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Electrochemical charging and electrocatalysis at hybrid films of polymer-interconnected polyoxometallate-stabilized carbon submicroparticles

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Abstract Using the layer-by-layer technique, carbon submicroparticles, that have been modified and stabilized with monolayers of Keggin-type phosphododecamolybdate ($\text{PMo}_{12}\text{O}_{40}^{3-}$), can be dispersed in multilayer films of organic polymers, poly(3,4-ethylenedioxythiophene), i.e., PEDOT, or poly(diallyldimethylammonium) chloride, i.e., PDDA, deposited on glassy carbon or indium-tin oxide conductive glass electrodes. The approach involves alternate treatments in the colloidal suspension of $\text{PMo}_{12}\text{O}_{40}^{3-}$ -covered carbon submicroparticles in the solution of monomer, 3,4-ethylenedioxythiophene or in solution of PDDA polymer. Electrostatic attractive interactions between anionic phosphomolybdate-modified carbon submicroparticles and cationic polymer layers permit not only uniform and controlled growth of the hybrid organic–inorganic film but also contribute to its overall stability. The system composed of $\text{PMo}_{12}\text{O}_{40}^{3-}$ -covered carbon submicroparticles dispersed in PEDOT is characterized by fast dynamics of charge transport and has been used to construct symmetric microelectrochemical redox capacitor. The PDDA-based system has occurred to be attractive for electrocatalytic reduction of hydrogen peroxide.

Keywords Phosphomolybdate · Monolayers · Carbon particles · Poly(diallyldimethylammonium) chloride · Poly(3,4-ethylenedioxythiophene) · Organic–inorganic networks · Multilayer composite films

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Introduction

Over the last several years, polyoxometallates (POMs) have been a subject of intense research not only due to their well-defined structure but also owing to their attractive catalytic properties and capability to undergo very fast and reversible multi-electron electrochemical reactions. Such inorganic metal–oxygen cluster compounds as POMs can form ordered self-assembled monolayers on common solid electrode substrates [1–7]. They can be combined with various inorganic cations and organic macromolecular compound (including conducting polymers) to form hybrid or composite materials [8–11]. A variety of well-defined multilayer assemblies of POMs with a precisely controlled thickness and layer sequence can be formed using the layer-by-layer method [12] based on electrostatic attractive interactions between oppositely charged species. The resulting organized multilayer systems on electrodes could have many applications ranging from electrocatalysis to charge storage. For practical purposes, it is necessary to maintain high electrical conductivity within the film on electrode that would facilitate fast delivery of charge to three-dimensionally distributed redox centers. The conductivity increase can be achieved by controlled incorporation and arrangement of carbon particles.

Due to high surface area, good electrical conductivity, exceptional physicochemical stability, and significant mechanical strength, carbon nanostructures are of considerable interest to the development of catalytic systems, fabrications of pigments [13] and fillers [14], development of high density charge storage devices [15] and emission systems [16], supercapacitors [17, 20, 23], nanoelectronic devices [18], probe tips for scanning probe nanoscopy [19], as well as novel hydrogen storage [21] and conductive [22] materials. The ability of Keggin-type POMs to undergo chemisorption on solid surfaces including metal and glassy carbon electrodes, powders

and fibers [1–7, 9, 24–27] can be explored to the formation of stable ionic monolayers on Pt [28] as well as on carbon [29] clusters. Formation of POM (e.g., phosphododecamolybdate, PMo_{12}) monolayers on carbon surfaces facilitates not only dispersion (under ultrasound) of the carbon black powder within the POM solution (due to the existence of repulsive forces between anionic POM layers) but also provides a driving force for the division of carbon black aggregates into much smaller particles [29]. The size of particles can be varied from the fractions of micrometers to tens of nanometers depending on the duration of the treatment. Obviously, by increasing the treatment time the size of particles can be decreased.

In the present work, we explore the ability of PMo_{12} to undergo chemisorption on carbon surfaces and to stabilize colloidal suspensions of carbon black particles [29]. We produce using the layer-by-layer approach hybrid films of alternating organic–inorganic layers that combine attractive mechanical and electrical properties of carbon particles, unique physicochemical characteristics of organic polymers (poly(diallyldimethylammonium) chloride, PDDA or poly(3,4-dioxyethylenethiophene), PEDOT) and rigid inorganic metal–oxygen clusters (PMo_{12}). Modification of carbon particles with polyanions permits not only their electrostatic interactions with positively charged polymer interlayers but also provides an effective route to the homogeneous dispersion of carbon black in such polymer matrices. The uniformity of distribution of carbon submicroparticles within three-dimensional multilayer films and their overall good conductivity should be of primary importance to energy-storage applications since these factors have positive impact on reversible capacity, especially at high current densities [23]. When it comes to electrocatalysis, an additional important issue is the possibility of generation of highly reactive mixed-valent $\text{Mo}^{\text{VI,V}}$ sites within PMo_{12} heteropolyanions [5, 27, 28, 30, 31] deposited on the carbon black surfaces. This research parallels our and others recent attempts to produce network multilayer films composed of carbon nanostructures (nanotubes) dispersed in polymer matrices [32–34].

