

# Screen-Printed Electrodes

Subjects: Engineering, Chemical

Contributor: Julio Bastos Arrieta, Karina Torres-Rivero

**Screen printed electrodes(SPE)** are disposable, low-cost and portable devices that include a miniaturized display of the working, reference and counter electrodes; based on conductive substrates like carbon nano allotropes (e.g. graphite, graphene) and metals (e.g. Au, Ag, Pt). This configuration is optimized to work with micro-volumes of samples. Their range of applications includes electrochemical analysis in environmental, clinical and agri-food fields.

Keywords: nanoparticles ; nanomaterials ; shape ; screen-printed electrodes ; electrochemistry ; surface-modification

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## 1. Introduction

Electrochemical methods are advantageous regarding miscellaneous instrumental analysis due to their low cost, simplicity, high sensitivity, ease of operation, rapid analysis, portability, and applicability for monitoring different samples in the environmental and pharmaceutical field. In recent years, research in the field of electrochemical sensors has evolved towards the simultaneous analysis of species and miniaturization of electrodes based on new materials and their strategic surface functionalization. Screen printing is a well-established method to produce thick-film electrochemical transducers <sup>[1]</sup>. This technology is highly reproducible and used for the preparation of single-use screen-printed electrodes (SPEs). SPEs composed of carbon nanoallotropes (e.g., carbon nanotubes, nanofibers, or graphene) represent a versatile sensing tool due to their suitability for incorporation in portable instrumentation <sup>[1][2][3]</sup>. Additionally, it has been reported how modifying their surface with metal nanoparticles (MNPs) leads to the enhancement of the electrochemical reactivity and sensitivity for specific analytes <sup>[4][5][6]</sup>.

The use of nanoparticles (NPs) to modify Screen Printed Electrodes (SPEs) offers significant advantages in enhancing the mass transference rate and the electrocatalytic activity of the electrode <sup>[7][8]</sup>. NPs exhibit a higher reactive surface, directly influenced by exposed atoms disposition, which results in more electrocatalytically active sites (edge and corner sites) <sup>[9]</sup>. This fact provides NPs of different sizes and shapes, preferential reactivity, and selectivity towards electrocatalytically detection of specific analytes, due to different charge distribution or polarization of the shaped entity, during the electrochemical determination <sup>[10]</sup>. Particularly, some studies have reported using SPEs modified with different MNPs to enhance the sensitivity towards the determination of different toxins in different samples; gold nanoparticles and graphene oxide modified screen printed carbon electrode to detect carbofuran <sup>[11]</sup>, reduced graphene oxide/gold nanoparticles/boronic acid nanocomposite modified screen printed electrode to determine glycoside in food samples <sup>[12]</sup>, Prussian blue nanoparticles-based screen printed electrodes to detect mustard agents <sup>[13]</sup>, a nanocomposite based on gold nanoparticles and graphene oxide quantum to modify screen printed electrodes for the voltammetric determination of Aflatoxin B<sub>1</sub> <sup>[14]</sup>, and dendritic platinum nanoparticles and gold nanoparticles on screen printed electrode to determine bisphenol A on tap water samples electrochemically <sup>[15]</sup>.

## 2. SPEs Modification by Physical Approaches

Some of the modification techniques rely on the physical incorporation of nanomaterials on SPEs surface without changing their chemical integrity to improve the electrode's electrocatalytic performance by increasing the effective surface area. Hence, low detection limits, fast responses, high sensitivity, and reproducibility can be obtained with the resulting nano-enabled sensor.

### 2.1. Drop-Casting Method

Several investigations have been reported using this methodology to modify screen-printed electrodes, using different NPs solutions: copper <sup>[16]</sup>, bismuth <sup>[17]</sup>, gold <sup>[18][19]</sup>, silver.

It is a simple technique where the screen-printed electrode surface is modified by using a solution that can be composed of particles such as nanotubes or nanoparticles <sup>[20]</sup>.

Usually, the NPs solution is placed onto the sensor surface. The solvent evaporation can be performed by introducing the sensor in an oven at a temperature at which the electrode is not damaged. The drop cast amount onto the electrode is the only parameter to be considered for this modification technique [3].

