full glass three electrode cell under an argon atmosphere. For the electrochemical characterization of the modified silica particles rod-shaped paraffin impregnated graphite electrodes with nominal diameters of 5 mm were used (VEB Elektrokohle, Berlin-Lichtenberg, Germany). For the electrochemical experiments with methyl viologen a glassy carbon disk electrode (Metrohm, Filderstadt, Germany) with an electroactive area of $A = 0.065$ cm^2 was employed [1]. The counter electrode was a platinum wire of $d = 1$ mm and the reference electrode a Ag/AgCl (sat.) system (BASi, West Lafayette, IN/USA; MF 2063, stored in 3 M aqueous NaCl). In all cases the supporting electrolyte was a 0.1 M KCl/H₂O solution (Millipore water) which was deaerated by argon bubbling. All potentials are given vs. Ag/AgCl.

The particles were placed on a glass plate as powder. They were immobilized by circularly grinding the electrode with the powder on the glass plate. Approximately 1 mm of the modified electrode rods were immersed into the electrolyte. After experiments, the electrodes were thoroughly polished on filter paper until signals in voltammograms had disappeared. Thus, the electrode was rubbed on different spots of the filter paper (*drawing* the number eight or a straight line) [16].

For the electrochemical characterization of methyl viologen scan rates of 0.05–1.003 V/s were applied. The concentrations were set to $c = 0.10$ –0.28 mM by taking appropriate aliquots from a stock solution ($c = 4.40$ mM) using an Eppendorf pipette.

3. Results and discussion

3.1. Mechanical attachment

After the attachment of **vio@S125** to the PIGE clearly visible films were obtained that were stable against rinsing with water. Thus, a release from the electrode surface upon immersion in an aqueous electrolyte is not expected.

Scanning electron micrographs of modified PIGEs were recorded to characterize the type of the particle coverage. Fig. 2A–C show three images recorded in secondary electron contrast mode with increasing magnification from A to C. Obviously, the particles form larger aggregates that are randomly distributed over the electrode surface. In addition, smaller, necklace-like, 2- or 3-dimensional aggregates composed of only a few particles and single particles exist as well (Fig. 2C).

Scanning electron micrographs (Fig. 2D) obtained from the detection of backscattered electrons exhibit a high material contrast between the graphite material (black, light C-atoms) and the silica based Stöber particles (white, heavy Si-atoms). A third phase is absent, indicating that no contaminations (e.g. from the grinding or cleaning process of the electrode) are present.

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