Large scale load of phosphotungstic acid on multiwalled carbon nanotubes with a grafted poly(4-vinylpyridine) linker

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**Abstract**

Multiwalled carbon nanotubes (MWNTs) were grafted with poly(4-vinylpyridine) (PV4P) in aqueous solution by in situ free radical polymerization of 4-vinylpyridine. The as-prepared PV4P-g-MWNTs hybrids can load phosphotungstic acid (PW) on a large scale by electrostatic interaction, which was characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The as-prepared PWs/PV4P-g-MWNTs hybrids were modified onto a carbon glassy electrode. Cyclic voltammograms (CVs) show that the electrochemical behavior of the modified electrode follows a four-one-electron surface-confined process of Keggin-type PWs. The modified electrode can be used as a nitrite sensor. The comparison of CVs shows that the response current of nitrite reduction at the electrode modified with PWs/PV4P-g-MWNTs hybrids is 15 times higher than that of PWs/MWNTs hybrids in a control experiment at 0.65 V (vs. AgCl). The amperometric i-t curve for the electrode modified with PWs/PV4P-g-MWNTs hybrids exhibits a linear concentration of NO\textsubscript{2}\textsuperscript{-} ranged from 1.2 to 17.5 \(\mu\text{M}\) with a detection limit of 0.2 \(\mu\text{M}\).

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1. Introduction

Polyoxometalate (POM) is of considerable industrial and academic interest in virtue of its thermal stability, good solubility, strong acidity, nanoscopic discrete topology, and reversible multi-electron redox activity of electrochemistry and photochemistry [1], thus a recently increasing interest is focused on POM used as advanced material [2], such as catalyst [3], sensor [4,5], fuel cells [6], molecular conductors [7], proton memory devices [8] and solid-state electronic devices [9]. In terms of possible components for electrochemical devices, POM is a promising candidate due to its ability to act as an electron reservoir, and shift multi-electrons while retaining its structural integrity [10], which make it ideal for use in the electrochemical sensors of NO\textsubscript{2} [11], BrO\textsubscript{3}\textsuperscript{-}, IO\textsubscript{3}\textsuperscript{-} [12], H\textsubscript{2}O\textsubscript{2} [13], L-cystine, the coenzyme nicotinamide dinucleotide [14], and so on. Among them, nitrite is widely believed to be toxic and carcinogenic. It is present in rot vegetables and salted foods as metabolites of nitrate. Moreover, nitrite is often used as food additive. Thus, the monitoring or removal of nitrite is of great interest in food safety and medical diagnosis [15].

In order to fabricate the nitrite sensors based POM, it is necessary to immobilize POM onto the electrode surface. Since POM is polyanion, it can be immobilized or embedded in positive matrix, such as polymer [16–19], surfactant [20,21], mesoporous silicone [22], Langmuir–Blodgett films [23]. On the other hand, among a vast of supports for POM, carbon nanotubes (CNTs) are interesting and useful materials, indeed, they combine high electrical conductivity with mechanical strength and chemical inertness [24]. These unique properties make them ideal candidates for the electrochemical applications [25]. POM can be adsorbed spontaneously on graphite walls of carbon materials [12,26] including CNTs. However, those adsorbed POMs are uneven distributed onto the surface of CNTs, and prone to loose from the graphite walls of CNTs [27]. In addition, CNTs can be easily modified with positive molecules and polymers by covalent bond or noncovalent adsorption, thus the functional molecule and polymer can be served as positive linker to deposit POMs onto CNTs by electrostatic deposition [28–31]. However, to the best of our knowledge, few efforts have been reported as this strategy to fabricate POMs/CNTs hybrids.

Herein, we choose PV4P as linker to prepare POM/MWNTs hybrids based on electrostatic deposition. It is well known that PV4P is base, and POM is acid. The pyridine group of PV4P can accept proton from POMs to charge positive, and thus loads negative POMs onto MWNTs by electrostatic interaction.

PV4P can be grafted onto MWNTs by a free radical polymerization of 4-vinylpyridine [32]. The strategy was used in organic
solution as N,N-dimethylformamide (DMF), and thus, the strategy is less “green”. Therefore, we report a green approach to graft PV4P onto MWCNTs to load a large amount of PWs in aqueous solution. Moreover, a potential application is investigated in detail on the detection of the nitrite at the PWs/PV4P-g-MWCNTs hybrids modified electrode.

