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Studies on phase and morphological evolution of silver vanadium oxides as a function of pH: evaluation of electrochemical behavior towards quantification of Pb^{2+} and Cd^{2+} ions

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Abstract

The effect of pH on morphological and phase evolution of silver vanadium oxide nanostructures are investigated under hydrothermal process. The results of powder x-ray diffraction (PXRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) disclosed that the morphological evolution of nanobelts into nanoring structures occurs at pH in between 4 and 5 with $\text{Ag}_2\text{V}_4\text{O}_{11}$ phase and nanobelt morphologies at pH from 6 to 7 with $\beta\text{-AgVO}_3$ phase. The prepared $\text{Ag}_2\text{V}_4\text{O}_{11}$ and $\beta\text{-AgVO}_3$ have been evaluated for the simultaneous quantification of Pb^{2+} and Cd^{2+} ions in aqueous solution using differential pulse anodic stripping voltammetry. The results reveal that $\text{Ag}_2\text{V}_4\text{O}_{11}$ shows better quantification result compared to $\beta\text{-AgVO}_3$.

1. Introduction

Silver vanadium oxides (SVO's) nanostructured materials, as one of the important group of ternary metal vanadates have drawn considerable research interest due to their potential applications in lithium batteries, photocatalysts, gas sensors, micro devices and bacterial inactivation owing to their unique electrochemical, ionic, catalytic, electrical, and anti-microbial properties [1–5]. Among SVO's, $\text{Ag}_2\text{V}_4\text{O}_{11}$ and $\beta\text{-AgVO}_3$ are known to be potential cathode materials for lithium batteries because of their high energy densities and long-term structural and chemical stabilities [6–8].

In the past decade, electrode modification with nanostructured materials for the detection of biomolecules and heavy metal ions have drawn extensive attention over conventional macro electrodes. This is because of their effective surface area, increased electroactive surface sites, enhanced mass transport, which in turn offer significant improvement in the sensitivity and selectivity of targeted species [9–12]. Very recently, metal vanadate nanostructures have been successfully employed as glassy carbon electrode (GCE) modifiers for the detection of biomolecules. For instance, Pei *et al.* reported the electrochemical determination of ascorbic acid, L-cysteine and tartaric acid by using copper vanadate nanobelts, manganese vanadate nanorods and calcium vanadate nanorods modified GCE, respectively [13–15]. As far as our knowledge concerned, the electrochemical detection of heavy metal ions using $\text{Ag}_2\text{V}_4\text{O}_{11}$ and $\beta\text{-AgVO}_3$ has not been reported in the literature.

In this context, significant effort has been focused on controlling the morphology and microstructure of $\text{Ag}_2\text{V}_4\text{O}_{11}$ and $\beta\text{-AgVO}_3$, which facilitates to tune and optimize the material properties. Hydrothermal approach is one of the well-known synthetic routes to fabricate $\text{Ag}_2\text{V}_4\text{O}_{11}$ and $\beta\text{-AgVO}_3$ nanostructures, where size and shape with desired chemical composition and crystal structure will be tuned by optimizing the processing parameters such as reaction time, temperature, precursor concentration, pH of the precursor solution, and surfactants/additives [5, 16–21]. Vanadium in its higher oxidation state (V^{5+}) gives variety of polyoxovanadate ions with different coordination geometries at different pHs [22, 23]. The effect of pH on morphological and phase evolution of silver vanadates is first of its kind studies carried out in the present investigation. The fundamental questions to be addressed in this research work have mainly originated from a recent research finding from our

own group [24, 25]. Therefore, we have attempted to investigate the effect of pH on the phase and morphological evolution of $\text{Ag}_2\text{V}_4\text{O}_{11}$ and $\beta\text{-AgVO}_3$ under hydrothermal process. To understand the electrochemical behavior, the prepared $\text{Ag}_2\text{V}_4\text{O}_{11}$ and $\beta\text{-AgVO}_3$ have been used as GCE modifier in the quantification of Pb^{2+} and Cd^{2+} ions in aqueous solution.

