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Electrochemical Detection of Vitamin D2 and D3 Based on a Au-Pd Modified Glassy Carbon Electrode

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In this work, the synthesis of AuPd bimetallic nanocrystals in an aqueous solution using a stabilizing agent and a reductant of triblock copolymer P123 and ascorbic acid, respectively, was proposed. Vitamins D_2 and D_3 were electrochemically detected in a mixed organic/water solution based on a glassy carbon electrode (GCE) modified by AuPd. The electrocatalytic response of D vitamins on the GCE surface was greatly affected by the organic/water ratio of the mixture. In the presence of the support electrolyte (lithium perchlorate), vitamins D_2 and D_3 exhibited well-defined peaks when the ethanol/water ratio was 40%/60%. This work also suggested the high sensitivity of the GCE toward the detection of vitamins D_2 and D_3. During the detection of vitamin D, vitamins A, K and E showed no obvious interference effects.

Keywords: Bimetallic nanocrystals; Vitamin D; Electrochemical determination; glassy carbon electrode; Osteoporosis

1. INTRODUCTION

Osteoporosis refers to a condition of either excessive bone loss or inadequate bone replacement after normal bone loss. Excessive bone loss will result in bones with poor density and a higher chance of breaking. People suffering from osteoporosis are diagnosed with poor bone density [1-4]. Osteoporosis may have a number of causes, including controllable causes such as cessation of smoking and inadequate calcium absorption and uncontrollable causes such as aging and female gender [5-8]. The exact role of vitamin D in the development of osteoporosis has always been under investigation. Owing to the need for the absorption of Vitamin D, scientists and doctors often recommend taking

adequate vitamin D and calcium throughout life for healthy bone development and to decrease the risk of osteoporosis [9, 10].

Based on several reports, the lack of vitamin D could contribute to bone loss, while other studies did not report this effect. In the case of osteoporosis development, absorption of vitamin D does not lead to an improvement in bone density, and osteoporosis could not be cured [11-13]. Nevertheless, further bone loss could be decelerated with the absorption of vitamin D; this phenomenon requires further investigation. It is also possible for vitamin D to facilitate the management of osteoporosis in other aspects. Possible risk of bone breaking is the primary concern for the development of osteoporosis. As shown in several reports, falling can be prevented by taking vitamin D, so vitamin D has an indirect effect on the prevention of bone breaking [14, 15].

Vitamin D is divided into two groups, namely, ergocalciferol (D_2) and cholecalciferol (D_3), which are obtained from the endogenous environment (exposure to sunlight) and exogenous environment (foodstuff), respectively. Ordinarily, vitamins D_2 and D_3 come from fresh salmon (D_3), cod liver oil (D_3), egg yolk (D_2 and D_3), and shitake mushrooms (D_2) [16, 17]. Furthermore, vitamins D_2 and D_3 can also be obtained from vitamin supplements.

The use of electrochemical techniques for the detection of vitamins D_2 and D_3 is considered to be highly challenging because these vitamins show poor solubility in aqueous solvents, and D_2 and D_3 show similar structures that are distinguished only by the presence of a double bond and a methyl group. Ordinarily, the detection of these vitamins is performed using other measurement methods (fluorescent, chromatographic, etc.) that require costly and time-consuming analysis and are unfavourable for point-of-care treatment and miniaturization [18-20]. Hence, the fabrication of electrochemical sensors that can be used for vitamin D_2 and D_3 detection has gained substantial attention because the use of these sensors can avoid the drawbacks of the conventional measurement methods. Electroanalysis has advantages such as suitability for point-of-care analysis and use of disposable and low-cost electrodes. Additionally, it ordinarily does not require a highly professional operator or the use of a specimen pre-treatment process.