Experimental

Electrochemical measurements were done with CH Instruments (Austin, U.S.A.) Model 750 Electrochemical Workstation. A standard three-electrode cell was used. Indium-tin oxide (ITO) covered conducting glass slides (geometric area, 1 cm^2) and glassy carbon disk (diameter, 3 mm) electrodes were typically used as working electrodes. Before modification, a glassy carbon electrode was activated by polishing with aqueous alumina slurries (size 5–0.5 μm) on a polishing cloth. The ITO electrode was rinsed with the mixture of 1 mol dm^{-3} KOH and methanol before use. The

counter electrode was made from Pt wire. All potentials were expressed versus the saturated (KCl) Ag/AgCl electrode. Scanning electron microscopy (SEM) images were obtained using Hitachi S 4200 instrument. The presence of molybdenum in the network films was confirmed using energy dispersive X-ray spectroscopy (EDS) unit for elemental analysis.

All chemicals were of analytical grade purity, and they were used as received. Phosphododecamolybdic acid, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo_{12}) was obtained from Fluka, and 3,4-dioxyethylenethiophene (EDOT) monomer was from Aldrich. Solutions were prepared using doubly distilled subsequently deionized (Millipore Milli-Q) water. Experiments were carried out at room temperature ($20 \pm 2 \text{ }^\circ\text{C}$).

To produce colloidal solution of polyoxometallate (PMo_{12})-modified (stabilized) carbon submicroparticles (CSMPs), approximately 30 mg of carbon black powder (Purex HS40 from Cofrablack, France) was dispersed in 10 cm^3 of 5 mmol dm^{-3} PMo_{12} aqueous solution. The initial suspension was sonicated for 12 h. Subsequently, it was centrifuged, and the supernatant solution was removed and replaced with fresh PMo_{12} solution. The centrifuging procedure was typically repeated 3–4 times. Each time PMo_{12} solution was decanted. Later, the particles were centrifuged and washed out with water at least 2–3 times. Then a stable colloidal solution of PMo_{12} -stabilized CSMPs was obtained. To fabricate (deposit) ultra-thin films of PMo_{12} -stabilized CSMPs on glassy carbon, the electrode substrate was dipped in the respective colloidal solution (described above) for 30 min. For comparison, simple modification of glassy carbon substrate by chemisorption of PMo_{12} [26] was achieved by dipping the electrode substrate for 10 min in an aqueous solution of 2 mmol dm^{-3} PMo_{12} .

Multilayer films composed of PMo_{12} -stabilized CSMPs and ultra-thin PEDOT (or PDDA), were assembled using the layer-by-layer method via alternate immersions for 30 min first in the suspension of PMo_{12} -stabilized CSMPs then in 0.2 mol dm^{-3} monomer solution of EDOT in 0.5 mol dm^{-3} H_2SO_4 (or in 1% PDDA solution in 0.05 mol dm^{-3} H_2SO_4). Fabrication of ultra-thin PEDOT (conducting polymer) required an electrochemical polymerization step through potential cycling (2 cycles at 50 mV s^{-1}) in external 2 mol dm^{-3} H_2SO_4 from -0.1 to 1.0 V . As a rule, the electrode was removed, rinsed with water and dried after each immersion. Since the procedure can be repeated more than ten times, the amount of dispersed carbon particles, organic polymer and inorganic POM clusters can be increased in a systematic manner to produce multilayer network films on the electrode surface.

To produce a solid-state microelectrochemical capacitor, two glassy carbon slide electrodes (geometric area, 2 cm^2), that had been modified (as described above) with multilayer films composed of PMo_{12} -stabilized CSMPs and ultra-thin PEDOT layers to act as redox capacitor half-cells, were assembled parallel in a sandwich configuration. They were tested in two-elec-

trode configuration where application of potential differences to the opposing carbon plate electrodes leads to displacement of the electrode potentials in opposite directions. A separator was in a form of the filter paper that had been pre-soaked in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ before introducing it into the capacitor cell.