Nevertheless, other investigations have reported drawbacks regarding this methodology: the so-called “ring coffee effect” [20][21], where the ring's periphery concentrates the non-volatile particles in contrast to the center. Marangoni effect, anisotropic nanoparticles, or even surfactants can reduce this effect, creating a uniform distribution of the drop cast nanoparticles on the sensor surface.

## 2.2. Spin Coating

The spin coating method allows producing a uniform distribution of the nanoparticles on the screen-printed electrode surface. This methodology is performed in four steps, (1) deposition in which the material (NPs solution) is deposited onto the sensor's surface; (2) spin up (acceleration); (3) spin off (deceleration), the applied solution is distributed via centrifugal force, the high spinning speed results in a uniformed layer; and (4) evaporation of the solvent is possible because of rapid rotation [22][23][24]. The coating solution viscosity and the rotation speed controlled the thickness of the deposited layer [22].

## 2.3. Spray Coating

Chomoucka et al. [25] and Mayousse et al. [26] have reported using this method to modify screen printed electrodes. Nanoparticles dispersed in an appropriate solvent (e.g., alcohol) are sprayed onto a substrate through jet/nozzle equipment. The liquid evaporates, allowing the NPs to settle on the surface [27][28].

## 2.4. Sputter Coating

Other investigations have reported the use of this technique to modify the sensor's surface [29][30]. The sputter coating is referred to the use of the energy of a partially ionized gas (usually argon) on the surface of a target (cathode) to pull out the atoms of the material one by one, and deposit them on the substrate [31].

## 2.5. Electrospray

This method relies on propelling nanoparticles using voltage [27]. The NPs are dispersed into droplets by an existing electrical field between a nozzle and the targeted substrate. The solvent is evaporated before reaching the surface, where the NPs are deposited [32]. Mettakoonpitak et al. [33] reported using electrospray for the deposition of silver nanoparticles on SPEs.

## 2.6. Chemical and Electrochemical Deposition

Chemical deposition takes place when reacting volatile precursors in the gas phase to form a layer that deposits on the desired surface, like SPEs. This approach includes homogeneous reactions occurring in the gas phase and heterogeneous chemical reactions which occur close to a heated surface, forming (nano)powders or (nano)coatings. For example, this strategy was used for the customized preparation of a nanocomposite modified SPE, that consisted of carbon black-Prussian blue NPs [34][35].

Similarly, electrochemical disposition is a modifying technique that can produce nanoparticles with controlled characteristics, size, morphology, and composition on an electrode's surface [36]. Typically, the oxidized species (metallic salts) are reduced at a fixed potential or current to obtain the metal particles grown on substrates. Using this methodology, it is possible to optimize the precursor solution parameters (e.g., salt type and concentration) and those regarding the electrochemical deposition. Even though bigger particles can be obtained using higher precursor concentrations, two parameters are critical in controlling NPs' size and shape: the deposition time and the applied potential or current [3].

Many studies have been performed using the electrodeposition and various salts precursor to modify screen-printed electrodes; Ag-NPs and Au-NPs [37] were electrodeposited using  $\text{AgClO}_4$  and  $\text{HAuCl}_4$ , respectively. Pt-NPs [38] using  $\text{K}_2\text{PtCl}_6$ , Cu-NPs [39] via  $\text{CuSO}_4$ , and NiO-NPs [40] employing  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

## 2.7. Ink Mixing and Printing Method

This technique incorporates into the ink preparation three components: conductive particles usually made of carbonous material, a binder paste mixture, such as resins or cellulose acetate, and even solvents such as terpineol, ethylene glycol, or cyclohexanone [41] that allow the particulate matter to transfer onto the electrode substrate, and the modifying agent, in this particular case, NPs [3]. Sometimes, screen-printed electrodes composed of graphite particles are electrochemically