Compared to monometallic materials, bimetallic NCs showed better catalytic behaviour owing to the synergistic effect of two distinct metals, and the chemical structures and compositions of bimetallic NCs are tunable [21-25]. Among various bimetallic systems, AuPd bimetallic NCs have attracted much attention owing to their extensive application as efficient catalysts in a wide variety of processes, including selective oxidation of alcohols [26-28], direct synthesis of H_2O_2 from H_2 and O_2 [29-31], decomposition of N_2O [32], Suzuki–Miyaura and Heck coupling reactions [33], and electrochemical reactions [34, 35].

In this study, a novel electroanalytical strategy was developed for the electrochemical detection of vitamins D_2 and D_3 using AuPd bimetallic NCs in a mixture of organic/water solution.

2. EXPERIMENTS

2.1. Synthesis of Au–Pd Bimetallic Nanodendrites

H_2PdCl_4 and $HAuCl_4$ were co-reduced using a distinct dropping addition method with ascorbic acid after the addition of Pluronic P123 (stabilizing agent) in order to prepare the Au–Pd bimetallic

nanodendrites. Specifically, an aqueous solution (5.0 mL) that contained ascorbic acid (88.0 mg) and Pluronic P123 (50.6 mg) was transferred to a vial (15 mL), followed by uniform mixing and constant stirring at 25 °C. Then, this mixture was added to another aqueous solution (5.0 mL) that contained H_2PdCl_4 and $HAuCl_4$ (6.25 μM each) through a peristaltic pump with a constant flow rate of 0.22 mL/min. Thus, a total concentration of 1.25 mM metal precursors was obtained with a varying ratio of Au/Pd in the terminal reaction solution. Meanwhile the metal ion/ascorbic acid/P123/H_2O molar ratio in the synthesis recipe was 1/40/0.7/44800. A dark brown solution was finally obtained after this mixed solution was stirred for one more hour at 25 °C, which was then centrifuged for 20 min at 10 000 rpm to yield the Au–Pd bimetallic nanodendrites. This was followed by washing three times with ultrapure water and re-dispersion in water before use.

2.2. Preparation of the Modified Glassy Carbon Electrode

First, the GCE was polished using alumina slurries (1.0, 0.5 and 0.3 mm). This was followed by complete rising with purified water, 3 min of sonication using ethanol and 3 min of sonication using water, along with air-drying. Subsequently a AuPd bimetallic NC dispersion (1 μL, 1 mg/mL) was dropped onto the surface of the GCE, followed by drying at ambient temperature. Prior to the electrochemical experiments, the surface of the electrode was treated in H_2SO_4 (0.1 M), voltammetric cycling was performed in the potential range of 0-1 V until a reproducible and evident response could be observed.

2.3. Measurements

A model PGSTAT 302 Autolab electrochemical system (Eco Chemie, Netherlands) was used for cyclic voltammetry (CV) and differential pulse voltammetry (DPV) analysis. The electrochemical cell used for the experiments consisted of a traditional triple-electrode configuration. The working, auxiliary and reference electrodes were a 3-mm glass carbon, a Pt wire, and Ag/AgCl (in 3.0 M KCl). Filled with their own organic mixtures for the measurement, the Ag/AgCl electrode was maintained for 1 d for further use in order to prevent the generation of possible potential junctions. All tests were performed under an inert atmosphere at 298 K (ambient temperature). CV was performed at a scan rate range of 10-300 mV/s, and the potential range was 0.0-1.0 V. DPV measurement was also carried out, where the step potential and pulse amplitude were 2 mV and 50 mV, respectively. We also applied a 50 ms pulse, a scan rate of 10 mV/s, and a sampling time of 20 ms, along with a 100 ms pulse interval. For the detection of vitamins D_2 and D_3, the applied potential range was 0.1-0.8 V. In addition, the electrochemical measurements were carried out in dichloromethane, acetonitrile and ethanol provided by Sigma-Aldrich.