2. Experimental section

2.1. Synthesis of silver vanadium oxides

In a typical synthetic process, 0.1819 g (1 mmol) of V_2O_5 powder was dissolved in 1 ml H_2O_2 (30%) and then it was diluted to 40 ml with distilled water. To this, 0.1699 g (1 mmol) of AgNO_3 was added and subjected for gentle stirring for 30 min. During this process, pH of the solution was adjusted to a specific value from 1 to 10 by adding 25% aqueous ammonia solution. At last, the resulting solution was transferred to a Teflon-lined stainless steel autoclave of volume capacity of 60 ml. The autoclave was sealed and kept in preheated hot air oven at 180 °C for 24 h. The products formed during the hydrothermal reaction were collected by centrifugation and washed thoroughly with distilled water followed by ethanol and finally dried in air at 70 °C for 8 h.

2.2. Electrode preparation

All solutions were prepared with distilled water with resistance not less than 18.2 M Ω cm. Initially, the GCE was mechanically polished with alumina slurry of different grades to mirror finish then rinsed and sonicated for about 3 min in distilled water followed by ethanol. Then, 5 mg of $\text{Ag}_2\text{V}_4\text{O}_{11}$ was dispersed in 5 ml distilled water by ultra-sonication for about 10 min to give a homogeneous suspension. Subsequently, the dispersed suspension (5 μl) was drop casted on the surface of the GCE and allowed to evaporate at room temperature for overnight. The $\beta\text{-AgVO}_3$ modified GCE was similarly prepared by the same procedure.

2.3. Analytical procedure

Electrochemical measurements of Pb^{2+} and Cd^{2+} ions were carried out using cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV) in the potential range -1.0 to 0.0 V with amplitude of 0.01 V and pulse width of 0.05 s. Known amounts of the analytes were taken in 10 ml electrochemical cell. The $\text{Ag}_2\text{V}_4\text{O}_{11}$ modified electrode was immersed into the cell containing 0.1 M KNO_3 , acetate buffer solution with pH of 5 and target metal ions, which were stirred for 3 min to pre-concentrate the metal ions at open circuit potential. Then, the pre-concentrated metal ions were reduced at a reduction potential of -1.2 V and subsequently stripped off from the electrode surface into the bulk of the electrolytic solution by sweeping the potential in the positive direction after 30 s of equilibration time.

2.4. Instrumentation

The identification of the phases was carried out by Panalytical X'Pert Pro MPD powder x-ray diffractometer (PXRD) using $\text{Cu-K}\alpha$ radiation at $\lambda = 1.5418$ Å. A software database published by the joint committee on powder diffraction standards (JCPDS) was used to analyze the x-ray diffractograms. Surface morphology and microstructure studies were carried out using a scanning electron microscope (SEM) (VEGA3 TESCAN) and transmission electron microscopy (TEM) (JEOL JEM-2100). Surface chemical composition and chemical states were identified by x-ray photo electron spectroscopy (XPS) (Thermo Fisher Scientific ESCLAB 250). Electrochemical measurements were carried out using electrochemical work station (CH Instruments, Texas, USA, model: CHI 619B) at room temperature with a standard three electrode configuration where modified GCE acts as working electrode, a platinum wire acts as counter electrode and Ag/AgCl acts as the reference electrode. The pH measurements were carried out using pH meter (Control Dynamics, Mumbai, India model: APX 175).

3. Results and discussion

The effect of pH on the phase formation and the morphology evolution under hydrothermal condition at 180 °C for 24 h by varying pH from 1 to 10 has been investigated using PXRD and SEM techniques. The PXRD patterns of the products prepared at various pHs from 1 to 9 are shown in figures 1(a)–(i). The products prepared (figures 1(a)–(c)) at pH of 1 to 3, exhibit an emerging of monoclinic $\text{Ag}_2\text{V}_4\text{O}_{11}$ phase (JCPDS 49-0166) with noticeable diffraction peaks. For the products prepared at pH of 4 and 5 display monoclinic $\text{Ag}_2\text{V}_4\text{O}_{11}$ phase as shown in figures 1(d), (figure S1 (stacks.iop.org/MRX/4/085039/mmedia)) and (e). Whereas, $\beta\text{-AgVO}_3$ phase was obtained when the pH is increased to 6 and 7 as shown in figures 1(f) and (g). Further increase in pH to 8 and 9, all the diffraction peaks (figures 1(h) and (i)) could be indexed to the $\beta\text{-AgVO}_3$ phase. As pH surpassed 10, there is no formation of the product. Therefore, it is clear that monoclinic $\text{Ag}_2\text{V}_4\text{O}_{11}$ phase was evolved between pH of 4 and 5. $\beta\text{-AgVO}_3$ phase was formed between pH of 6 and 9. The overall results of phase and morphology of synthesized products as a function of pH are summarized in table S1.