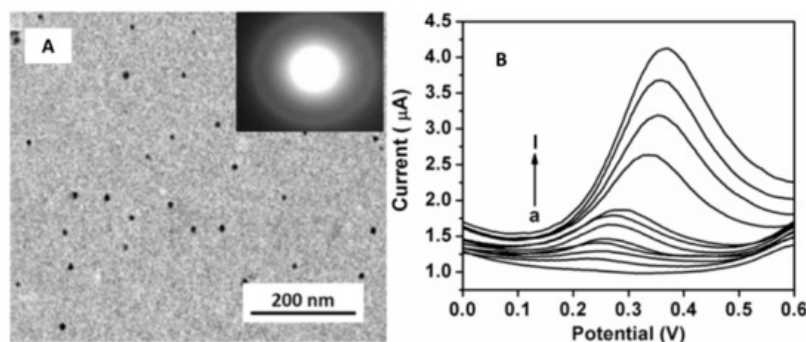
activated to enhance their electrochemical performance [42]. Additionally, a pre-treatment could be performed in carbon-based electrodes to improve the electron transfer rates between the electrode surface and the compounds in solution [41][43].

It is possible to mention some studies reporting the utilization of this modifying technique: nanocomposite consisting of bismuth nanoparticles and amorphous carbon [44], silver and carbon nanoparticles conductive inks [45], silver nanoparticles ink [46][47], and gold nanoparticles ink [48].

### 3. SPEs Modification with Morphologically Different NPs Systems

#### 3.1. Spherical Nanoparticles

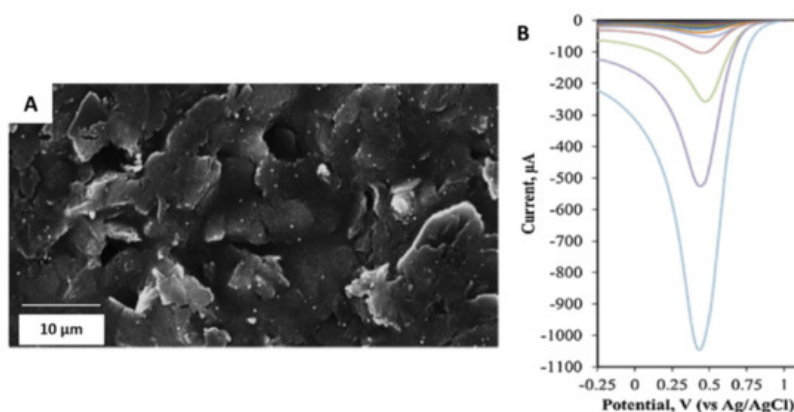
Several investigations include the synthesis of nanoparticles with a spherical shape. These NPs have been used to modify SPEs with different applicability in numerous fields. Singh et al. [49] prepared a graphene oxide-cyclodextrin composite with platinum nanoparticles (GR/CD/Pt). This nanocomposite was incorporated into the SPEs by printing it upon the working electrode's top, obtaining the GR/CD/Pt/SPE, further used for cysteine determination. The modified SPE were characterized by employing scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), Fourier transform infrared (FT-IR), and thermogravimetric analysis (TGA). Figure 2A shows a TEM image of the GR/CD/Pt with spherical-shaped particle structure. A coating of platinum NPs over GR/CD composite with an average diameter of 15 nm can be observed.



**Figure 2.** (A) TEM micrograph of GR/CD/Pt composite. (B) CV response of cysteine at the SPE modified with the GR/CD/Pt in a concentration range of 0.5–170  $\mu\text{M}$  in 0.1 M PBS buffer pH 7.4. Reproduced with permission of Singh et al., Journal of Electroanalytical Chemistry; published by Elsevier, 2018 [49].

Moreover, an electrochemical characterization of the GR/CD/Pt/SPE was performed using cyclic voltammetry (CV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS). DPV studies (Figure 2B) exhibited two ranges in which current and cysteine concentrations had a linear correlation from 0.5 to 40  $\mu\text{M}$  and from 40 to 170  $\mu\text{M}$  with a limit of detection (LOD) of 0.12  $\mu\text{M}$ .