Results and discussion

Fabrication and characterization of PMo_{12} -stabilized carbon particles

The procedure of fabrication of the colloidal suspension of carbon submicroparticles (CMPs) in water [29] has involved a few exposures of carbon black to PMo_{12} aqueous solutions, followed by multiple centrifuging and washing steps (to remove PMo_{12} -rich solution phases) as described in Experimental Section. Fig. 1 illustrates scanning electron microscopic (SEM) images of carbon particles (Fig. 1a) and after (Fig. 1b) the treatment with PMo_{12} . Most of carbon black structures had formed fairly sizeable clusters with diameters in μm range

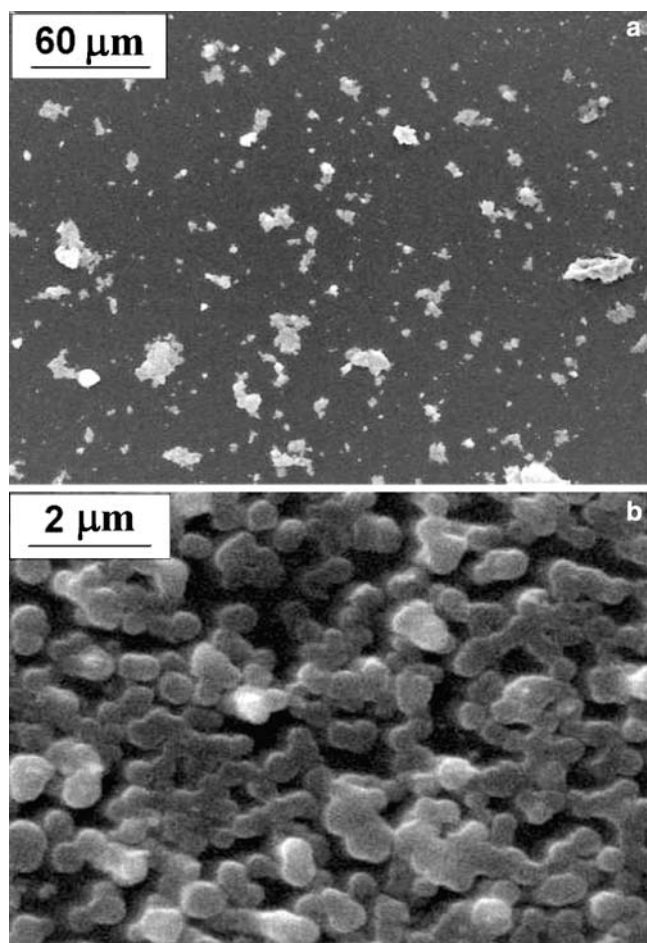


Fig. 1 SEM images of carbon black particles before (a) and after (b) the treatment with PMo_{12}

before they were exposed to PMo_{12} (Fig. 1a). Following conditioning in PMo_{12} solutions, the average diameters of carbon particles decreased to 100–200 nm (Fig. 1b). The result shall be interpreted as follows. The electrostatic repulsive interactions between the negatively charged PMo_{12} (chemisorbing on carbon black), when combined with the force of ultrasound bath, are expected to breakdown the larger carbon clusters (agglomerates) to smaller submicro-structures that are subsequently stabilized by PMo_{12} . Apparently, the adsorption of PMo_{12} constitutes the sufficient driving force [29] for the gradual division of carbon black clusters into smaller units [29].

It is evident from the cyclic voltammetric responses (recorded in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$) of Fig. 2 that PMo_{12} can be adsorbed not only on (a) glassy carbon but also on (b) ITO electrodes; and PMo_{12} -stabilized CSMPs

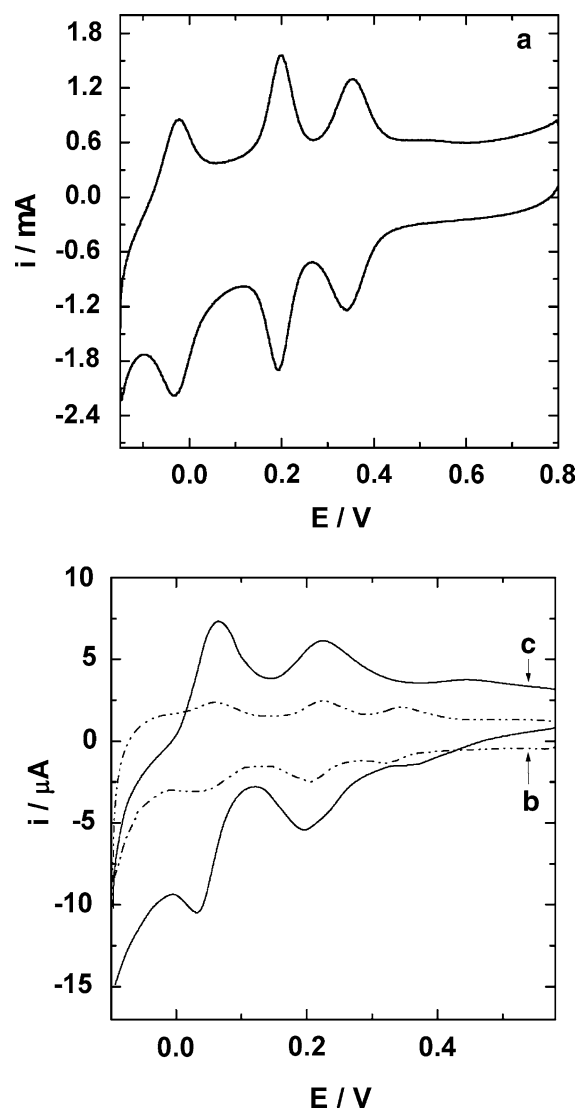
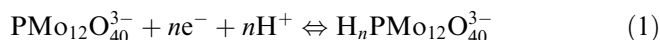


