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Research Paper

Fabrication of Silver Oxide and Nickel Oxide Nanoparticles by Green Synthesis Method Using *Malva Sylvestris* Plant Extract

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ABSTRACT

This paper reports the green preparation of silver oxide and nickel oxide nanoparticles. The *malva sylvestris* extract was used as the green reductant and capping agent. The prepared nanoparticles were characterized using XRD, SEM, FT-IR, and EDX analysis. The XRD analysis discloses that the prepared silver oxide nanoparticles comprise both Ag_2O and Ag metal phases. In addition, it was found that the prepared nickel oxide nanoparticles have an amorphous structure. The FT-IR results show the presence of metal-oxide bonds at the wavenumber range 750-600 cm-1. Also, the green synthesis of the metal oxide nanoparticles was confirmed by the existence of the organic functional groups on the surface of the prepared samples. The SEM images show the spherical nanoparticles in the size range below 50 nm for both prepared nanoparticles. These results reveal the superior ability of the *malva sylvestris* extract to prepare the fine metal oxide nanoparticles. In this research, synthesized Ag_2O nanoparticles (Ag_2O NPs) and NiO nanoparticles (NiO NPs) were used as modifiers for carbon paste electrode (CPE) and their effect on the electrochemical determination of Quercetin (QCT) was investigated by using differential pulse voltammetry (DPV).

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1. Introduction

In recent years, great attention has been devoted to nanomaterials and their applications in the field of manufacturing high-tech products [1, 2]. Nanomaterials have been utilized as a significant part of modern technology, such as catalysis, energy conversion, hydrogen production, medical treatment, solar harvesting technology, etc. [1-3]. The controlling structure and morphology of nanomaterials are the most important issues that many research groups have considered. In this regard, the physicochemical properties of the nanomaterials could be tuned using the appropriate preparation method [4, 5]. Generally, the preparation approach of nanomaterials is divided into two categories of chemical and physical processes [6]. In the physical process, the nanomaterials are synthesized using non-solvent-based methods such as ball milling, laser ablation, etc. On the contrary, the preparation of nanoparticles in the solvent media lies in the chemical synthetic approach. The chemical preparation of nanomaterial is associated with using poisonous reagents that not only pose potential hazards to the environment but also substantially increase the cost of production. Therefore, the utilization of cost-effective and environmentally friendly reagents has received much attention [6-8]. Green chemistry is a substitute for the conventional method of preparation of nanomaterials. In the green preparation approach, the biological reagents are used as reductant or stabilization agents [9]. The tuning of the physicochemical properties of the nanomaterials using biological reagents is much easier than using chemical agents due to the mid-reactive and non-toxic nature of biological agents [9]. The common biological materials that have been used for green synthesis include micro-organisms (bacteria, algae, and fungus) and plant extracts (steam, flower, leaf, and seed). The metal and metal oxide nanoparticles have been synthesized using the bacteria media [7]. For instance, Korbekandi et al. used *Lactobacillus casei* for the synthesis of Ag nanoparticles [9]. The *spirulina platensis* bacteria was used for the preparation of CuO nanoparticles [9].

The plant extracts contain bioactive materials such as polyphenols, tannin, proteins, glycosides and flavonoids, which are able to reduce and stabilize metal ions to form fine nanoparticles. In this regard, *Aloevera* plant extract was used to prepare Au and Ag nanoparticles [10]. Thema et al. prepared NiO nanoparticles using *Agathosma betulina* extract [11]. Logambal et al. reported the green synthesis of CuO nanoparticles using *Couroupita guianensis* extract [12]. One of the most interesting plants which are rich in polyphenole is *malva sylvestris*. The medical properties of *malva sylvestris* have been acknowledged as anti-inflammatory and antioxidant agents. Also, the abundance of polyphenol compounds in the *malva sylvestris* makes it appropriate for the green synthesizing of nanoparticles [10, 11]. Owing to superior characteristics such as electronic, optical and catalytic properties, the metal oxides nanoparticles are widely used. In this regard, NiO and Ag_2O have received much attention as a result of their excellent catalytic properties. For example, Wang et al. studied the catalytic properties of $Ag/Ag_2O/CeO_2$ composite for photocatalytic hydrogen production [12]. Guo et al. prepared the Ag_2O modified CuO nanosheet and studied their catalytic properties for water oxidation [13]. Also, Zahra et al. reported the NiO/ZrO_2 mixed oxides for oxygen evolution reaction [14]. In this report, we prepared the silver oxide and nickel oxide nanoparticles using the green synthesis approach. The *malva sylvestris* extract was used as a reductant and capping agent to prepare silver oxide (Ms-Ag_2O NPs) and nickel oxide nanoparticles (Ms-NiO NPs). The prepared samples were characterized using XRD, SEM, and FT-IR analysis. Further, the carbon paste electrode was modified with Ms-Ag_2O NPs (Ms-Ag_2O/CPE) and Ms- NiO NPs (Ms-NiO/CPE) separately. The Ms-Ag_2O/CPE and Ms-NiO/CPE were used to investigate the electrochemical behaviour of QCT by differential pulse voltammetry (DPV) technique