Other studies carried out by Cunha-Silva and Arcos-Martinez [50] functionalized a SPE with rhodium nanoparticles (Rh-NPs) using the chronoamperometric technique. The obtained sensor was used for bromide anion determination in seawater, surfactant, and pharmaceutical samples. Figure 3A shows that the SPEs surface modified with the electrodeposited rhodium nanoparticles at  $-0.25$  V for 480 s. Figure 3B exhibited the voltammograms obtained using the modified electrodes in 0.05 M phosphate-buffered saline (PBS) with 0.05 M of NaCl as supporting electrolyte. The bromide concentration ranged from 0 to 40 mM.

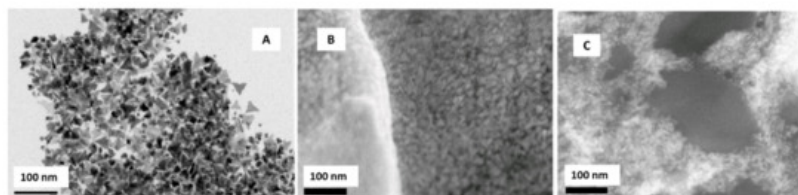


**Figure 3.** (A) SEM micrograph of Rh-NPs deposited on SPEs. (B) Cathodic stripping voltammograms of modified electrodes recorded using 150  $\mu\text{L}$  drop of supporting electrolyte with bromide. The cathodic linear sweep voltammetry scan was from 1.11 to  $-0.25\text{ V}$  at a scan rate of  $0.10\text{ Vs}^{-1}$ . Reproduced with permission of Cunha-Silva and Arcos-Martínez, *Sensors and Actuators B: Chemical*; published by Elsevier, 2019 [50].

### 3.2. Triangle Shaped Nanoparticles

Baradoke et al. [51] developed triangular ruthenium nanoplates (Ru-NPLs) to modify graphene screen-printed electrodes to determine  $\beta$ -Nicotinamide adenine nucleotide in its reduced form (NADH), which is related to depression, neurodegenerative diseases (Parkinson and Alzheimer), and even cancer.

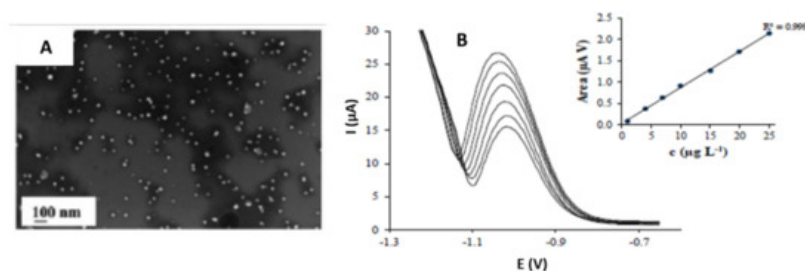
The authors synthesized these Ru nanoplates through a hydrothermal reduction of a ruthenium salt ( $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ) with formaldehyde in the presence of polyvinylpyrrolidone (PVP). TEM micrographs show very thin triangular nanoplates with an edge length of  $18 \pm 3\text{ nm}$  (Figure 4A).



**Figure 4.** (A) TEM micrograph of Ru-NPLs obtained through the hydrothermal reduction of Ru salt by formaldehyde in the presence of PVP. SEM micrographs of Ru-NPLs in  $\text{H}_2\text{O}$ , (B) in ethanol, (C) modified screen-printed graphene electrode. Reproduced with permission of Baradoke, Pastoriza-Santos y González-Romero, *Electrochimica Acta*; published by Elsevier, 2019 [51].

After the synthesis, the nanoplates were incorporated, using the drop-casting method, to graphene screen-printed electrodes (Ru-NPLs-SPEGPH). Water (Figure 4B) and ethanol (Figure 4C) were used as casting solvents to deposit the Ru-NPLs onto SPEGPH; the first led to the formation of large aggregates of nanoparticles. The second permitted a more homogeneous distribution of the Ru-NPLs. The authors performed a polymerization at pH 7.2 to incorporate the Ru-NPLs on screen-printed carbon electrodes using a poly(o-phenylenediamine) (PoPD) film. Finally, the study of the NADH oxidation on modified SPEGPH was performed. Analytical determination showed that the highest NADH oxidation current was obtained when NADH had direct contact with Ru-NPLs, while the SPEGPH modified with the Ru-NPLs and the PoPD film offered an improved and stable electrocatalytic activity toward the NADH oxidation, exhibiting a very low detection limit (LOD) ( $4.0 \pm 0.9\text{ }\mu\text{M}$ ), wide linear range, and good reproducibility.