Fig. 2 Cyclic voltammetric responses of PMo_{12} monolayer adsorbed on a glassy carbon and b ITO electrodes. Curve c shows the response of PMo_{12} -modified CSMPs assembled on ITO. Electrolyte: $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. Scan rate: 50 mV s^{-1}

(PMo_{12} -CSMPs) can readily be attached to the surface of the ITO electrode. The spontaneous deposition of PMo_{12} -CSMPs on ITO was achieved by simple dipping of the electrode substrate in its colloidal suspension. The attachment of CSMPs was presumably facilitated by the presence of interconnecting PMo_{12} polyanions capable of chemisorbing on both indium tin oxide [3, 9] and carbon particles [29]. It is likely that PMo_{12} can undergo adsorption at carboxylic and other oxygen containing functionalities existing at carbon surfaces [35]. PMo_{12} has some oxidizing capabilities [26] leading to the interfacial oxidation of carbon particles to form surface carboxylic groups; they are presumably involved in the chemical adsorption of PMo_{12} [35] via its hydroxyl groups [36].

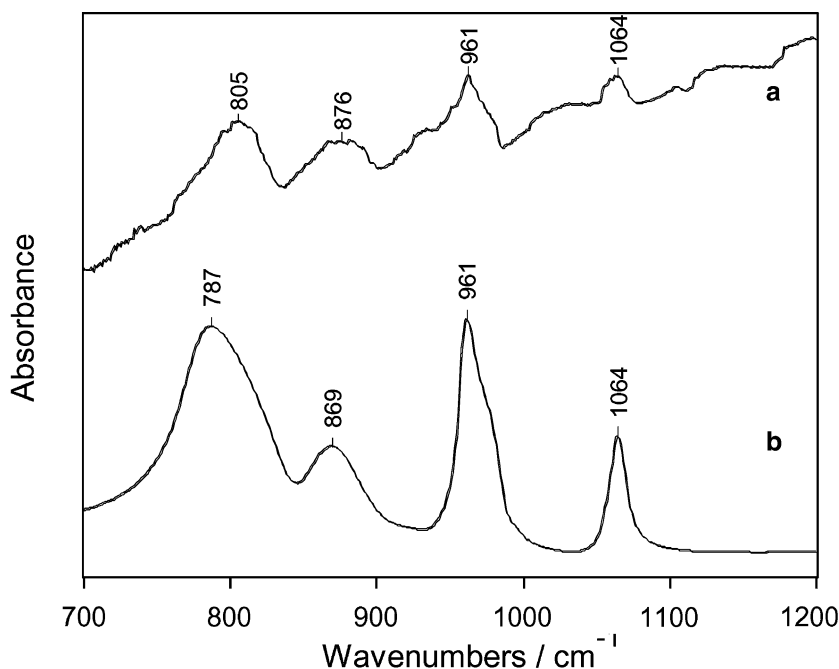
All cyclic voltammograms illustrated in Fig. 2 exhibit peaks characteristic of PMo_{12} in the potential range from -0.1 to 0.45 V. They shall be interpreted [26] in terms of three consecutive two-electron reversible well-defined processes leading to the formation of mixed-valent $\text{Mo}^{\text{VI,V}}$ ionic sites in the partially reduced heteropolyblue molybdate, $\text{H}_n\text{PMo}_{12}\text{O}_{40}^{3-}$:



(where n is ideally equal to 2, 4 or 6). Formal potentials of redox reactions of PMo_{12} chemisorbed on CSMPs are slightly shifted towards more positive values when compared to the simple PMo_{12} monolayer on glassy carbon. There are also some irregularities in the relative ratios of peaks in the case of PMo_{12} -CSMPs (Fig. 2, Curve c). These observations may reflect some changes in the thermodynamics of electrode processes caused by differences in the strength of adsorption of PMo_{12} to CSMPs in comparison to that on ITO or glassy carbon.