3. RESULTS AND DISCUSSION

As indicated in Fig. 1, the electrocatalytic response of vitamins D_2 and D_3 at the AuPd modified GCE was characterized via CV, where the scan rate and the potential range were 50 mV/s,

and 0.0-1.5 V, respectively. These tests were performed in dichloromethane, ethanol or acetonitrile with vitamins D_2 and D_3 (1.0 mM), where the support electrolyte was lithium perchlorate (0.1 M). We note that these vitamins were collected from a stock solution, with respective organic solvent. GCE exhibited the oxidation peak of vitamin D_2 at +0.67 V in ethanol, at +1.0 V in acetonitrile and at +1.36 V in dichloromethane. For the electro-oxidation of either of these vitamins, the recorded response of AuPd-modified GCE was varied according to the type of the test organic solvent.

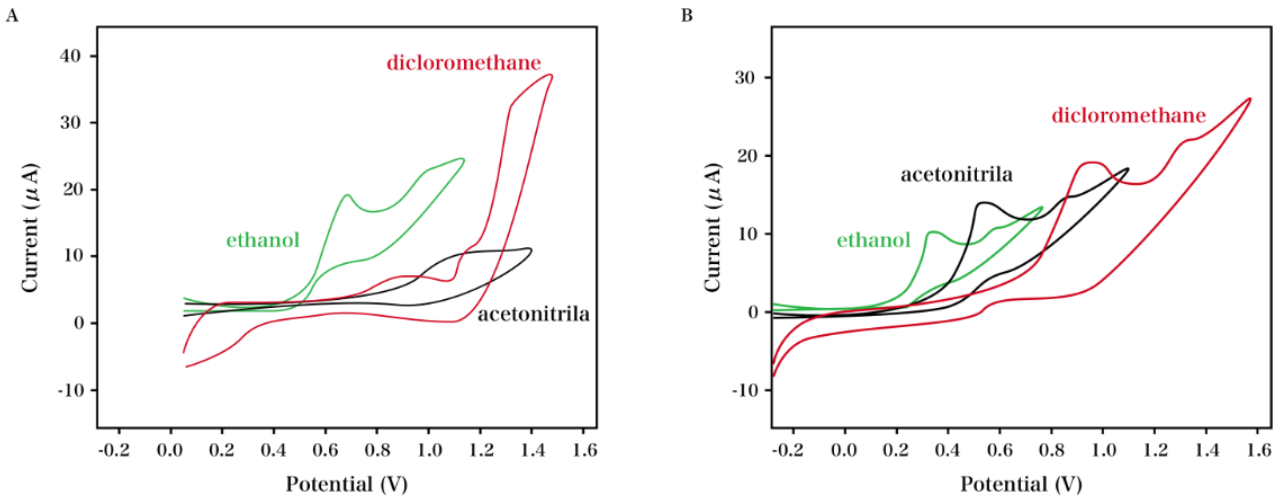

Figure 1. CVs of vitamins D_2 and D_3 (1.0 mM) in ethanol, acetonitrile, and dichloromethane. Scan rate: 50 mV/s, pH: 7.

