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Hydrothermal synthesis and electrochemical sensing properties of copper vanadate nanocrystals with controlled morphologies

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Abstract: Morphology-controlled synthesis of copper vanadate nanocrystals is of great significance in electrochemical sensing applications. A facile hydrothermal process for synthesizing copper vanadate nanocrystals with various morphologies (e.g., nanoparticles, nanobelts and nanoflowers) was reported. Phase, morphology and electrochemical performance of the as-synthesized copper vanadate nanocrystals were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and cyclic-voltammogram (CV) techniques. The results revealed that the morphologies of the $Cu_3V_2O_7(OH)_2\cdot 2H_2O$ (CVOH) nanocrystals could be controlled by changing copper salts, surfactants and pH values. The CVOH samples showed enhanced electrochemical response to ascorbic acid. Comparatively, the CVOH nanobelts had the higher electrochemical sensing performance than those of CVOH nanoparticles and nanoflowers. The CVOH-nanobelts-modified GCEs had a linear relationship between the peak currents in their CVs and ascorbic acid concentration. The CVOH nanocrystals can be used as potential electrochemical active materials for the determination of ascorbic acid.

Key words: copper vanadate nanocrystals; hydrothermal synthesis; electrochemical sensors; ascorbic acid

1 Introduction

Ascorbic acid (AA) is one of the most important vitamins due to its antioxidant and other benefits for human bodies [1]. AA is often added to various foods and pharmaceutical products for prevention of some diseases. The detection and quantitative determination of AA for the quality control in producing pharmaceuticals is essentially important. Therefore, there is an urgent need in developing easy-to-use and inexpensive methods to detect AA [2]. Electrochemical methods for accurate determination of analytes have attracted increasing attention because of their intrinsic advantages of rapid response, high sensitivity, easy operation and low cost [3]. Glassy carbon electrodes (GCE), carbon paste (CP) electrodes and gold arrays microelectrodes, which were functionalized by various active materials, have been used to detect various analytes [4−6]. Nanocrystals of metal oxides, carbon and metals were widely used to modify the electrodes' surfaces to facilitate the electron transfer between target analytes and electrode surfaces and then to improve their performance [7−12]. The morphologies and sizes of the nanocrystals highly affect the modification [13] and electrochemical property of electrodes [7]. Metal vanadate nanocrystals have been reported in electrochemical applications [14−18]. Among those metal vanadates, copper vanadate nanocrystals showed a great potential in the surface modification of electrodes because of their unique electrochemical performance [11,16].

Controlled synthesis and electrochemical applications of copper vanadate nanocrystals with unique morphologies and sizes are the most interesting research topics. Their electrochemical properties are highly influenced by the morphologies and sizes that are largely determined by synthetic processes and starting reactants. As a typical phase, CuV_2O_6 nanocrystals have been

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synthesized via various processes (i.e., solid-state reaction, sol-gel process, hydrothermal method) using different starting materials (i.e., V_2O_5 + $Cu(NO_3)_2$ [19], NH_4VO_3 + $Cu(NO_3)_2$ [20], V_2O_5 hydrogel + Cu_2O [21]). Hollow $Cu_{0.95}V_2O_5$ microspheres and CuV_2O_6 nanoparticles have been synthesized using VO_2 and $Cu(NO_3)_2$ as precursors in the polyvinyl pyrrollidone solutions [22]. Also, $Cu_2V_2O_7$ nanoparticles have been synthesized using a thermal-decomposition method [11]. Recently, $Cu_3(OH)_2V_2O_7{\cdot}nH_2O$ nanoparticles have been synthesized by hydrothermal methods using V_2O_5 + $Cu(NO_3)_2$ [23] or V_2O_5 + $CuSO_4{\cdot}7H_2O$ [24] as the starting materials. $Cu_3(OH)_2V_2O_7{\cdot}2H_2O$ samples with different morphologies and sizes by a sol-gel process or chemical precipitation method were also reported [25,26]. In addition, $Cu_3V_2O_8$ nanoparticles have been gotten with $CuSO_4{\cdot}5H_2O$ and NH_4VO_3 as materials under the assistance of different Schiff base ligands via a simple precipitation approach [27,28]. However, the synthesis of copper vanadate nanocrystals with controlled morphologies using simple and cost-effective methods is still full of challenges.