Figure 3 (curve a) shows the FTIR spectrum of (PMo_{12} -stabilized CSMPs attached to Au-covered glass slide. For comparison, the FTIR response of pure solid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$ in KBr) is provided (curve b). The assignment of the bands has been made according to data published elsewhere [36]. Following adsorption of PMo_{12} on CSMPs, the positions of $\text{Mo-O}_c\text{-Mo}$ and $\text{Mo-O}_e\text{-Mo}$ vibration modes for corner (O_c) and edge oxygen (O_e) atoms are somewhat shifted to higher wavenumbers: from 787 and 869 cm^{-1} (crystalline PMo_{12}) in Fig. 3b to 805 and 876 cm^{-1} (PMo_{12} -CSMPs) in Fig. 3a. The reported changes are the most pronounced for $\text{Mo-O}_c\text{-Mo}$ vibrations. They may reflect strengthening (shortening) of Mo-O bonds due to the possibility of changes in electron densities as a result of interfacial charge transfer between $\text{PMo}_{12}\text{O}_{40}^{3-}$ anion and the surface of carbon particles. Alternatively, following adsorption on carbon, weakening of repulsive interactions between oxygen atoms (leading to shortening of Mo-O bonds) can be envisioned. Most likely, the chemical adsorption process on carbon particles involves corner (and to small extent edge) oxygens in PMo_{12} . Further, the vibrations of the central tetrahedron PO_4 are independent from the rest of the polyanion. Consequently, the maximum of $\text{P-O}_p\text{-Mo}$ (where O_p is an oxygen atom from the $-\text{PO}_4$ heterogroup) stretching mode is centered at $1,064$ cm^{-1} for PMo_{12} adsorbed on CSMPs (Fig. 3a), and it does not differ from that characteristic of crystalline PMo_{12} (Fig. 3b). Also the maximum of the Mo-O_t (where O_t is a terminal oxygen atom) stretching mode peak at 961 cm^{-1} is unchanged. The above observations imply that the overall physico-chemical identity of PMo_{12} heteroanion is retained following adsorption on CSMPs.

Fig. 3 FTIR spectra of **a** phosphododecamolybdic acid in KBr and **b** PMo_{12} -modified CSMPs assembled on gold-coated glass slide



Layer-by-layer formation of polymer films with dispersed carbon particles

By performing alternate treatments in PMo_{12} -stabilized CSMPs colloidal suspensions and in the monomer (EDOT) solutions hybrid films consisting of PMo_{12} -stabilized CSMPs and ultra-thin PEDOT interlayers can be successfully grown. Indeed, a systematic increase of voltammetric peak currents has been observed (Fig. 4a). In the layer-by-layer method, PMo_{12} (that is chemisorbed on carbon particles) retains its negative charge necessary for electrostatic attraction of positively charged ultra thin PEDOT layers. Because PEDOT does not show well-defined voltammetric peaks and its electrochemical charging contributes mostly to background currents, the voltammetric response of the film of Fig. 4a is dominated by three sets of voltammetric peaks originating from PMo_{12} . But the increase of currents related to the oxidation of PEDOT at more positive potentials, i.e., higher than 0.75 V (Fig. 4a), implies that the polymer is present in the film, and its loading increases following application of alternate immersions. Judging from the charges under the second reduction peak of PMo_{12} (adsorbed on CSMPs) at about 0.23 V, the increase in loading of PMo_{12} is fairly monotonic (Fig. 4c) and it is on the level $0.3 \times 10^{-10} \text{ mol cm}^{-2}$ per immersion cycle. It is noteworthy that the values of the PMo_{12} peak currents are proportional to the scan rate up to ca. 2 V s^{-1} (Fig. 4b) what is consistent with the surface type behavior of our multilayer system as well as with the fast dynamics of charge propagation. The presence of both conducting polymer and electronically

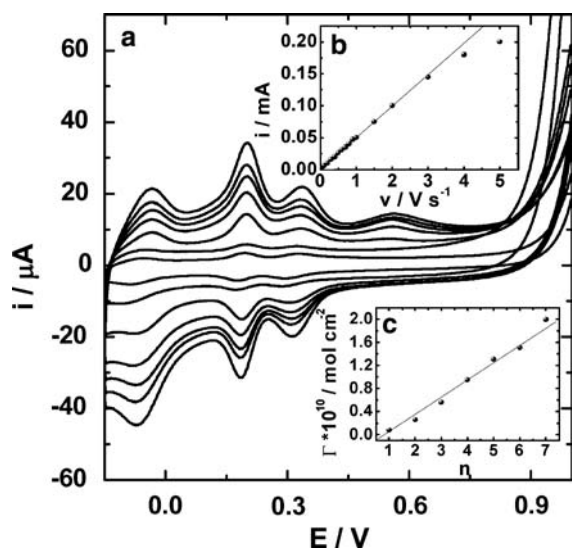


Fig. 4 a Cyclic voltammograms recorded at 50 mV s^{-1} (in argon-saturated $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$) following application from 1 to 7 cycles of alternate treatments in the colloidal solution of PMo_{12} -protected CSMPs and 0.2 mol dm^{-3} solution of EDOT. Inset **b** illustrates the dependence of the second reduction PMo_{12} peak (at about 0.2 V) on scan rate, v . Inset **c** shows the dependence of the loading of PMo_{12} (adsorbed on CSMPs) on a number of the alternate immersion cycles. Electrode substrate: glassy carbon

conducting carbon particles is expected to facilitate charge propagation within the film.