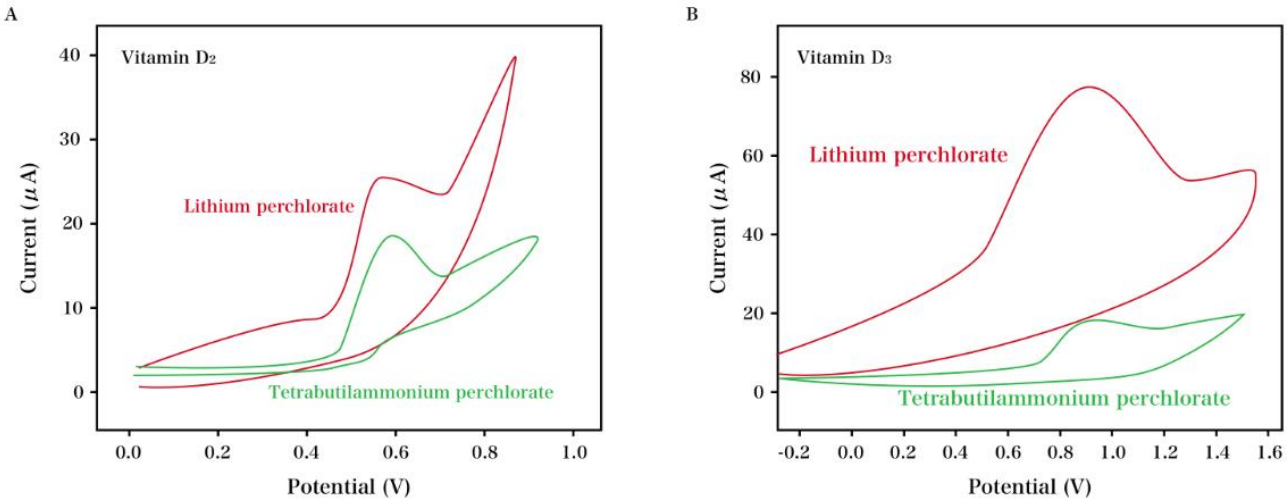

Figure 2. Effect of the supporting electrolyte lithium perchlorate and tetrabutylammonium perchlorate in ethanol after addition of vitamins D_2 and D_3 (1.0 M). Scan rate: 50 mV/s, pH: 7.

As shown in Fig. 1B, vitamin D_3 showed a similar oxidation potential to the above two vitamins, but exhibited varied peak current intensities. This may be cause by the differences between the molecular structures of the vitamins. It can be seen that the oxidation potentials of ethanol were less positive than those in other solvents, suggesting better catalysis to vitamins D_2 and D_3, as well as

less toxicity. In the next step, a test using tetrabutylammonium perchlorate or lithium perchlorate as a support electrolyte was carried out in the presence of both vitamin D_2 and vitamin D_3 dissolved in ethanol in order to evaluate the effect of support electrolyte in the electro-oxidation process. Hence, it was chosen to be the test organic solvent to achieve greater solubility of the D vitamins. The electrolyte that contained lithium perchlorate and ethanol was employed in subsequent tests owing to the greater current responses obtained for lithium perchlorate (Figs. 2A and 2B). These results showed that the electrocatalytic oxidation of vitamins could be directly affected by the type of solvents as well as the support electrolytes. The peak current decreases gradually with successive CV scans, which is a phenomenon of the weak adsorption of an oxidation product [36]. The less positive oxidation potentials of vitamins D_2 and D_3 were observed at the AuPd-modified GCE in the electrolyte that contained lithium perchlorate and ethanol. All the results above give evidence for the irreversible nature of the electrochemical process of D_2 and D_3 [37].

A series of measurements were performed in the mixed solution that contained lithium perchlorate electrolyte; different ethanol/water ratios of 20 %, 40 %, 60 % and 80 % ethanol (v/v); and vitamins D_2 or D_3 (1.0 mM) in order to investigate the electrochemical performance of vitamin D at the AuPd-modified GCE. As can been seen, the percentage of organic solvent strongly affects the peak potential and peak current for the oxidation of vitamins D, in a quite distinct way for vitamins D_2 and D_3. Fig. 3 presents the results of CV measurements. Compared to other ethanol ratios, vitamin D_2 measured in 20 % ethanol exhibited an obviously lower peak current, possibly because vitamin D_2 detected in the water-rich solutions was less soluble, along with the preferential hydration of the surface of the electrode and the following less efficient diffusion of the ethanol solvated molecules to the surface of the electrode. As the ethanol content increased, solvation of the electrode surface was observed in the presence of the mixed solution of water and ethanol, resulting in increased solubility of vitamin D_2. For organic solvent fractions higher than 60 %, the peak potential is shifted towards positive values. This can be associated with a change in the reaction plane position away from the electrode surface because now both electrodes and analytes are solvated mostly by ethanol [38].