In addition, triangular-shaped nanoparticles were synthesized for the voltammetric determination of heavy metal ions. Torres-Rivero et al. [5][52] synthesized silver nanoparticles (Ag-nanoseeds and Ag-nanoprisms) by the seed mediated approach [53][54]. SEM and TEM images showed that the Ag-nanoprisms had triangular morphology with a size between 14.25 and 16.46 nm (Figure 5A). After the nanoparticle synthesis, the investigators performed a modification onto the screen-printed carbon nanofibers electrodes (SPCNFE) surface by a drop-casting strategy [4][5] using the Ag-nanoseeds (Ag-NS-SPCNFE) and the Ag-nanoprisms (Ag-NPr-SPCNFE). The electrochemical study was completed to verify the enhancement of the voltammetric response provided by silver nanoparticles. In a previous study, the Pb(II) and Cd(II) ions were determined in an acetic acid/acetate buffer [5]. In contrast, in another investigation, As(V) ions were detected in a HCl electrolyte [52] using the differential pulse anodic stripping voltammetry technique.



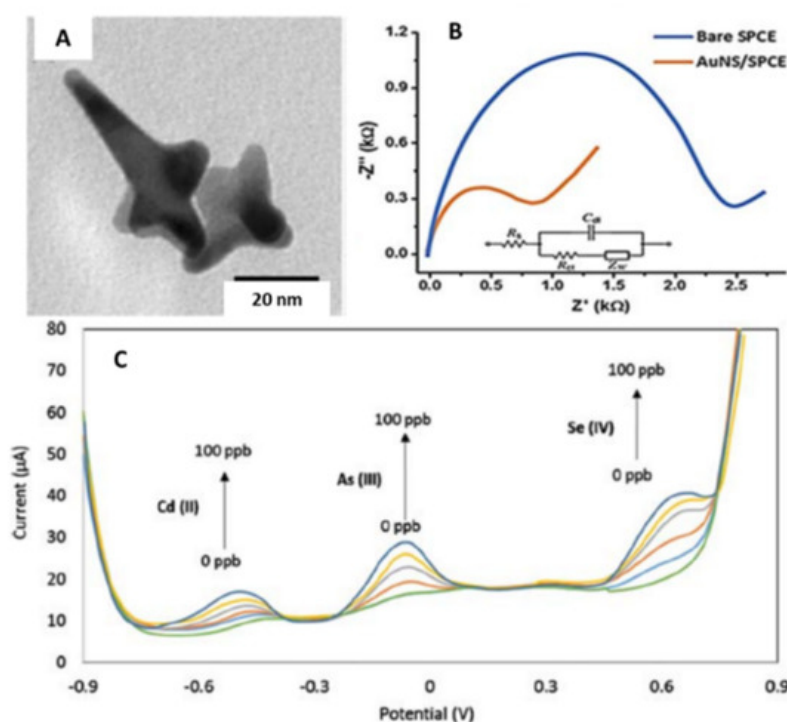
**Figure 5.** (A) SEM micrograph of AgNPr (800  $\mu\text{L}$  of Ag Seeds solution). (B) Differential pulse anodic stripping voltammograms of As(V) and its calibration plot in  $0.01\text{ mol L}^{-1}$  pH 2 applying  $-1.30\text{ V}$  and a deposition time of 120 s. Reproduced with permission of Torres-Rivero et al., *Nanomaterials*; published by MDPI, 2020 [52].

To perform the electrochemical study, As(V) ions were deposited at a deposition potential of  $-1.3$  V for a deposition time of 120 s. The scanning potential was from  $-1.2$  to  $-0.6$  V, where the As(V) peak was exhibited at  $-1.0$  V (Figure 5B).