In this work, a new and facile hydrothermal process was developed to synthesize copper vanadate nanomaterials with various morphologies, and their applications in electrochemical detection of AA were systematically investigated. The optimal hydrothermal conditions were explored by adjusting acid radicals, additives and pH values, which are the key factors affecting the morphologies [29−32]. The copper vanadate nanocrystals with typically unique morphologies (i.e., nanoparticles, nanobelts, and nanoflowers) have been used as the active materials to modify GCEs, which were used as the working electrodes to detect ascorbic acid on the basis of the electrochemically sensing mechanism.

2 Experimental

2.1 Materials and methods

NH_4VO_3 (AR grade) and $Cu(CH_3COO)_2{\cdot}H_2O$ (AR grade) were purchased from Tianjin Guangfu Fine Chemical Research, China. $CuSO_4{\cdot}5H_2O$ (AR grade, Tianjin Kemiou Chemical Reagent Co., Ltd, China), $CuCl_2{\cdot}H_2O$ (AR grade, Tianjin Fengchuan Chemical Reagent Co., Ltd., China) were also used as copper sources. $Cu(NO_3)_2{\cdot}3H_2O$ (AR grade) and poly-vinylpyrrolidone (PVP) were obtained from Sinopharm Chemical Reagent Co., Ltd., sodium dodecyl benzene sulfonate (SDBS) and hexadecyltrimethy ammonium bromide (CTAB) were purchased from Tianjin Fu Chen Chemical Reagents Factory and China National Pharmaceutical Group Corporation, respectively. All chemicals were used as received.

Copper vanadate samples were synthesized under different conditions, by varying copper sources ($CuSO_4$, $Cu(NO_3)_2$, $Cu(CH_3COO)_2$, or $CuCl_2$), Cu^{2+} concentration (0.03−0.075 mol/L), surfactants (PVP, SDBS or CTAB), pH values (3−11) and hydrothermal reaction time (12−24 h). The details for hydrothermal synthesis of copper vanadate nanocrystals are listed in Table 1.

In a typical synthesis (S6 in Table 1), 0.1404 g (~1.2 mmol) of NH_4VO_3 was dissolved in 30 mL of distilled water at 80 °C under magnetic stirring, and

Table 1 Summary of experimental parameters for hydrothermal synthesis of copper vanadate nanocrystals

Sample No.	Copper source	Cu^{2+} concentration/ (mol·L^{-1})	Surfactant/ concentration/%	Time/h	pH	Morphology of products
S1	$CuSO_4$	0.03	PVP / 2.7	24	4	Nanoflowers
S2	$CuSO_4$	0.03	PVP / 3	24	3	Broken nanobelts
S3	$CuSO_4$	0.03	PVP/3	24	5	Irregular flakes and particles
S4	$CuSO_4$	0.03	PVP / 1.5	24	4	Nanobelts with particles
S5	$CuSO_4$	0.03	PVP / 0.3	20	5	Nanobelts with particles
S6	$CuSO_4$	0.03	PVP / 0.3	24	3	Nanobelts
S7	$CuSO_4$	0.03	PVP / 0.3	24	7	Non-uniform nanoparticles
S8	$CuSO_4$	0.03	PVP / 0.3	24	11	Irregular particles
S9	$CuSO_4$	0.03	SDBS / 0.3	20	5	Pieces with particles
S10	$CuSO_4$	0.03	CTAB / 0.3	20	5	Pieces with particles
S11	$CuSO_4$	0.03	−	20	5	Strings with particles
S12	$CuSO_4$	0.075	−	12	5	Irregular particles with microrobs
S13	$Cu(NO_3)_2$	0.075	−	12	5	Irregular particles
S14	$Cu(CH_3COO)_2$	0.075	−	12	5	Nanoparticles
S15	$CuCl_2$	0.075	−	12	5	Irregular particles