



Fabrication, characterization, electrochemistry, and redox-induced electrochromism of viologen-functionalized silica core-shell nano-composites



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ARTICLE INFO

Article history:

Received 29 May 2017

Received in revised form 1 August 2017

Accepted 28 August 2017

Available online 31 August 2017

Keywords:

Core-shell nano-composites

Viologen

Layer-by-layer assembly

Electrochemistry

Electrochromism

ABSTRACT

Electroactive viologen-functionalized silica core-shell nano-composites have been prepared and characterized using thermogravimetry, field emission transmission electron microscopy, and infrared, UV–vis absorption, and X-ray photoelectron spectroscopy. The viologen monolayer functionalized nano-silica core (nano-SiO₂VBen) was obtained via a substitution reaction of propylamine–modified silica nanoparticles (nano-SiO₂NH₂) with N,N'-di(bromomethylbenzyl)-4,4'-bipyridium dibromide (VBenBr₂). The nano-SiO₂VBen core was positively charged and could thus act as a support for the construction of the shell layer of viologen multilayers through, alternatively, the electrostatic adsorption of poly(sodium-*p*-styrenesulfonate) (PSS) and VBenBr₂. Dynamic light scattering and morphological studies revealed that the dynamic sizes of the nanoparticles increased in the following order: nano-SiO₂NH₂, nano-SiO₂VBen, and nano-SiO₂VBen@(PSS/VBen)_n. This was due to the assembly of organic multilayers around the nanoparticles and formation of aggregates. Cyclic voltammograms of nano-SiO₂VBen- and nano-SiO₂VBen@(PSS/VBen)_n-modified electrodes showed two couples of redox waves in the potential range from 0 to –1.2 V (vs Hg/Hg₂Cl₂), corresponding to the redox processes of viologens in the nano-composites. Compared to their precursor of VBenBr₂, the nano-SiO₂VBen and nano-SiO₂VBen@(PSS/VBen)_n composites could be more strongly adsorbed on the electrode surface without co-adsorption of the polymeric supporter (Nafion), which can be attributed to a stronger molecular interaction between the present nano-composites and electrode surfaces. Finally, the redox-induced electrochromic properties of VBenBr₂ and nano-composites were investigated in the solutions or polymer gel electrolytes, and the results suggest that both viologen organic electrolyte and nano-composites could act as potential candidates for the development of redox-based electrochromic indicators and displays.

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1. Introduction

Viologens are *N,N'*-disubstituted-4,4'-bipyridinium dications that have been widely investigated due to their reversible redox properties and the reversible color change from colorless to blue or violet that occurs during their first redox process [1–3]. They are important electron mediators for light-harvesting compounds/complexes, quantum dots, dyes, and photosynthetic reaction centers [4–8]. Further, they have been utilized as substituents or building blocks for the development of electrochromic displays [9–

11] and even electrochromic papers through the incorporation of viologens in the matrix of papers [12], redox-controlled molecular sensors for supramolecular devices and machines [13,14], redox indicators for O₂ and amines [15,16], and mediators for catalytic reduction of organic dyes [17]. Researchers have synthesized many viologens with various alkyl chains, viologen dendrimers, and poly (viologen) derivatives in the past several decades to achieve this wide range of functions and/or applications [18–21]. Electrochemical studies of viologen-modified electrodes have revealed two couples of well-reversible redox waves in the potential range from 0 to –1.2 V (vs Hg/Hg₂Cl₂); the substituents (alkyl chains) and the anionic counter ions in viologens can slightly influence the redox potentials and formation of the reduced viologen dimers [1,2,12,18].

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Recent developments in supramolecular chemistry, molecular assembly, and nanoscale science and technology have created new uses for viologens, which have been covalently and non-covalently immobilized on electrode surfaces to produce well-organized thin films [21,22] and on the surfaces of inorganic materials (including carbon nanotubes, graphene, and quantum dots) to produce various organic–inorganic hybrid materials [23–25]. These films and hybrid materials are generally prepared based on intermolecular electrostatic interaction, gold–thiol bonding, and silane coupling [21–26]. Further, monolayers of amphiphilic viologens can be produced at the air–water interfaces and then transferred onto the electrode surfaces using the Langmuir–Blodgett (LB) technique [27]. It has been reported that the electrochemical properties of the viologen-immobilized electrodes depend on the chemical structure of the viologens, electrolytes in the solutions, and arrangement and orientation of the viologens in the LB films [22,27].

However, viologen LB films have weak stabilities in electrolyte solutions. To counteract this, some viologenthioles and viologen silane derivatives have been synthesized and immobilized using the self-assembling and layer-by-layer (LBL) techniques [28–30]. In these techniques, viologens are attached through Au–S or Si–O bonding, resulting in the formation of more stable viologen-modified electrodes and organic–inorganic hybrid materials [21,29]. Electrochemical and spectroscopic studies have revealed that these viologen-covered thin films can act as candidates for the development of chemically modified electrodes, electron mediators of light-harvesting units, and redox-based molecular switches and electrochromic devices [15,20,26]. Viologen derivatives can also be directly synthesized and immobilized on the electrode surfaces through the electrochemical reduction of viologen phenyl diazonium salts [31] or by electropolymerization of a branched monomer [32,33]. In these cases, the morphology and thickness of the viologen polymer thin films can be controlled during their formation. For example, porous polyviologen materials can be prepared on the electrode surfaces, which can be used for anion recognition and organic rechargeable batteries [32,33].