2. Experimental

2.1. Chemicals and materials

MWCNTs were obtained from Chengdu organic Chemics Co., Ltd. (purified >95% out diameter 10–20 nm, length ~30 μm) and purity [33] as follows: The raw MWCNT was sonicated in water for several minutes to disperse them, and then H2O2 (18%) solution was added. The mixed solution was boiled for several hours until the H2O2 was decomposed. Then, concentrated HCl was added and the solution was refluxed for 8 h to dissolve the metal particles inside the raw MWCNTs. After cooling and filtering through a 0.45 μm PTFE filter membrane, the filtered mass was collected and dried at 100 °C in vacuo.

4-Ethenylpyridine and PV4P (Mw. 20,000) was purchased from ACROS. The other chemicals were obtained from Shanghai Jingchun Co., Ltd., NaNO2, NaOH, and HCl solution was freshly prepared before use. Water was purified by a Milli-Q system.

2.2. Preparation of PV4P-g-MWCNTs hybrids

A 100 mL flask was charged with a magnetic bar, 45 mg of MWCNTs, 1.8 mL of 4-ethenylpyridine and 60 mL of water. This mixture solution was flushed with nitrogen for 15 min, sonicated for 30 min and then stirred at room temperature for 12 h. 4-Ethenylpyridine started polymerization under continuous stirring at 65 °C after 18 mg K2S2O8 was added. This reaction was stopped after 48 h, when the mixture was cooled to room temperature. PV4P-g-MWCNTs hybrids were obtained from the sediment by dumping off the supernatant. In order to remove free PV4P, PV4P-g-MWCNTs hybrids were dispersed in 1 M HCl solution under 30 min ultrasonication, and centrifuged at 13,000 rpm for 1.5 h. This procedure was repeated thrice. PV4P-g-MWCNTs hybrids were neutralized by 1 M NaOH, recovered by centrifuging at 3000 rpm, rinsed with alcohol at least for twice, and dried in vacuum for 48 h at 100 °C before characterization.

2.3. Preparation of PWs/PV4P-g-MWCNTs hybrids

5 mg PW and 5 mg PV4P-g-MWCNTs hybrids were sonicated and dispersed in 5 mL water. PWs will be deposited onto MWCNTs by electrostatic interaction with PV4P linker. The mixture solution was centrifuged, and the unsorbed PW solution was dumped off. PWs/PV4P-g-MWCNTs hybrids were collected from centrifugal content, rinsed with water and ethanol at least for twice, and dried in vacuum for 48 h at 100 °C before characterization.

2.4. Preparation of PWs/MWCNTs hybrids

The PWs/MWCNTs hybrids were prepared according to the report of Ref. [34]. 4 mg MWCNTs were added to 1.0 mM PWs aqueous solution (20 mL), and sonicated for 15 h in an ice water bath. After sonication, an inky and stable suspension was obtained. This suspension was centrifuged to remove insoluble amorphous carbon, and the supernatant was filtered through PTFE filter to remove free PW and catalyst metal salts, and then the filter residues were rinsed with water and acetone to remove the adsorbed PW. PWs/MWCNTs hybrids were collected by centrifugation, and dried in vacuum for 48 h at 100 °C before characterization.

2.5. Preparation of PWs/PV4P hybrids

1 mg PW and 1 mg PV4P were sonicated and dispersed in 5 mL water. PWs will be combined with PV4P by electrostatic interaction. The mixture solution was centrifuged, and the unsorbed PW solution was dumped off. PWs/PV4P hybrids were collected from centrifugal content, rinsed with water and ethanol at least for twice, and dried in vacuum for 48 h at 100 °C before characterization.

2.6. Characterization

Fourier transform infrared spectroscopy (FT-IR) was recorded on a Nicolet NEXUS70 spectrometer after baseline-correct. Thermogravimetric analysis (TGA) was recorded on Netzsch STA 449C analyzer at a heating rate of 10 °C/min under nitrogen. X-ray photoelectron spectroscopy (XPS) was recorded on an ESCALAB-MKII spectrometer with an unmonochromated Al Kα X-ray source (1486.6 eV) for excitation at a base pressure of 1 × 10−6 Torr. High-resolution spectra, at an energy resolution of 0.85 eV, were obtained at a perpendicular takeoff angle, using the pass energy of 20 and 0.05 eV steps.

Scanning electron microscopy (SEM) observation was performed on a Hitachi S-4800 scanning electron microscope operated at an accelerating voltage of 5 kV.

Transmission electron microscopy (TEM) observation was performed on a JEOL 1000 microscope equipped with a CCD camera, operating at 200 kV using a high-brightness LaB6 electron gun.