The authors observed an excellent linear response between the peak area and the As(V) concentration. The researchers also pointed out that even the obtained limits of detection using Ag-NPr-SPCNFE ( $1.2$  and  $2.6 \mu\text{g}\cdot\text{L}^{-1}$ ) were lower than similar studies. The linear range's highest limit is restricted to a lower concentration value ( $25 \mu\text{g}\cdot\text{L}^{-1}$ ). Finally, the modified electrode was tested in spiked water samples obtaining results comparable to those obtained with inductively coupled plasma-mass spectrometry (ICP-MS) measurements.

### 3.3. Star-Shaped Nanoparticles

In addition to the traditional shapes, new and novel shaped nanoparticles have been developed. Lu et al. [55] synthesized gold nanostar (Au-NS) to modify screen-printed carbon electrodes (SPCE) for the simultaneous detection of Cd(II), As(III), and Se(IV). The morphology and size of the Au-NS were estimated using TEM images (Figure 6A). The average tip-to-tip diameter was  $49 \pm 14$  nm, and the number of spikes per nanostar ranged from 4 to 10. Additionally, the behavior of the gold nanostars on the SPCE was studied using electrochemical impedance spectroscopy. The charge transfer resistance decreased significantly from  $2.4$  k $\Omega$  (bare electrode) to  $0.8$  k $\Omega$  (Au-NS-SPCE) (Figure 6B). This difference was related to the augmented area due to the Au-NS coating the SPE surface.



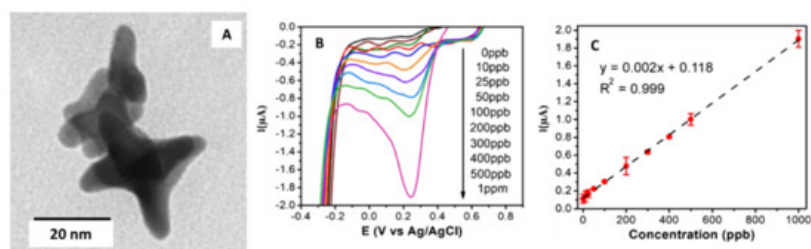
**Figure 6.** (A) TEM micrograph of gold nanostars. (B) Nyquist plot of the bare and gold nanostar modified screen-printed electrode in the presence of the redox probe  $10 \text{ mM Fe(CN)}_6^{3-/4-}$ . (C) SWASV curves of the AuNS-modified SPCE for the simultaneous detection of Cd(II), As(III), Se(IV) in a concentration range of 0 to  $100 \mu\text{g L}^{-1}$ . Reproduced with permission of Lu et al., *Analytical and Bioanalytical Chemistry*; published by Springer, 2020 [55].

The modified electrode was used to perform an electrochemical study using the Britton–Robinson buffer (BRB). The boric acid was excluded from the buffer, resulting in a modified solution of equal amounts of phosphoric and acetic acid ( $0.1 \text{ M}$  pH 2.0) (mBRB). Square wave anodic stripping voltammetry (SWASV) was used to detect Cd(II), As(III), and Se(IV) simultaneously. They were deposited using a deposition potential of  $-0.9$  V for a deposition time of 180 s. The stripping potential was from  $-0.9$  to  $0.9$  V, with an amplitude of  $70 \text{ mV}$ , a period of  $20 \text{ ms}$ , a step increment of  $11 \text{ mV}$ , and a sampling width of  $5 \text{ ms}$ . Figure 6C shows the corresponding voltammograms of the simultaneous detection of the mentioned metal ions. Cd(II), As(III), and Se(IV) exhibited peaks at approximately  $-0.48$ ,  $-0.09$ , and  $0.65 \text{ V}$  (vs. Ag/AgCl), respectively. The obtained LODs were  $1.62$ ,  $0.83$ ,  $1.57 \mu\text{g}\cdot\text{L}^{-1}$  for Cd(II), As(III), and Se(IV), respectively. However, the authors reported the formation of arsenic triselenide ( $\text{As}_2\text{Se}_3$ ), which is a highly stable and insoluble compound that could affect the stripping response of the As(III) and Se(IV). Finally, the Au-NS-SPCE was tested with real water samples. The results showed the proposed method could represent a reliable method to detect Cd(II), As(III), and Se(IV) simultaneously in environmental samples.