2. Experimental

2.1. Preparation of plant extract from Malva sylvestris

First, 10 g of the *malva sylvestris* leaves were ground using mortar to form fine powder. Then, the powder was dispersed into 100 mL of deionized water and heated at 80 °C for 2 hours. The mixture was separated using filter paper, and then a light yellow filtrate solution was collected for use in nanoparticle synthesis.

2.2. Preparation of silver oxide and nickel oxide nanoparticles

A certain amount of silver nitrate (0.1 g) was dissolved into 25 mL of the *malva sylvestris* extract. The solution was heated at 60 °C for 6 hours. The prepared dark brown solid was collected using centrifugation at 6000 rpm for 15 min. The collected solid was washed several times using deionized water/ethanol solution and finally dried in an oven at 100 °C for 5 hours. The same procedure was followed for preparation of NiO nanoparticles using $Ni(NO_3)_2.6H_2O$ precursor.

2.3. Preparation of Ms-Ag_2O/CPE and Ms-NiO/CPE

The Ms-Ag_2O/CPE and Ms-NiO/CPE electrodes were prepared by mixing certain amounts of graphite powder (0.5 g) and Ms-Ag_2O NPs or Ms-NiO NPs (0.004 g) separately in mortar for 30 min. After the preparation of homogenous powder, a certain amount of paraffin oil (6 to 8 drops) was added to create a carbon paste. Then, the well-mixed pastes were packed stiffly into a syringe with 2 mm diameter and 10 mm depth. A copper wire was put into each of the packed carbon pastes to establish electrical connections.

2.4. Characterization

The crystallinity and phase structure of the prepared silver oxide and nickel oxide nanoparticles were studied using X-ray diffraction (XRD) analysis (Philips X'pert Pro MPD, Cu-Kα radiation λ = 1.54 Å). The morphology of the prepared nanoparticles was studied using scanning electron microscopy (SEM) (TESCAN Mira3), which was equipped with an energy-dispersive detector to determine the components and elemental analysis of the prepared nanoparticles. The FT-IR spectra of the prepared samples were recorded on a Shimadzu Varian 4300 spectrometer. The electrochemical behaviours of QCT at the surfaces of Ms-Ag_2O/CPE and Ms-NiO/CPE and CPE were studied using the DPV method.

3. Results and discussion

Fig. 1a,b show the XRD analysis for the prepared silver oxide and nickel oxide nanoparticles. The XRD pattern reveals that the prepared silver oxide nanoparticles include both Ag_2O and Ag phases. As shown in Fig. 1a, the prepared silver oxide using the *malva sylvestris* represents the diffraction peaks at 2θ = 33.27°, 38.39°, 56.21° and 77.57° which are attributed to the hexagonal phase of Ag_2O (marked with •). Moreover, the cubic phase of Ag metal (marked with ♣) is clearly observed at 44.51°, 66.69° and 77.57° [15]. Due to the electron donation ability of flavonoid groups, the reduction of silver ions into silver metal is attributed to the presence of these compounds in *malva sylvestris* extract. The hydroxyl groups in flavonoid play a pivotal role in chelating silver ions and reducing them by donating electrons [16].