2.7. Electrochemical investigation

We used a 15 mL glass electrochemical cell containing three electrodes: (1) a glassy carbon disk working electrode (3 mm in diameter) embedded in Teflon, (2) a platinum wire counter electrode, and (3) a saturated KCl Ag/AgCl electrode as the reference electrode. Before use, glassy carbon electrodes were polished with 0.5 μm alumina, washed with double-distilled water, then immersed for 20 min in a sonicator bath, and finally washed in double-distilled water.

To modify the glassy carbon electrode with MWCNTs, PWs/MWCNTs, PWs/PV4P or PWs/PV4P-g-MWCNTs hybrids, 1.0 mg of these materials were dispersed in 100 μL of the de-ionized water, and then a 2.5 μL of this suspensions solution was mixed with a 2.5 μL of Nafion® 117. The mixture was spread and air-dried on a glassy carbon electrode at room temperature.

A three-electrode setup was configured with CHI 660C interfaced to a personal computer at room temperature for the electrochemical characterization of as-prepared modified glassy carbon electrode. The electrolytic solution was bubbled with nitrogen for 15 min before electrochemical experiment.

3. Results and discussion

3.1. Characterization of PV4P-g-MWCNTs hybrids

The PV4P-g-MWCNTs hybrids were prepared by free-radical polymerization of 4-vinylpyridine on the surface of MWCNTs with K2S2O8 as a radical initiator in aqueous solution. Free PV4P and residual catalyst were removed by a series of centrifugation and decantation steps. The procedure was similar to that used for grafting poly(sodium 4-styrenesulfonate) to single walled carbon nanotubes (SWCNTs) in water [35]. In contrast to neat MWCNTs, PV4P-g-MWCNTs hybrids can be easily dispersed in acid water after protonation. As shown in Fig. 1Aa, 0.05 wt% MWCNTs are precipitated in 1 M HCl solution after 30 min ultrasonication. However, 0.05 wt% PV4P-g-MWCNTs hybrids are well dispersed in 1 M HCl
solution even for 6 months under the same conditions (Fig. 1Ab). The result indicates that surface modification of MWCNTs has significant influence on the stability and dispersion of MWCNTs in acid solution. In order to make it clear that the PV4P was not adsorbed onto the surface of MWCNTs via $\pi-\pi$ interaction, but grafted to the surface of MWCNTs with covalent bond during polymerization, a control experiment was carried out. MWCNTs (1 mg) were precipitated after 30 minutes ultrasonication in 1 mL of 1 M HCl solution containing 200 mg PV4P. The result indicated that the ungrafted PV4P failed to disperse and stabilize MWCNTs in 1 M HCl solution [32].

The FT-IR spectra of PV4P-g-MWCNTs hybrids are shown in Fig. 1B in comparison with those of MWCNTs and PV4P, the absorptions of 1597, 1556 and 1415 cm$^{-1}$, present at FT-IR spectra of PV4P-g-MWCNTs hybrids and PV4P, can be assigned to the ring vibration of pyridine group in PV4P [32], indicating PV4P has been grafted to the surface of MWCNTs. The broad peak at 1636 cm$^{-1}$, present at FT-IR spectra of MWCNTs and PV4P-g-MWCNTs hybrids, is due to stretch vibration of carbonyl group, which resulted from MWCNTs purification [36].

The morphology of PV4P-g-MWCNTs hybrids and MWCNTs was investigated by SEM and TEM as shown in Fig. 2. MWCNTs are clean,
and the diameter of MWCNTs is estimated to be ca. 10–20 nm. After the PV4P was grafted to the MWCNTs, MWCNTs were wrapped in a thick layer of PV4P, and the thickness of PV4P layer is estimated to be ca. 2–5 nm.

3.2. Characterization of PWs/PV4P-g-MWCNTs hybrids

The PWs/PV4P-g-MWCNTs hybrids were prepared by electrostatic interaction of negative PWs and protonated PV4P grafted to MWCNTs, which was investigated by FT-IR in Fig. 3A. The FT-IR spectra of PWs/PV4P-g-MWCNTs hybrids were compared with those of pure PWs. As shown in Fig. 3Aa, the FT-IR characteristic bands of PWs/PV4P-g-MWCNTs hybrids at 1081, 895, 892 and 813 cm\(^{-1}\) are ascribed to the band vibration of P–W, W–O, W–O–Wcorner (i.e., between the corner-sharing WO\(_6\) octahedra) and W–O–Wedge (i.e., between the edge-sharing WO\(_6\) octahedra) [37], respectively, indicating that the primary Keggin PWs was presented in the hybrids frameworks. On the other hand, the PWs/PV4P-g-MWCNTs hybrids exhibit a red shift in spectra by 4–6 cm\(^{-1}\) compared with those of pure PWs, as shown in Fig. 3Ab, which is attributed to the strong linkage of PW clusters to the grafted PV4P matrix.