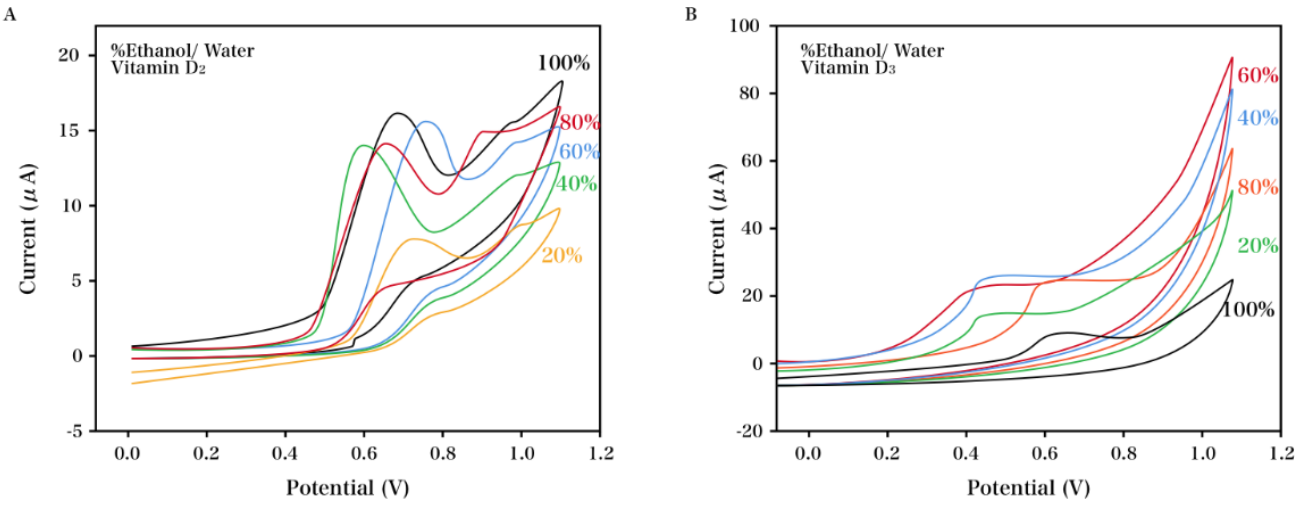

Figure 3. CVs in lithium perchlorate with ethanol/water of varying proportions after addition of vitamins D_2 and D_3 (1.0 mM). Scan rate: 50 mV/s, pH: 7.

Vitamin D_3 exhibited significantly different electrochemical performance. With an increase in the ethanol fraction, an initial increase in the peak current followed by a decrease were observed. Meanwhile, an increase in the peak potential value to 60 % was observed, followed by a further shift to more positive values.