Dutta et al. [56] presented the gold nanostars synthesis by Good's buffer method [57][58], which was used to modify a carbon paste screen-printed electrode (CPSPE) for the electrochemical detection of Cr(VI) in water.

Figure 7A shows a TEM micrograph of the synthesized Au-NS. The diameter of the Au-NS inner sphere, which ranged from 10 to 22 nm. Additionally, the star diameter ranged from 30 to 52 nm.



**Figure 7.** (A) TEM micrograph of gold nanostars. (B) Linear sweep voltammograms obtained with the SPE modified with the gold nanostar in 0.1 M  $\text{H}_2\text{SO}_4$  with Cr(VI) additions between 0 and 1000  $\mu\text{g}\cdot\text{L}^{-1}$ . (C) Calibration curve obtained for the Cr(VI) additions. Reproduced with permission of Dutta et al., *Microchimica Acta*; published by Springer, 2019 [56].

CPSPEs were modified by drop-casting with increasing quantities of Au-NS solutions (from 7.5 to 66  $\mu\text{L}$ ). The authors determined that the optimal amount of Au-NS solution was 22  $\mu\text{L}$ , which offered the highest current density for Cr(VI). The modified electrode was used to detect Cr(VI) in water using linear sweep voltammetry (LSV) (see Figure 7B); also, a linear relationship between the current and the Cr(VI) concentration is observed (see Figure 7C). The potential was scanned from  $-0.7$  to  $0.8$  V with a scan rate of  $0.05$   $\text{V}\cdot\text{s}^{-1}$ . All measurements were performed in 0.1 M sulfuric acid. The limit of detection and quantification were 3.5 and 10  $\mu\text{g}\cdot\text{L}^{-1}$ , respectively. Electrode sensitivity was found to be  $20$   $\text{nA}\cdot\text{ppb}^{-1}\text{cm}^{-2}$ .

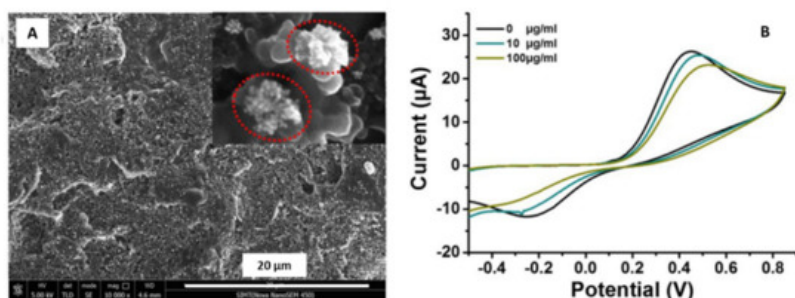
In addition, a study with the presence of possible interferents, Ni(II), Zn(II), Fe(III), Cr(III), Pb(II), As(III), Cu(II), Se(IV), and Cd(II) was performed. The authors studied the response of the modified CPSPE with 100  $\mu\text{g}\cdot\text{L}^{-1}$  Cr(VI) and 1  $\text{mg}\cdot\text{L}^{-1}$  of each metal ion. They could observe no significant change in the LSV peak current value in the presence of metal ions.

Finally, a determination of Cr(VI) in contaminated groundwater was carried out. The results were contrasted with ICP analyses to assess the accuracy of the voltammetric sensor. Recoveries percentages ranged from 95% to 97%.

### 3.4. Nanoflowers Shaped Nanoparticles

Glycated hemoglobin (HbA1c) is now considered a promising biomarker for the diagnosis of type II diabetes (T2D) [59][60]. Wang et al. [61] developed an electrochemical biosensor using a screen-printed electrode modified with gold nano-flowers (AuNFs) to quantify the HbA1c.