The above concept is not limited to PEDOT: an analogous multilayer systems can be fabricated by alternate formation of ultra-thin layers of PMo_{12} -stabilized CSMPs and PDDA (Fig. 5). To demonstrate growth of the film, voltammetric curves have been recorded each time after formation of an additional PMo_{12} -stabilized CSMPs (inorganic)–PDDA (organic) bilayer. The preparative procedure is analogous to that described for Fig. 4 except that alternate treatments in the polymer solutions do not have to be followed by electro-polymerization steps in the external supporting electrolyte. The growth and distribution of PMo_{12} -CSMPs and PDDA seem to be less uniform (Fig. 5b) than in the case PEDOT-containing system (Fig. 4c). By plotting the film loading (calculated from the charge under the most positive PMo_{12} reduction peak), a linear dependence versus a number of treatments in PMo_{12} solutions (slope; $0.4 \times 10^{-10} \text{ mol cm}^{-2}$ per immersion cycle) has been obtained.

Figure 6 illustrates a cartoon how PMo_{12} -stabilized CSMPs are expected to be dispersed within multilayer polymer-containing films of Figs. 4 and 5. The distribution of CSMPs is probably not so ideal in the real film but, nevertheless, PMo_{12} -stabilized CSMPs are expected to appear alternately (due to application of the layer-by-layer technique) and fairly uniformly. The multilayer films are stable because of the existence of electrostatic attraction interactions between PMo_{12} anions and positively charged polymer backbone.

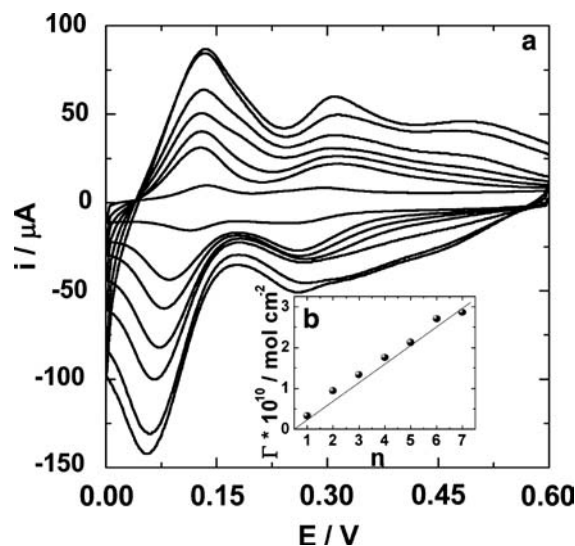
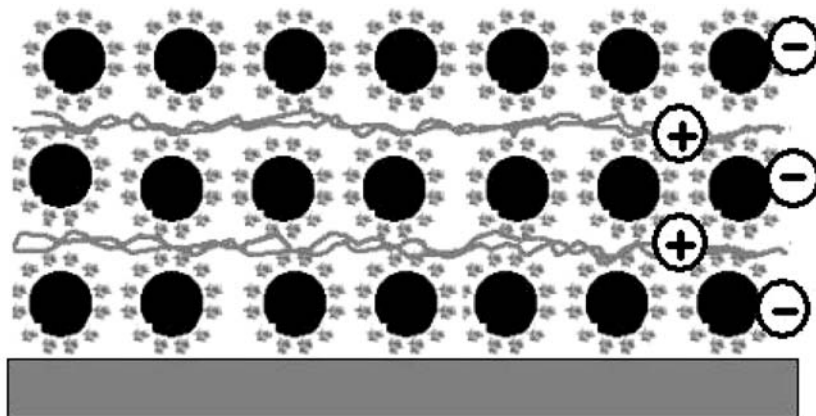


Fig. 5 a Cyclic voltammograms recorded following application of 1–7 cycles of alternate treatments in the colloidal solution of PMo_{12} -protected CSMPs and the cationic polymer (PDDA) solution. Inset **b** shows the dependence of the loading of PMo_{12} (adsorbed on CSMPs) on a number of the alternate immersion cycles. Electrolyte: $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. Scan rate: 50 mV s^{-1} . Electrode substrate: ITO

Fig. 6 Cartoon illustrating formation of the multilayer film composed of positively charged polymer layers and negatively charged PMo_{12} -modified CSMPs dispersed within