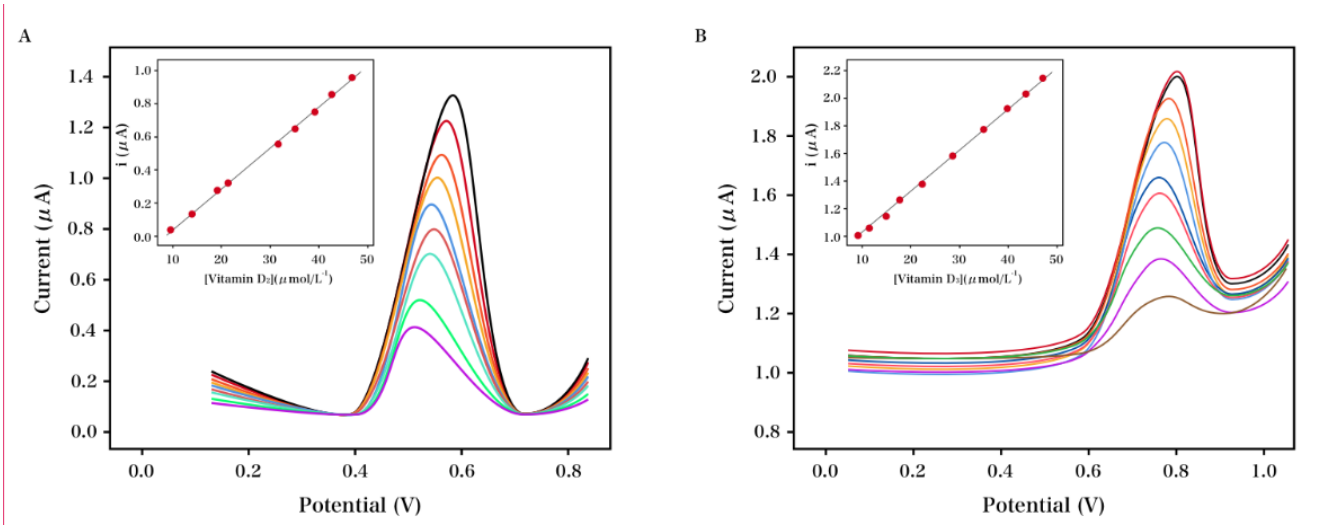

Figure 4. DPVs obtained at the AuPd-modified GCE for varying concentrations of vitamins D_2 and D_3. Plots of currents intensities versus the concentration of vitamins D_2 and D_3 are shown in the insets. Scan rate: 10 mV/s, sampling time: 20 ms, pulse interval: 100 ms.

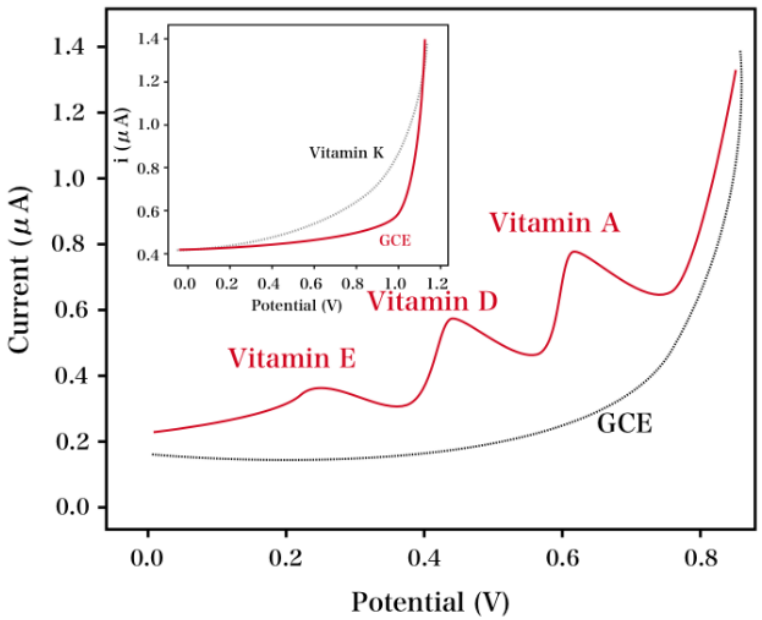

Figure 5. DPVs of the interference from vitamins A, K_1, and E for vitamin D. DPVs obtained for the AuPd-modified GCE toward the detection of vitamin K shown in the inset. Scan rate: 10 mV/s, sampling time: 20 ms, pulse interval: 100 ms.

As indicated in Fig. 4, the detection of vitamins D_2 and D_3 at the AuPd-modified GCE in a mixture of ethanol/water (v/v: 40 %/60 %) and lithium perchlorate was characterized via the DPVs. A linear increase in the peak oxidation currents was observed with the vitamin D_2 and D_3 concentrations. For vitamins D_2 and D_3, the linear concentration intervals were 1 to 10 μM and 5 to 50 μM, respectively. The detection potential of +0.4 V vs. Ag/AgCl could still maintaining high sensitivity and diminishing possible interference from other electroactive spices at high potentials [39, 40]. It can be seen that the quantification of vitamin D was possible at trace levels, the electrocatalytic activity of the AuPd-modified GCE was remarkable, and there is potential for application in the detection of vitamins D_2 and D_3 in real specimens. For vitamins D_2 and D_3, the limit of detection (LOD) was 0.15 and 0.18 μM, respectively. As shown in Table 1, the LOD of the AuPd-modified GCE was lower than those reported in two recent studies, indicating that the AuPd-modified GCE is applicable for the detection of vitamins D.