Figure 1. PXRD patterns of the products synthesized at different pHs.

SEM images of synthesized products at various pHs under hydrothermal condition of 180 °C for 24 h has been investigated and the results are shown in figure 2. SEM images of the products prepared at pH of 1 and 2 (figures 2(a) and (b)) reveal that the products consist of aggregated nanobelt-like morphology. Well defined nanobelts having different widths and lengths of several tens of micrometers are observed when the product is prepared at the pH of 3 (figure 2(c)). As the pH increased to 4 and 5, the obtained products are mainly composed of nanobelts with considerable amount of nanoring structures (figures 2(d) and (e)). The detailed information of the interesting nanoring morphologies of $\text{Ag}_2\text{V}_4\text{O}_{11}$ has been discussed and the results are shown in figures 3 and S2. The SEM images of typical nanoring structures of $\text{Ag}_2\text{V}_4\text{O}_{11}$ obtained at pH of 4 and 5 are shown in figures 3 and S2, respectively. The nanobelts having width of 150–400 nm, thickness of about 50–80 nm, and typical length up to several micrometers are observed. The observed nanorings are in circular shape with smooth and flat surfaces, whose diameters are in the range of 3.0 μm –6.0 μm . The SEM images showed that there appear three typical forms of nanoring structures in the products: free standing circular rings, tape-like ring structures, and loop-like ring structures. The earlier report on $\text{Ag}_2\text{V}_4\text{O}_{11}$ rings showed the formation of perfect free-standing rings, micro loops with uniform and varied diameters [21]. Different from that report, tape-like ring structures and micro loops with uniform diameters are observed in the present experiment. The morphology of the products composed of only nanobelts when the pH increases to 6 and 7 (figures 2(f) and (g)). When the pH further increased to 8 and 9 nano/micro belts were observed (figures 2(h) and (i)). The performed phase and morphological investigations at various pHs revealed that the morphological evolution of nanobelts to nanoring structures occurs at pH of 4 and 5 for $\text{Ag}_2\text{V}_4\text{O}_{11}$ and nanobelts for $\beta\text{-AgVO}_3$ at pH of 6 and 7.

Effect of reaction time on the product formation has been investigated. On performing the hydrothermal reaction for different intervals of time with pH from 6 to 9, it is noticed that the formation of phase pure $\beta\text{-AgVO}_3$ with well-defined nanobelt morphology appears at pH of 6 for the duration of 3 h (figures 4(a) and (b)). Figure 4(b) presents the high-magnification SEM image, shows that the thickness and width of nanobelts are 40–50 nm and 170–200 nm, respectively, with length up to several micrometers. With prolonged hydrothermal treatment, there is no obvious change in phase and morphology of the $\beta\text{-AgVO}_3$. This indicates that $\beta\text{-AgVO}_3$ phase with nanobelt morphology can form quickly and retains the same features during further hydrothermal treatment. As noted from literature survey, there is a report of synthesis of $\beta\text{-AgVO}_3$ in the form of nanoribbons by pyridine assisted hydrothermal route at 180 °C for 3 h [16] and another report of hydrothermal synthesis of $\beta\text{-AgVO}_3$ nanobelts at 150 °C for 4 h [26].

The morphology and structure of the $\text{Ag}_2\text{V}_4\text{O}_{11}$ and $\beta\text{-AgVO}_3$ prepared at pH of 4, and pH of 6 for 3 h respectively, were further investigated by TEM and HRTEM analysis. Figures 5(a)–(c) displays the TEM images

Figure 2. SEM images of the products synthesized at (a) pH = 1, (b) pH = 2, (c) pH = 3, (d) pH = 4, (e) pH = 5, (f) pH = 6, (g) pH = 7, (h) pH = 8, and (i) pH = 9.