This reaction is similar to that of the reduction reaction in presence of citrate ions, as follows [17]:

$$2Ag^{+} + C_6H_5O_7^{3-} \longrightarrow 2Ag^{0} + H^{+} + CO_2 + C_5H_4O_5^{2-}$$

In addition, Fig. 1b shows the diffraction peaks for the prepared nickel oxide nanoparticle using the *malva sylvestris* extract. The amorphous nature of the prepared nickel oxide was confirmed using the XRD analysis. Besides, there is a broad peak around 2*θ* = 34.78° which featuresthe NiO phase (047-1049) [18].

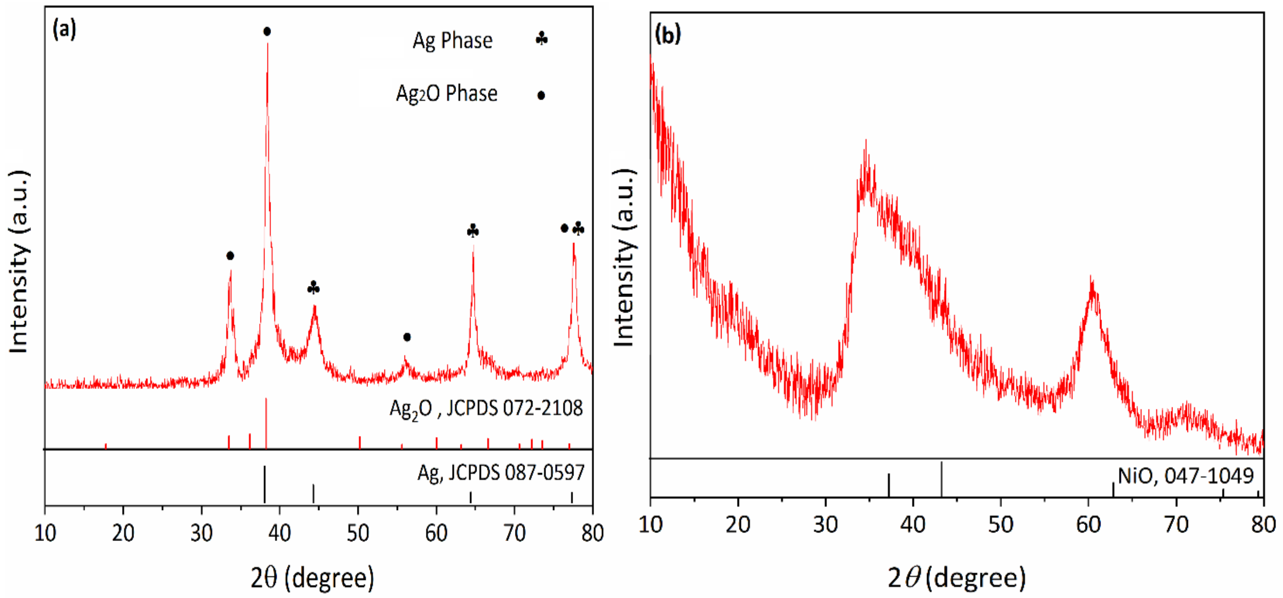
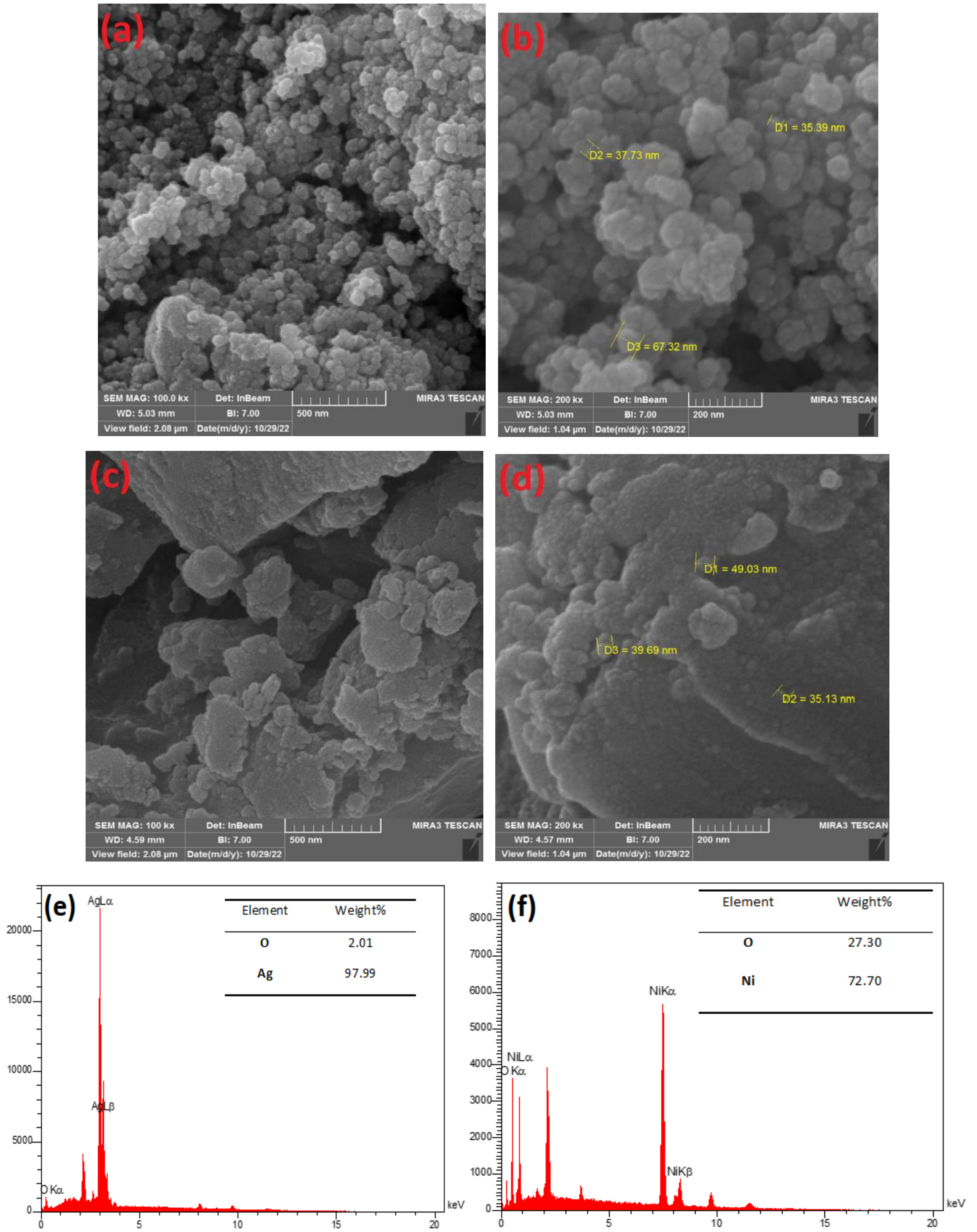