Table 1. Comparison of varying electrodes toward the Vitamin D detection.

Electrode	Vitamin D_2		Vitamin D_3		
	Linear range (μM)	Detection of limit (μM)	Linear range (μM)	Detection of limit (μM)	Reference
Glassy carbon electrode	1-10	0.118	—	—	[41]
SiO_2/GO/$Ni(OH)_2$	0.05-5	0.00326	—	—	[42]
GCE	—	—	10-40	3	[43]
Poly (alizarin red S)/MWCNT	—	—	0.5-80	0.22	[44]
AuPd modified GCE	1-10	0.05	5-50	0.18	This work

In ten successive measurements in the aforementioned electrolytes, the AuPd-modified GCE exhibited a constant response, and no obvious electrocatalytic activity loss was observed. Meanwhile, a relative standard deviation (RSD) of 2.6 % was obtained. For comparison, we also assessed the possible interference effects from other vitamins. Additionally, the interference effects from vitamins A, E and K were also studied during vitamin D detection. As shown in Fig. 5, the mixture of ethanol/water (v/v: 40 %/60 %) in lithium perchlorate after the addition of vitamin D was mixed with vitamins A, E and K. Based on the GCE detection, vitamins A, E and D detected by the GCE exhibited three separate and well-defined peaks. Within the test range, vitamin K_1 exhibited no signal, suggesting that vitamin K_1 had no effect on the vitamin D detection.

Vitamin D_3 in real specimens was detected in a mixed solution of organic/water solvents using the GCE, with the performance of the solution and the sensor studied herein. The tablets containing calcium (high concentration) and vitamin D_3 were purchased from chain drugstores to prepare the real specimen. Specifically, after crushing and solubilisation using 40 % ethanol/60 % water solution, these tablets were kept under ultrasound treatment for 10 min to thoroughly solubilize vitamin D_3. This was followed by introducing the as-prepared 40 % ethanol/60 % water mixture + vitamin D_3 into the electrochemical cell with GCE prior to further experiments. The DPV involved the use of a calibration technique to determine the amount of vitamin D_3 in real specimens, with the obtained results displayed in Table 2. These results indicated the efficiency of the mixture of organic solvent 40 % ethanol/60 %

water, and the feasibility of using this mixture with GCE in the detection of vitamin D_3 in real specimens. We also performed the detection using high-performance liquid chromatography for comparison. As shown in Table 2 and Table 3, the obtained results indicate that the proposed electrochemical sensor exhibits similar performance to that of the HPLC.

Table 2. Recovery of the detection of Vitamin D_3 in drug specimen.

Vitamin D_3 (μM)	Found (μM)	HPLC (μM)	Recovery (%)
2	1.97	2.01	98.5
4	4.08	4.06	102
8	7.89	7.92	98.63
12	12.12	12.14	101

Table 3. Recovery of the detection of Vitamin D_2 in tablets.

Vitamin D_2 (μM)	Found (μM)	HPLC (μM)	Recovery (%)
10	10.22	10.23	102.2
15	14.91	15.09	99.4
20	21.08	21.96	105.4
30	32.61	33.07	108.7

4. CONCLUSIONS

In this work, a reproducible and simple technique was proposed for the preparation of Au–Pd bimetallic nanocomposite. We studied the electrochemical performance of vitamins D_2 and D_3 in a solvent (mixed solution of ethanol/water) using the AuPd-modified GCE. The performances varied because every analyte within the solvents showed varying solubility. In the case of our study, the optimum proportion between ethanol and water was 40 %/60 %. The DPV method provided an inexpensive and fast measurement and no interference effects were observed. In addition, this method can be miniaturized and employed for point-of-care quantification of vitamin D in real analysis.

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