Figure 3. SEM images of typical nanoring structures of $\text{Ag}_2\text{V}_4\text{O}_{11}$ obtained at pH of 4: (a) free standing circular ring, (b) loop-like ring structure, and (c) tape-like ring structures.

of $\text{Ag}_2\text{V}_4\text{O}_{11}$ nanobelts and rings. TEM image of $\text{Ag}_2\text{V}_4\text{O}_{11}$ nanobelts (figure 5(a)) shows that the width of the individual nanobelts around 150–300 nm with length up to several micrometers. Figures 5(b) and (c) depict the loop-like, and tape-like ring structures of $\text{Ag}_2\text{V}_4\text{O}_{11}$, respectively. Figure 5(d) is a representative of HRTEM image of a single nanobelt, exhibits crystalline structure and clear lattice fringes. The interplanar spacing can readily be resolved to 5.9 Å, corresponding to the (20 $\bar{1}$) plane of $\text{Ag}_2\text{V}_4\text{O}_{11}$. Combined with the SAED pattern recorded on an individual nanobelt, it is revealed that the as-prepared nanobelts oriented along the [30 $\bar{2}$] crystal plane. Figure 6(a) displays the high-magnification TEM image of $\beta\text{-AgVO}_3$ nanobelts prepared at pH of 6 for 3 h, shows that the width of the individual nanobelts around 160–180 nm with length up to several micrometers and it can be observed that the presence of some tiny particles with the diameter of 20–30 nm on the surface of $\beta\text{-AgVO}_3$ nanobelts. The appearance of these nanoparticles is due to decomposition of $\beta\text{-AgVO}_3$ during the bombardment of high energy electron beam in the process of TEM analysis [27]. Figure 6(b) shows the typical HRTEM image and SAED patterns of an individual $\beta\text{-AgVO}_3$ nanobelt. The lattice fringes with interplanar distance of 3.07 Å matches well with the d_{310} lattice spacing of $\beta\text{-AgVO}_3$ phase. In addition, the lattice fringes with interplanar

Figure 4. High magnification SEM image (a) and PXRD pattern (b) of the product prepared at pH of 6 for the time interval of 3 h.

Figure 5. TEM images of (a) nanobelts, (b) loop-like ring morphology, and (c) tape-like ring morphologies of Ag₂V₄O₁₁ synthesized at pH of 4 and (d) representative HRTEM image of single nanobelt with SAED pattern.

distance of 2.38 Å is corresponding to d_{111} of the Ag phase (JCPDS 04-0783), formation of which can be ascribed to the bombardment of high electron beam during TEM characterization.

The XPS analysis was performed to evaluate the surface chemical composition and purity of the product, and to explore the valence state of silver and vanadium in the product. Figure 7(a) represents the XPS survey spectrum of the product obtained at pH of 4, which revealed that the surface is composed of C, O, V, and Ag, depicting the purity of the product. The XPS spectrum (figure 7(b)) of Ag 3d region shows two strong peaks at 367.5 eV and 373.4 eV, which are ascribed to binding energies of Ag 3d_{5/2} and Ag 3d_{3/2} of Ag⁺ state, indicating the valence state

Figure 6. TEM image of (a) nanobelts of β -AgVO₃ synthesized at pH of 6 for 3 h and (b) corresponding HRTEM image of nanobelt with SAED pattern.

of silver is +1 in the obtained product. Figure 7(c) depicts two peaks at 516.9 eV, and 524.4 eV respectively, corresponding to V 2p_{3/2} and V 2p_{1/2} of V⁵⁺. Figure 8(a) illustrates the XPS survey spectrum of the product obtained at pH of 6, in which peaks of Ag 3d, V 2p, O 1s, and C 1s can be observed. In figure 8(b), two Ag 3d strong peaks at 367.4 eV and 373.2 eV could be found, attributing to binding energies of Ag 3d_{5/2} and Ag 3d_{3/2} of Ag⁺ state. Figure 8(c) shows two peaks at 516.4 eV, and 524.2 eV corresponding to V 2p_{3/2} and V 2p_{1/2} of V⁵⁺ state respectively. From the XPS analysis it is clear that there is no content of Ag⁰ in the synthesized products.