Fig. 1. XRD patterns of the prepared silver oxide (a) and nickel oxide (b).

Fig. 2 shows the SEM images for the prepared silver oxide and nickel oxide nanoparticles using the *malva sylvestris* extract. As is clear form Fig. 2a,b, the silver oxide nanoparticles have spherical morphology with the average size below 50 nm. However, the nickel oxide nanoparticles represent the agglomerated particles with a size of hundreds nanometer (Fig. 2c). But, Fig. 2d reveals that the agglomerated particles are composed of finer spherical particles in the size range below 50 nm.



Element	Weight%
O	2.01
Ag	97.99

Element	Weight%
O	27.30
Ni	72.70

Fig. 2. SEM images and EDX spectra of the green synthesized of silver oxide (a, b, e) and nickel oxide (c, d, f) nanoparticles using the *malva sylvestris* extract.

In addition, Fig. 2e,f show the EDX spectra for the prepared silver oxide and nickel oxide, respectively. From Fig. 2e, the green synthesized silver oxide nanoparticles are mainly comprised of Ag (97.99 wt%) and O (2.01 wt%) elements without any observable metal impurity. Similarly, Fig. 2f, discloses the elemental analysis for the green synthesized for nickel oxide nanoparticles. The prepared nanoparticles are constructed of Ni (72.70 wt%) and O (27.30 wt%) elements without any metal impurity. The presence of carbon is attributed to the *malva sylvestris* extract used for the preparation of nanoparticles.