Solid-state microelectrochemical capacitor

Because the data of Fig. 4b clearly imply fast dynamics of charge transport, the hybrid organic (PEDOT)–inorganic (PMo_{12} -stabilized CSMPs) multilayer films should be of importance to the construction of microelectrochemical (redox) capacitors. To execute a diagnostic experiment, two glassy carbon slides (that had been modified with the multilayer films as for Fig. 4) were assembled in a sandwich configuration [37, 38] and separated with the H_2SO_4 pre-soaked filter paper as described in Experimental section. Figure 7 illustrates a typical cyclic voltammetric response recorded in two-electrode configuration where application of potential differences to the opposing glassy carbon slides results in the displacement of the electrode potentials in opposite directions. The voltammogram is characterized by two sets of approximately symmetrical peaks around the zero point. They presumably originate from the existence of mixed-valent $\text{Mo}^{\text{VI,V}}$ sites in the hybrid multilayer films

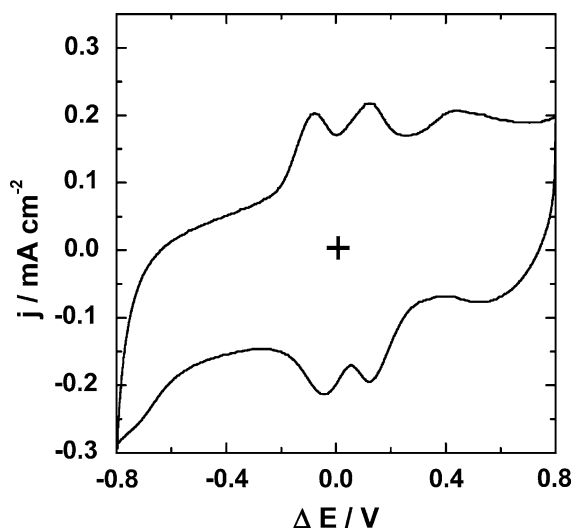


Fig. 7 Steady-state voltammetric responses (recorded in two-electrode mode) of two PEDOT-based (PMo_{12} -modified CSMPs containing) films deposited (as for Fig. 4) on two glassy carbon slides, separated with filter paper (pre-soaked with 0.5 mol dm^{-3} H_2SO_4) and assembled opposite each other in a sandwich configuration. Scan rate: 20 mV s^{-1}

(fabricated and assembled at ambient conditions) between which electron transfers are feasible upon application of small potential biases as in classical biamperometry [37, 38]. When referring to the data of Fig. 4, one can expect that application of larger potential differences (up to 0.8 V) should force both the PMo_{12} and PEDOT to undergo redox processes. They include multielectron reductions of PMo_{12} at the negative electrode and electrochemical charging (oxidation) of the polymer at the positive electrode. As long as the potential differences did not exceed +0.8 V, the system behaved reproducibly and it was stable during the seven-day long experiments; after this period, the cell was intentionally dismantled.

Figure 8 illustrates typical charging/discharging cycles of the capacitor recorded at the current density of $5 \times 10^{-5} \text{ A cm}^{-2}$. The essentially linear charging–discharging profiles were observed, and this characteristic did not change even when the potential limit was extended from 0.8 to 1.0 V (for simplicity not shown here).

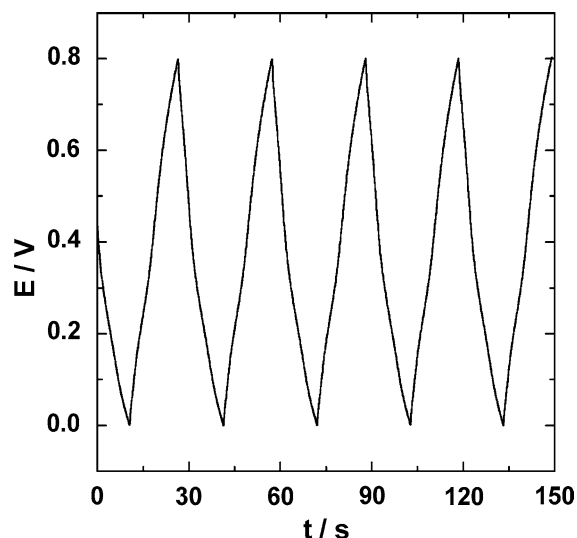


Fig. 8 Galvanostatic (current, $5 \times 10^{-5} \text{ A cm}^{-2}$) charging/discharging curves of a symmetrical electrochemical capacitor utilizing two glassy carbon slide electrodes modified with PEDOT-based (PMo_{12} -modified CSMPs containing) films (as for Fig. 4 and 7)

Under the current of Fig. 8, the average capacity determined in repeating cycles was not impressive, 0.6 mF cm^{-2} (it should be remembered that ultra-thin films of Fig. 4 were utilized), the present capacitor cell showed a sustained cycleability over a fairly long period of time (more than 1,000 cycles). Although no attempt was made to optimize the construction of our electrochemical capacitor, the parameters obtained here make the system potentially attractive for the accumulation of charge with the use of electrodes modified with hybrid conducting polymer films containing POM and dispersed carbon particles. The results should be improved by optimization of the thickness and morphology of the active material deposited on glassy carbon slides. Further research is along this line.