In addition to immobilization on the electrode surfaces, viologen polyelectrolytes have recently been anchored on the surfaces of nanoparticles such as nano-SiO₂ and graphene oxide, forming core-shell viologen-functionalized nanocomposites [34,35]. Electrochemical studies of viologen-functionalized nano-SiO₂ have revealed that the values of the semi-quinone formation constant K_{sem} in the modified silica material were greater than those found in dissolved methyl viologen. These observations indicated that, compared to methyl viologen, there was a stabilizing effect of the solid supporting matrix/electrode with respect to disproportionation of the anchored viologen mono radical cations [34]. Viologens can also be anchored to the side chains of poly(vinylbenzyl chloride) to produce redox-active colloidal particles. These particles can be used as battery materials that display reversible cycling, accessing up to 99% of their capacity and achieving $99 \pm 1\%$ coulombic efficiency over 50 cycles through bulk electrolysis, a feature that has been attributed to efficient, long-distance intraparticle charge transfer [36].

We studied here the immobilization of viologens on the surface of nano-SiO₂ particles and their electrochemical and redox-based electrochromic properties. The commercially available nano-SiO₂ particles were first modified by a monolayer of propylamine to form nano-SiO₂NH₂ (Fig. 1) hybrids through a silane coupling reaction of nano-SiO₂ with 3-aminopropyltrimethoxysilane [37,38]. After an interfacial substitution reaction of nano-SiO₂NH₂ with N,N'-di(bromomethylbenzyl)-4,4'-bipyridium dibromide (VBenBr₂), positively charged, viologen monolayer-covered nano-SiO₂VBen hybrids were obtained. These particles then acted

as a positively charged nano-core to adsorb poly(sodium-*p*-styrenesulfonate) (PSS) and VBenBr₂ alternatively to produce core-shell nano-SiO₂VBen@(PSS/VBen)_n composites. Unlike their precursor, VBenBr₂, both nano-SiO₂VBen and nano-SiO₂VBen@(PSS/VBen)_n composites could form stable casting films on the electrode surfaces without the addition of Nafion, a widely used co-adsorbent that supports the formation of stable casting films of electroactive molecules. Cyclic voltammograms of nano-SiO₂VBen and nano-SiO₂VBen@(PSS/VBen)_n composites revealed two couples of redox waves in the potential range of 0 and –1.2 V (vs Hg/Hg₂Cl₂), which was attributed to reversible electron transfer between the viologens and the electrode surface. Finally, the redox-induced electrochromic properties of the present viologen derivative and nano-composites were investigated via two routes: by the addition of reductant to the suspension of nano-composites [39]; and by encapsulation of the viologen or nano-composite polyelectrolyte gel between two indium tin oxide (ITO) electrodes followed by the use of applied voltages [40,41]. These redox-induced color change phenomena suggested that both viologen organics and nano-composites can act as alternative candidates for the development of redox-induced electrochromic indicators and displays.

2. Experimental

2.1. Materials

Ludox AS40 particles, containing 40 wt. % SiO₂ (diameter ~12 nm) and PSS (Mw ~70,000, DP ~340), were purchased from the Sigma-Aldrich Co. 3-Aminopropyltrimethoxysilane, ammonium hexafluorophosphate, and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMI][TFSI]) were obtained from J&K Scientific LTD. 4,4'-Bipyridyl (BPy) and α,α' -dibromo-*p*-xylene were obtained from Alfa Aesar[®]. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) was obtained from the Sigma-Aldrich Co. Polyethylene glycol 200 (PEG-200) and ferrocene were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as received without further purification.

2.2. Synthesis of viologen-functionalized silica nano-cores

The precursor, VBenBr₂ (Fig. 1), was synthesized according to the method described in the literature [22,23]. Mixtures of 3.38 g α,α' -dibromo-*p*-xylene and 0.5 g 4,4'-bipyridyl (molar ratio 4:1) were stirred in dichloromethane at room temperature for 10 hours. The precipitate was filtered and washed with dichloromethane to remove unreacted reactants and then dried under a vacuum at room temperature. Because VBenBr₂ was not soluble in acetone, it was changed to VBen(PF₆)₂ (for the construction of electrochromic configuration) by the addition of 20 mL VBenBr₂ (1.0 g) aqueous solution into 20 mL of saturated NH₄PF₆ solution. After stirring overnight, the precipitate of VBen(PF₆)₂ was filtered, washed with plenty of water, and dried in a vacuum at room temperature.

Nano-SiO₂NH₂ hybrids were synthesized as follows: ludox silica nanoparticle solution (10 g) was first suspended in a mixed methanol and DMF (100 mL) solvent, and then it was stirred with 0.6 g 3-aminopropyltrimethoxysilane at 60 °C for 48 hours [37,38]. The suspension was then isolated by centrifugation at 4,000 rpm. The white nano-SiO₂NH₂ precipitate was washed with DMF and methanol and finally dried in a vacuum.

The nano-SiO₂VBen hybrids (nano-cores) were prepared by refluxing mixtures of nano-SiO₂NH₂ and VBenBr₂ in methanol overnight. The precipitate was isolated by centrifugation at 4,000 rpm. The pale-yellow powders of nano-SiO₂VBen were washed with methanol and dried in a vacuum.

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