The mass ratio of PWs loaded onto MWCNTs in PV4P-g-MWCNTs hybrids was investigated in the nitrogen atmosphere by TGA (Fig. 3) and their results were listed in Table 1. Fig. 3B shows TG curves for PWs/PV4P-g-MWCNTs hybrids as well as the reference substances, MWCNTs, PV4P and PV4P-g-MWCNTs hybrids. The weight loss observed in the temperature range of 30–100 °C is due to the release of adsorbed water in MWCNTs, PV4P and PV4P-g-MWCNTs hybrids. A small weight loss present at TG curve of PV4P started at 142 °C is attributed to the degradation of PV4P oligomers (Fig. 3B). In 150–800 °C interval of the temperature, the MWCNTs remained stable, no further weight loss is observed (Fig. 3B), whereas PV4P-g-MWCNTs hybrids and PV4P started to degrade at the temperature of less than 350 °C, and continued to lose weight up to 430 °C (Fig. 3Bb and c) [32]. The water loss of PWs/PV4P-g-MWCNTs hybrids is observed at 30 °C, but up to 150 °C. PV4P degradation occurred at 350 °C, but lasted up to 500 °C. A new slow weight loss started at 530 °C, and continued to 740 °C, which is attributed to the decomposition of PWs cluster.

The XPS survey profiles of MWCNTs, PV4P-g-MWCNTs and PWs/PV4P-g-MWCNTs hybrids were shown in Fig. 4A. A 4f signal arises in the range from 33 to 40 eV (Fig. 4B), indicating PWs present in PV4P-g-MWCNTs hybrids. C 1s spectrum has its main features at 284.3 eV, as shown in Fig. 4Ca, which originated from sp\(^2\) carbon atoms of MWCNTs backbone, and its low shoulder peak is generated from carbon atoms in oxygenated groups: hydroxyl (component centered at 286.2 eV) and carbonyl (287.2 eV) [38]. After PV4P was grafted onto MWCNTs, a new shoulder peak upgrades at 286.2 eV (Fig. 3Bb), which is assigned to C–N bond of pyridine group at PV4P chains. These shoulder peak of PWs/PV4P-g-MWCNTs hybrids became much lower than that of PV4P-g-MWCNTs hybrids, which can be interpreted as the block-off of C 1s signal at 286.2 eV from PWs layer. N 1s signal of PV4P-g-MWCNTs hybrids can be observed at ca. 400 eV (Fig. 3Bb), where no obvious N 1s signal is present at PWs/PV4P-g-MWCNTs hybrids (Fig. 3C), indicating that N 1s signal is screen off by PWs (Fig. 3D). The O 1s signal of MWCNTs is dominant at 532.5 eV (Fig. 3Ea), which resulted from the purification of MWCNTs. By comparison with that of MWCNTs, the O 1s signal of PV4P-g-MWCNTs hybrids is much lower (Fig. 3Eb). As discussed above, the O 1s signal is diminished signal of PWs. After PWs were deposited onto PV4P-g-MWCNTs hybrids, the O 1s signal of PWs/PV4P-g-MWCNTs hybrids intensified and located at 531.0 eV (Fig. 3Ec). This O 1s signal is mainly derived from the group W–O of PWs, which accounted for the intensification of O 1s signal at XPS curve of PWs/PV4P-g-MWCNTs hybrids.

The structure of PWs/PV4P-g-MWCNTs hybrids was investigated by TEM as shown in Fig. 5A and B. MWCNTs were enwrapped by the thick matrix of PWs and PV4P, which made a faint to the observation on the walled structure of MWCNTs. The diameter of PWs/PV4P-g-MWCNTs hybrids is estimated to be 15–30 nm, and as a result of PV4P grafted and PW loads, the thickness of MWCNTs is increased by ca. 5–10 nm (Fig. 5A). The high-resolution micrograph reveals that PWs are well-distributed in the PV4P layers, not aggregated on the surface of MWCNTs (Fig. 5B). It should be noted that PWs will remain in the PV4P layers even after multiple rinses with water and ethanol, which can be ascribed to the electrostatic interaction between PWs and PV4P. For comparison, the structure of PWs/MWCNTs hybrids was also investigated by TEM as shown in Fig. 5C and D. PWs/MWCNTs hybrids are smooth free of particles deposition and polymer wrap (Fig. 5C). The diameter of PWs/MWCNTs hybrids is estimated to be ca. 10–20 nm, close to the value of net MWCNTs. The high-resolution micrograph reveals few