In order to reveal the growth process of Ag₂V₄O₁₁ nanobelts and nanoring structures, time dependent intermediate hydrothermal experiments were conducted for the precursor solution at pH of 4. The morphologies of the intermediate products were investigated by SEM. Figure 9 depicts the morphological evolution of Ag₂V₄O₁₁ obtained at the pH of 4, with different hydrothermal durations. Figure 9(a) presents SEM image of the product synthesized for 2 h. It is observed that a significant quantity of tiny nanobelt like structures appeared on longer nanobelts. On proceeding the hydrothermal reaction to 6 h, well defined nanobelts were observed (figure 9(b)). With the hydrothermal reaction time increased to 16 h and 20 h (figures 9(d) and (e)), bending of the nanobelts had been observed and finally ring structures were appeared as the hydrothermal reaction duration maintained for 22 h (figure 9(f)).

The formation of various forms of nanoring structures from self-coiling of as-formed polar nanobelts can be explained by spontaneous polarization induced self-coiling mechanism which was reported earlier by several research groups [21, 28–30]. The polar surface dominated Ag₂V₄O₁₁ nanobelts originate from the way of packing of atoms in the crystal structure. Ag₂V₄O₁₁ crystallizes in monoclinic system with a space group of C2/m and it is isostructural with Cu_xV₄O₁₁. Ag₂V₄O₁₁ crystal structure is constructed with quadruple [V₄O₁₂]_n chains which built up from [V₄O₁₆] units made of distorted VO₆ octahedra by sharing their apexes. These quadruple [V₄O₁₂]_n chains further linked up by corner shared oxygens, forming continuous [V₄O₁₁]_n sheets separated by silver atoms [31, 32]. Under hydrothermal reaction of the solution at pH of 4 and 5, nanobelts dominated by polar surfaces are first formed along the [3 0 $\bar{2}$] plane. Due to the uncompensation of surface charges during the growth, nanobelts may tend to fold themselves as their length increases in order to minimize their polar surface area. The stable shape of the nanobelt is determined by the minimization of the total energy contributed by electrostatic energy and elastic energy produced by bending of the nanobelt. On prolonging the hydrothermal treatment, curved nanobelts are observed which on further hydrothermal duration self-coil into various ring structures. When polar surface induced electrostatic energy is greater than the elasticity, the nanobelts tend to self-coil into a ring structure. In the preset experimental results, two typical coiling possibilities can be observed. One possible way is that the nanobelts coiled by side by side surface of the nanobelts to form perfect ring structure and another way is that the stacking top and bottom surfaces to form tape-like ring structure. The synergetic effects of both stacking possibilities give rise to loop-like ring structure. The proposed self-coiling growth process evidently confirmed from the SEM images in which coiling of Ag₂V₄O₁₁ nanobelts are undoubtedly observed (figure 9(f)).

The formation of Ag₂V₄O₁₁ phase at the pH of 4 and 5 can be explained as follows: It is well known that the composition of the vanadium (V) species in aqueous solution mainly depends on the pH of the solution. Several oxo and peroxo vanadium (V) derivatives in aqueous solution at different pHs have been investigated and characterized [22, 23, 33]. The dissolution of V₂O₅ in H₂O₂ leads to the formation of unstable diperoxo

Figure 7. (a) XPS survey spectrum of $\text{Ag}_2\text{V}_4\text{O}_{11}$ obtained at pH of 4; (b) XPS spectrum of the Ag 3d region; (c) XPS spectrum of the V 2p region.

Figure 8. (a) XPS survey spectrum of $\beta\text{-AgVO}_3$ synthesized at pH of 6 for 3 h; (b) XPS spectrum of the Ag 3d region; (c) XPS spectrum of the V 2p region.

Figure 9. The morphological evolution of $\text{Ag}_2\text{V}_4\text{O}_{11}$ obtained at pH value of 4, with different hydrothermal durations (a) 2 h, (b) 6 h, (c) 10 h, (d) 16 h, (e) 20 h, and (f) 22 h.