In order to study the functional groups on the surface of the green prepared nanoparticles using *malva sylvestris*, the prepared samples were analyzed using FTIR spectroscopy, shown in Fig. 3a,b. Clearly, the presence of C-O, C=O and N-H groups were confirmed on the surface of both samples at around 1048, 1658 and 1411 cm^{-1}, respectively. These characteristic absorption peaks affirm the residual organic species on the surface of nanoparticles, which are also indisputable evidence for successful sample preparation via the green synthetic route. The stretching vibration for hydroxyl groups is observed at around 3350-3400 cm^{-1}. The absorption peaks related to the metal-oxygen bonds for Ag-O and Ni-O appeared at 758 and 630 cm^{-1}, respectively [19, 20].

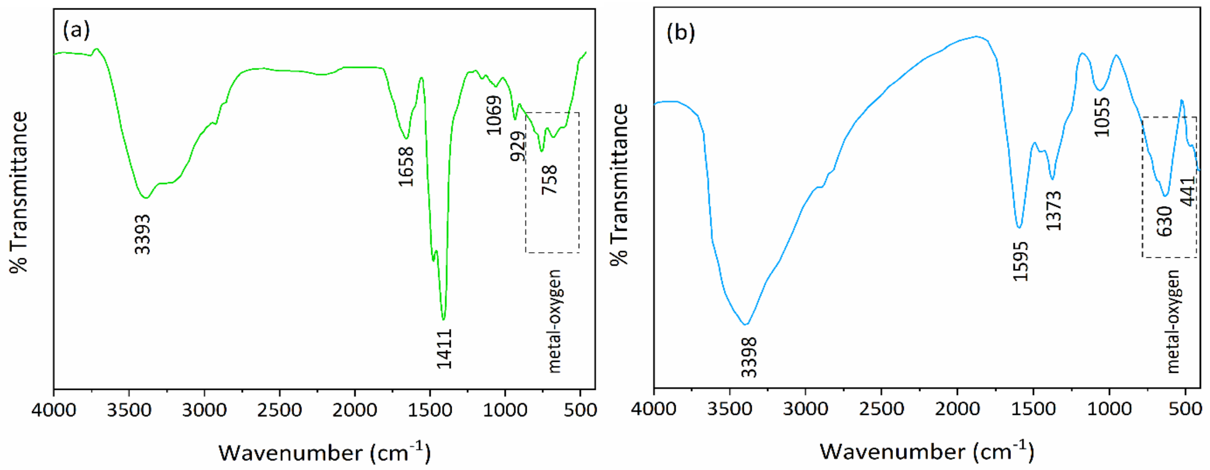


Fig. 3. FT-IR spectra of the prepared of silver oxide (a) and nickel oxide (b) nanoparticles.

Table 1 summarizes the recent literature on green synthesis of metal oxide nanoparticles and reveals the potential of the *malva sylvestris* extract for synthesizing metal oxide nanoparticles.

Table 1. The comparison between the *malva sylvestris*-mediated green synthesize of nanoparticles and previously reported green synthesize of metal oxide nanoparticles.

Nanoparticle	Plant extract	Particle size (nm)	Refrence
Ag/Ag_2O and NiO	Malve sylvestris	< 50	This work
NiO	Agathosma Betulina	26	[21]
NiO	Aegle marmelos	8-10	[22]
NiO/MgO	Pomegranate	---------	[23]
CuO	Gloriosa superba	5-10	[24]
CuO	Allium sativum	20-40	[25]
Ag/Ag_2O	Eupatorium Odoratum	8-20	[26]

4. Application of synthesized Ag_2O NPs and NiO NPs as modifier of carbon paste electrode

In recent decades, metal oxide (MOX) nanoparticles have attracted significant attention due to their chemical characteristics and functional properties, such as high electrical and thermal conductivity, and they have been considered important as modifiers for electrochemical sensors [27]. On the other hand, Quercetin (QCT) is a kind of flovanol that naturally occurs in various plants. QCT shows antibacterial, anti-allergic, antioxidant and antitumor activities due to its scavenging properties, but overdoses of QCT can lead to serious diseases such as kidney cancers and stomach upset [28]. Therefore, it is important to detect QCT levels with a high degree of accuracy and sensitivity. Fast, low-cost, and available electrochemical methods are some of the best methods for these determinations [29,30]. In this research, synthesized Ag_2O NPs and NiO NPs were used as modifiers for carbon paste electrode (CPE) and their effect on electrochemical determination of QCT was investigated by using differential pulse voltammetry (DPV).