Electrocatalytic reduction of hydrogen peroxide

Hydrogen peroxide has been chosen as a model system to probe reductive electrocatalytic capabilities of the multilayer film composed of PMo_{12} -CSMPs dispersed

within PDDA (as for Fig. 5). We explore here the ability of the partially reduced PMo_{12} (to heteropolyblues) to catalyze the reduction of hydrogen peroxide [39]. Fig. 9a shows responses (recorded in the presence of hydrogen peroxide) of the films of the increasing thicknesses, i.e., increasing numbers of PMo_{12} -stabilized CSMPs and PDDA bilayers. It is noteworthy that bare ITO barely shows any electrocatalytic reactivity towards reduction of H_2O_2 (Fig. 9, curve a). The data of Fig. 9 are consistent with the increasing electrocatalytic reactivities of the films upon (a) increasing the film thickness (population of PMo_{12} redox centers) and (b) concentration of hydrogen peroxide in the solution. Although the multilayer hybrid film is not optimum here, at least in terms of the choice of conducting polymer matrix and population of PMo_{12} -stabilized CSMPs, the research seems to be of importance to the development of electrocatalytic (e.g., amperometric) sensors or biosensors and for the fuel cell technology.

Conclusions

Carbon particles are gradually divided via multiple treatments in PMo_{12} solutions. Subsequently produced carbon submicroparticles are stabilized through the adsorption of anionic PMo_{12} monolayers on their surfaces to form aqueous colloidal suspensions. The layer-by-layer method is successfully utilized to assemble PMo_{12} -modified particles within multilayer films (deposited on ITO or glassy carbon) composed of positively charged PDDA or PEDOT. Due to the presence of dispersed carbon particles, distribution of charge is facilitated in the films. Our preliminary results with microelectrochemical redox capacitor indicate that hybrid organic-inorganic films, in which electrical conductivity of carbon black is combined with high redox conductivity of PEDOT and reversible electrochemical behavior of PMo_{12} , could be considered as materials for electrochemical charging. Due to the presence of reactive PMo_{12} centers, electrocatalytic reduction of hydrogen peroxide at the polymer-based films containing PMo_{12} -modified CSMPs is feasible.

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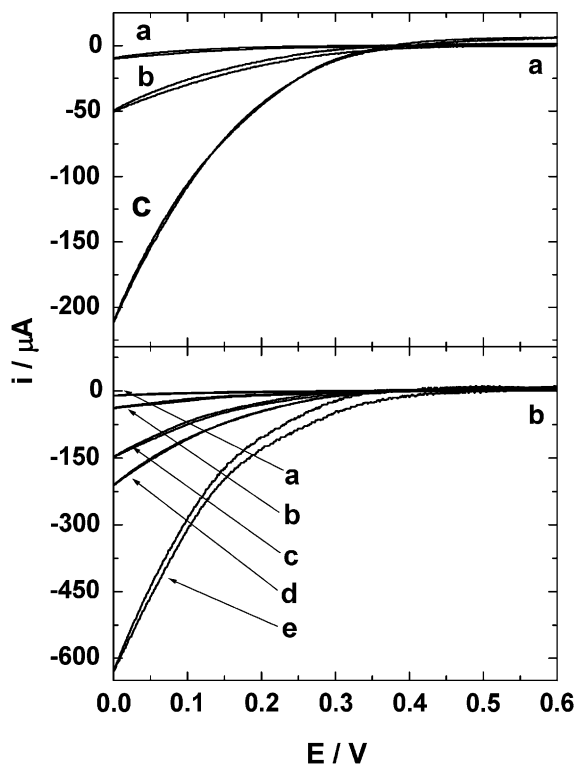


Fig. 9 Cyclic voltammetric responses for the electrocatalytic reduction of hydrogen peroxide at PDDA-based (PMo_{12} -modified CSMPs containing) films. **a** Dependencies of the electroreduction currents (H_2O_2 concentration, 0.01 mol dm^{-3}) on the loading PMo_{12} -modified CSMPs resulting from the deposition of **b** one and (c) seven layers of carbon particles; curve **a** shows response of bare ITO. **b** Dependencies of the currents on concentration of H_2O_2 : **b** 1×10^{-4} , **c** 1×10^{-3} ; **d** 1×10^{-2} , and **e** $1 \times 10^{-1} \text{ mol dm}^{-3}$ recorded for the film composed of six layers of PMo_{12} -modified CSMPs; curve **a** stands for the background response of the modified ITO electrode in the absence of H_2O_2 . Electrolyte: $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. Scan rate: 50 mV s^{-1}

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