$[\text{VO}(\text{O}_2)_2]^-$ and monoperoxo $[\text{VO}(\text{O}_2)]^+$ vanadate species. The unstable aqueous solution of $[\text{VO}(\text{O}_2)_2]^-$ and $[\text{VO}(\text{O}_2)]^+$ species undergoes progressive decomposition with evolution of oxygen gas leading to the formation of oxovanadate species $[\text{VO}_2]^+$ and $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$ at nearly pH of 2 [33]. When the pH of the solution is adjusted between 3 and 5, hexa coordinated decavanadate anion $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$ are the main vanadium species [22]. Whereas, further increase in pH between 6 and 9, vanadium coordination decreases from 6 to 4, leading to the four coordinated vanadate species, difunctional $[\text{H}_2\text{VO}_4]^-$ [34]. On hydrothermal treatment of the solution of pH 4 and 5, at the initial stage of the reaction, we could expect that the decavanadate anion $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$ gets protonated leading to the formation of $[\text{VO}(\text{OH})_3(\text{H}_2\text{O})_2]$ and $[\text{VO}(\text{OH})_3(\text{H}_2\text{O})]^-$ species in accordance with

Figure 10. Overlaid voltammograms of bare glassy carbon electrode (bGCE) in absence of metal ions (a), bGCE (b), β -AgVO₃-GCE (c) and Ag₂V₄O₁₁-GCE (d) in presence of 10 mM solution of each of Pb²⁺ and Cd²⁺ ions, in acetate buffer solution (pH = 5) containing 0.1 M KNO₃ as a supporting electrolyte. Scan rate is 50 mV s⁻¹.

Figure 11. Overlaid differential pulse anodic stripping voltammograms of the GCE modified with Ag₂V₄O₁₁ at different concentrations of Pb²⁺ and Cd²⁺ ions after a deposition time of 120 s at -1.20 V, respectively.

partial charge model [25, 35]. Upon further hydrothermal treatment, polycondensation of [VO(OH)₃(H₂O)₂] and [VO(OH)₃(H₂O)]⁻ in the presence of Ag⁺ ions resulting in the formation of [V₄O₁₁]²⁻ layers, where Ag⁺ ions can accommodate within these layered framework in order to compensate negative charge.

3.1. Electrochemical performance of Ag₂V₄O₁₁ and β -AgVO₃: simultaneous measurement of Pb²⁺ and Cd²⁺ ions

Electrochemical performance of Ag₂V₄O₁₁ synthesized at pH of 4 and β -AgVO₃ synthesized at pH of 6 for the time duration of 3 h has been investigated. Electrocatalytic behavior of the Ag₂V₄O₁₁ and β -AgVO₃ modified GCE has been recorded in presence of 10 mM of metal ions using CV and DPASV. Figure 10 depicts the overlaid CVs of Pb²⁺ and Cd²⁺ ions at modified and unmodified electrodes. No peak current signals were observed for bare glassy carbon electrode (bGCE) in absence of metal ions (figure 10(a)). Whereas, significant anodic and a tiny cathodic signals were observed in the presence of metal ions (figure 10(b)). However the CVs were recorded

Figure 12. Calibration plots for Cd²⁺ and Pb²⁺ ions under optimized conditions.

Table 1. Comparison of the silver vanadium oxide nanostructure modified GCE performance with literatures reports for the detection of heavy metal ions.

Electrode	Metal ions	Deposition time (s)	Linear range ($\mu\text{g l}^{-1}$)	Limit of detection LOD ($\mu\text{g l}^{-1}$)	Ref.
Ac-Phos SAMMS/CPE	Pb ²⁺	120	10–200	10	[37]
	Cd ²⁺			10	
Thiolated CAL-SPEs	Pb ²⁺	600	5–100	5	[38]
Bismuth film/SPE	Pb ²⁺	120	20–300	10	[39]
	Cd ²⁺			8	
Diacetyldioxime/CPE	Pb ²⁺	300	100–1500	10	[40]
	Cd ²⁺			40	
PANI/GCE	Pb ²⁺	120	0–2000	20	[41]
	Cd ²⁺			15	
Ag ₂ V ₄ O ₁₁ /GCE	Pb ²⁺	120	10–100	3.5	This work
	Cd ²⁺			5.5	

Ac-Phos SAMMS/CPE—carbon paste electrode modified with thiol self-assembled monolayer on mesoporous silica; Thiolated CAL-SPEs—tetra-tert-butyl-tetrakis-(2-mercaptoethoxy)-calix [4] arene; Bismuth film/SPE—bismuth film screen-printed electrode; Diacetyldioxime/CPE—diacetyldioxime carbon paste electrode; PANI/GCE—polyaniline glassy carbon electrode; Ag₂V₄O₁₁/GCE—silver vanadate glassy carbon electrodes.