As shown in Fig. 4a,b, compared to an unmodified carbon paste electrode, the electrochemical response was greatly improved for QCT electrooxidation. Also, Ag_2O NPs, compared to NiO NPs, have a slightly superior effect on the electrochemical response of QCT, which can be due to their higher electrical conductivity. According to the obtained results, it is clear that the addition of Ag_2O and NiO nanoparticles exerts a significant catalytic effect on the electrochemical reduction of QCT, leading to a decrease of overpotential in the process and an enhancement in the peak current. Therefore, Ag_2O nanoparticles and NiO nanoparticles modified carbon paste electrode proposed for the determination of QCT as electrochemical sensors.

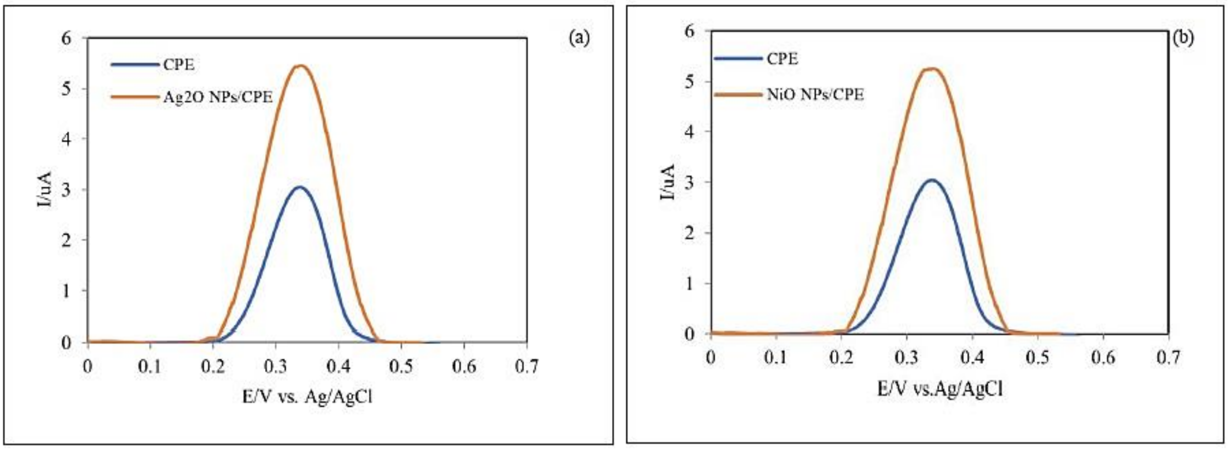


Fig. 4. DPV voltammograms of 0.1 M phosphate buffer solution at (pH 6) in the presence of QCT at the CPE and CPEs modified with Ag_2O NPs (a) and NiO NPs (b) synthesized via *malva sylvestris* extract.

5. Conclusions

In summary, we have presented a green approach for preparing silver oxide and nickel oxide nanoparticles. The *malva sylvestris* extract was used to prepare samples. The crystallinity and phase structure of the prepared samples were studied using XRD analysis, which revealed the hexagonal phase of Ag_2O for the prepared silver oxide nanoparticles. In addition, the existence of the Ag metal phase was proved in the sample. Besides, the amorphous structure was confirmed for the prepared nickel oxide nanoparticles. The ability of *malva sylvestris* extract to prepare metal oxide nanoparticles was revealed using SEM analysis, which showed nanospherical particles with a size of around 50 nm for both prepared nanoparticles. The prepared silver oxide and nickel oxide nanoparticles were used to detect QCT. The DPV results for Ms-Ag_2O/CPE and Ms-NiO/CPE CPE electrochemical sensors display an excellent electrochemical response for QCT.

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