Table 1
The composition of samples determined by TGA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PWs (wt%)</th>
<th>PV4P (wt%)</th>
<th>MWCNT (wt%)</th>
<th>H2O (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWs/PV4P-g-MWCNTs</td>
<td>39.0%</td>
<td>14.1%</td>
<td>36.9%</td>
<td>10.0%</td>
</tr>
<tr>
<td>PW4P-g-MWCNTs</td>
<td>54.4%</td>
<td>43.3%</td>
<td>2.3%</td>
<td>4.0%</td>
</tr>
<tr>
<td>PV4P</td>
<td>94.8%</td>
<td>2.5%</td>
<td>0.5%</td>
<td></td>
</tr>
<tr>
<td>MWCNT</td>
<td>99.5%</td>
<td>0.5%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
PWs on the surface of MWCNTs. It has been reported that MWCNTs can be solublized and functionalized by PWs [34]. However, these PWs will be desorbed from MWCNTs in the process of rinse, because they were deposited onto MWCNTs by weak molecular interaction of PWs and MWCNTs. The result confirmed that the positive PV4P can be served as an effective polymer linker to load the negative PW onto the surfaces of MWCNTs by electrostatic adsorption.

3.3. Electrochemical investigate of PWs/PV4P-g-MWCNTs hybrids

PW is electroactive, it is capable of 3–4 electron transfer. Fig. 6 shows cyclic voltammograms (CVs) of the glassy-carbon electrode modified with PWs/PV4P-g-MWCNTs hybrids at different scan rates in N2-saturated 0.5 M H2SO4 solution. The electrode modified with PWs/PV4P-g-MWCNTs hybrids exhibits four redox couples at the formal potential of 0.062, −0.20, −0.31 and −0.61 V, respectively, which are corresponding to four one-electron processes of the Keggin-type PWs [39,40]. The redox couple peaks (II) and (III) are overlapped, and the peaks (I) and (IV) are well separated. As shown in Fig. 6 inset, the plots of the anodic and cathodic currents of the peaks (IV) are linear against the scan rate, indicating a surface-confined redox process for the electrode modified with PWs/PV4P-g-MWCNTs hybrids in N2-saturated 1.0 M H2SO4 solution [41].

As shown in Fig. 7, the effects of pH on the electrochemical behaviors of PWs/PV4P-g-MWCNTs hybrids were studied by
recording CVs in different pH solution which is determined by a pH meter. As pH value increased from −0.30 to 2, the redox peaks (I) and (IV) current decreased, while the ones (II) and (III) increased. The redox peaks (II) and (III) are well refined and well distinguished during pH value range from 0.70 to 1, indicating that a fast and reversible electron transfer occurred at the redox peaks (II) and (III) in this pH interval. The CVs at pH 2.0 is similar to that at pH 3.0, while the current of CVs at pH 3.0 decreased, which resulted from the PWs desorption off PV4P-g-MWCNTs hybrids when pH is higher than 0.2. On the other hand, the pH value of solution had significant influence on the peaks potential, especially peaks (III), which will shift negatively by increasing pH from −0.30 to 2. The average of the anodic and the cathodic peak potentials was estimated as the formal potential. The dependence of the formal potentials (III) on pH value was shown in Fig. 7 inset, the slopes of formal potential vs.

pH in this pH range is 0.061 V pH−1, which is close to the theoretical value of 0.059 V pH−1 for the 1e−/1H+ redox process.

3.4. Electrocatalytic reduction of nitrite at PWs/PV4P-g-MWCNTs hybrids modified electrode

To illustrate the potential use of PWs/PV4P-g-MWCNTs hybrids in the electrochemical sensors, the reduction of nitrite was evaluated as the electrocatalytic activity of the glassy carbon electrode modified with PWs/PV4P-g-MWCNTs hybrids.