in the same domain in presence of 10 mM of metal ions using at β -AgVO₃ (figure 10(c)) and Ag₂V₄O₁₁ (figure 10(d)) modified electrodes to distinguish the electro-catalytic activity of the electrodes. From the figures 10(c) and (d), it is observed that the electrochemical performance of the Ag₂V₄O₁₁ modified GCE (figure 10(d)) has showed an impressive improvements within the voltammetric signal in the form of current than β -AgVO₃ and unmodified electrode in presence of Pb²⁺ and Cd²⁺ ions. Hence GCE modified with Ag₂V₄O₁₁ could be used as an electrochemical sensing platform for the simultaneous detection of Pb²⁺ and Cd²⁺ ions in aqueous solution.

In order to achieve the maximum efficiency of the Ag₂V₄O₁₁ modified GCE in the electrochemical quantification of Pb²⁺ and Cd²⁺ ions, DPASV were used. The respective potential observed for lead and cadmium ions in the present investigation which were similar to the reported data [36]. In the present electrochemical study, the anodic (oxidation) peaks were significant over the cathodic (reduction) peaks. Hence the anodic peaks were systematically studied by using another sensitive electrochemical technique such as DPASV to get the better analytical response in the form of sensitivity and limit of detections. However, to evaluate the analytical applicability of the proposed electrochemical sensing platform, it has been successfully applied to quantify the metal ions from various industrial effluents and environmental samples. It is adequate to construct a calibration plot with the standard solutions of target analytes. The DPASV under optimized conditions were showed a linearity in the range 10–100 ppb (figure 11) and it has been performed by the successive addition of 10 ppb of analytes and its calibration plots were shown in figures 12(a) and (b). The response of oxidation peak current of metal ions as a function of concentration of metal ions increases linearly up to 100 nM and limit of detection was found to be 3.3 and 3.5 ppb (3 σ) for Pb²⁺ and Cd²⁺ ions respectively. Therefore, the Ag₂V₄O₁₁ modified GCE can be used as potential candidate for the quantification of Pb²⁺ and Cd²⁺ ions in real sample matrices. The proposed silver vanadium oxide nanostructure modified sensor has been compared with the existing sensors and it is tabulated in table 1.

Figure 13. Overlaid differential pulse anodic stripping voltammograms of the GCE modified (a) β -AgVO₃ nano/micro belts, (b) Ag₂V₄O₁₁ aggregated nanobelts, (c) Ag₂V₄O₁₁ nanobelts, (d) β -AgVO₃ nanobelts, and (e) Ag₂V₄O₁₁ nanobelts with ring structures in presence of 50 ppb of Pb²⁺ and Cd²⁺ ions after a deposition time of 120 s at -1.20 V, respectively.

The results reveal that the silver vanadium oxide nanostructure modified sensor exhibits comparatively better analytical responses [37–41].

Additionally, effect of the morphology of the silver vanadium oxide on electrochemical detection ability for Pb²⁺ and Cd²⁺ ions has been carried out. Overlaid differential pulse anodic stripping voltammograms of the different morphology of the silver vanadium oxide nanostructures modified GCE is shown in figure 13. From the figure it is clear that the sensitivity for Pb²⁺ and Cd²⁺ ions is as follows: Ag₂V₄O₁₁ nanobelts with ring structures > β -AgVO₃ nanobelts > Ag₂V₄O₁₁ nanobelts > Ag₂V₄O₁₁ aggregated nanobelts > β -AgVO₃ nano/micro belts.

4. Conclusion

In the present study, we investigated the effect of pH on the formation of silver vanadates and their morphological evolution under hydrothermal process. The performed phase and morphological investigations at various pH values revealed that the morphological evolution of nanobelts into nanoring structures occurs at pH of 4 and 5 with Ag₂V₄O₁₁ phase and nanobelt morphologies at pH of 6 and 7 with β -AgVO₃ phase. Electrochemical characterization of GCE's modified with Ag₂V₄O₁₁ and β -AgVO₃ revealed that the GCE modified with Ag₂V₄O₁₁ could be used as an electrochemical sensing platform for the simultaneous detection of Pb²⁺ and Cd²⁺ ions within the world real samples.

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