Fig. 8 depicts the comparison on the CVs of the electrode modified MWCNTs, PWs/MWCNTs and PWs/PV4P-g-MWCNTs hybrids responding to 5 mM NO2−. On the CVs of the electrode modified with PWs/PV4P-g-MWCNTs hybrids (Fig. 8Aa and b), a reductive
current wave of NO\textsubscript{2} starts at ca. 0.54 V, and increases rapidly when the applied potential shifts negatively from 0.54 V to −0.80 V, indicating that the catalytic process of NO\textsubscript{2} reduction is dependent on the applied potential of the modified electrode. No obvious characteristic PWs is present on the CVs of the electrode modified with PWs/MWCNTs hybrids (Fig. 8Ba), indicating that few PWs were deposited onto MWCNTs for this modified electrode, which is consistent with TEM observation. The reduction of NO\textsubscript{2} occurred at ca. −0.20 V (Fig. 8Bb), which is lower than that of PWs/PV4P-g-MWCNTS hybrids by 0.74 V. Moreover, the response current of NO\textsubscript{2} reduction is 15 times less than that of PWs/PV4P-g-MWCNTS hybrids at 0.65 V. In order to make clear that the role of PV4P for PWs immobilization and the effect of PWs for NO\textsubscript{2} detection, a PWs/PV4P hybrids modified electrode was prepared. Fig. 8Ca shows its CV characteristic with a Keggin PW in 0.5 M N\textsubscript{2}-saturated H\textsubscript{2}SO\textsubscript{4} solution. Fig. 8Cb reveals its CV similar to that of PWs/PV4P-g-MWCNTS hybrids when NO\textsubscript{2} was added, indicating that PV4P served as PW linker and the reductive current originated from the catalytic effect of PW. On the other hand, this reductive current of NO\textsubscript{2} is much lower than that of PWs/PV4P-g-MWCNTS hybrids, reflecting that MWCNTs can enhance the catalytic effect of NO\textsubscript{2} due to its high conductivity and surface area. For comparison, the bare electrode is also studied, no obvious current response was observed when 5 mM NO\textsubscript{2} was introduced (Fig. 8Da and b). The results demonstrated that PWs/PV4P-g-MWCNTS hybrids have the advantages over PWs/MWCNTS hybrids and MWCNTS on the response of NO\textsubscript{2} in two aspects: the higher sensitivity and the lower overpotential.

As shown in Fig. 9, the potential of the amperometric i-t curve is optimized at 0.65 V for the detection of NO\textsubscript{2}, and the response current of nitrite reduction increased in N\textsubscript{2}-saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} solution upon successive addition of 1.25 μM NO\textsubscript{2}. Fig. 9 inset shows that a linear relationship of the NO\textsubscript{2} concentration ranged from 1.2 to 17.5 μM was obtained at the electrode modified with PWs/PV4P-g-MWCNTS hybrids, over the range, the higher concentration of NO\textsubscript{2} produce a negative deviation from linearity due to diffusion obstacle of NO\textsubscript{2}. The detection limit valued by signal-to-noise ratio, is 0.2 μM, which is much lower than those of 0.1 mM.
reported for the carbon paste electrode modified with polyoxometalate/bacterial cellulose composite [17].

3.5. Electrochemical stability of PWs/PV4P-g-MWCNTs hybrids modified electrode

The PWs/PV4P-g-MWCNTs hybrids modified electrode kept remarkably stable under operation and storage. The operational stability of the modified electrode was measured by the same modified electrode under continuous response to N2-saturated 0.5 M H2SO4 solution in the presence of 1.25 μM NO3-. There is 1.0% relative standard deviation for 7 successive determinations. The storage stability of the modified electrode was also investigated, and the response current for 15 days remained at 90.2% value of initial response after stored at 4 °C in N2-saturated 0.5 M H2SO4 solution.

4. Conclusion

Overall, PV4P-g-MWCNTs hybrids were synthesized in aqueous solution, and the PV4P was grafted to MWCNTs by in situ free radical polymerization. PV4P can be protonated, and thus PV4P-g-MWCNTs hybrids can be easily dispersed and stabilized in aqueous solution. As a positive linker, PV4P can be used to immobilize negative PW onto MWCNTs by electrostatic interaction and the as-prepared PWs/PV4P-g-MWCNTs hybrids show four-one-electron surface processes of Keggin-type PW. A potential application for PWs/PV4P-g-MWCNTs hybrids was demonstrated in the detection of toxic and carcinogen NO3-, and the electrochemical study shows that PWs/PV4P-g-MWCNTs hybrids can efficiently catalyze on the reduction of NO3-, which suggests a promising candidate for NO2 sensor in food safety and medical diagnosis.

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