AuNFs were electrochemically deposited on the screen-printed carbon electrode (Figure 8A). A capture molecule (4-Mercaptophenylboronic acid or 4-MPBA) was used to catch the HbA1c; mediated by the boric acid and the 4-MPBA, interacting with the target sugar subunit HbA1c. Once the HbA1c was immobilized on the SPCE, it could produce a reduction of  $\text{H}_2\text{O}_2$  due to its catalytic property. This allows the study of the electrochemical response, as there is a proportionality between the amount of the captured HbA1c and the reduced  $\text{H}_2\text{O}_2$  on the modified electrode (see Figure 8B).

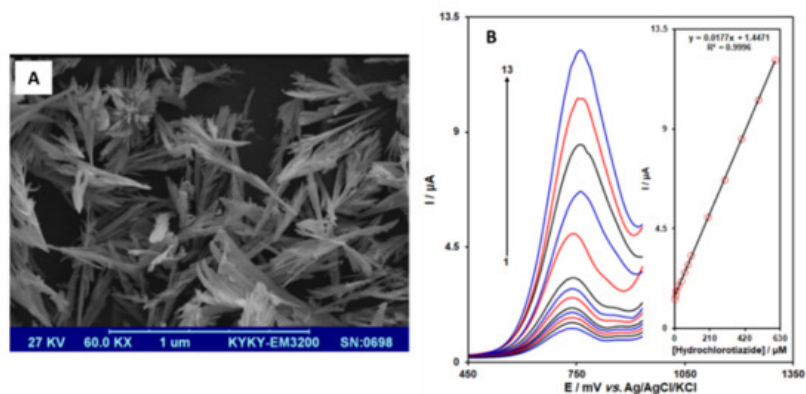


**Figure 8.** (A) SEM micrograph of gold nanoflowers deposited onto the Screen Printed Carbon Electrode (SPCE). (B) Cyclic voltammograms obtained for the modified electrode detecting HbA1c in 2.5 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  containing 0.1 M KCl. Reproduced with permission Wang et al., *Talanta*; published by Elsevier, 2019 [61].

The voltammetric results confirmed the modified electrode's successful application to quantify the glycosylated hemoglobin in the range between 5 and 100  $\mu\text{g}\cdot\text{mL}^{-1}$ . The proposed electrode was also tested in human blood, reaching a recovery rate between 99% and 103.8%. The authors suggested a promising potential method to monitor real samples of diabetes patients and are extended to detect glycoprotein biomarker of other chronic diseases, such as cancer.

Other studies used rare earth elements combined with metal oxide nanocomposites to develop novel nanostructures, enhancing the catalytic activity to fabricate efficient sensors. In that sense, Rezaei et al. [62] synthesized lanthanum-doped zinc oxide nanoflowers to modify a graphite screen-printed electrode for the detection of hydrochlorothiazide (HCT). The HCT is a drug extensively used for hypertension treatment, increasing the excretion of sodium chloride and water from the kidney [63]. The HCT is also used for heart failure treatment, liver cirrhosis, and kidney disorders [64]. The authors prepared the  $\text{La}^{3+}$ -doped ZnO nanoflowers using nano-powders: zinc acetate, lanthanum nitrate, and thiourea ammonia. This last reagent was used as a complexing agent.

After the nanoflowers synthesis, they were characterized by SEM, as shown in Figure 9A.



**Figure 9.** (A) SEM micrograph of  $\text{La}^{3+}$ -doped ZnO nanoflowers. (B) Differential pulse voltammograms obtained for the  $\text{La}^{3+}/\text{ZnO}/\text{SPE}$  in the presence of different concentrations ranging from 1 to 600  $\mu\text{M}$  of hydrochlorothiazide. Inset figure corresponds to the calibration plot for the HCT determination. Reproduced with permission of Rezaei et al., International Journal of Electrochemical Science; published by ESG, 2019 [62].

Graphite screen-printed electrodes were modified by the drop-casting strategy. The modified sensor was characterized using cyclic voltammetry and differential pulse voltammetry (DPV) (See Figure 9B). Firstly, a pH study was performed. The authors concluded that HCT is a pH-dependent molecule, determining the higher oxidation current values for hydrochlorothiazide occurred at pH 7.0.

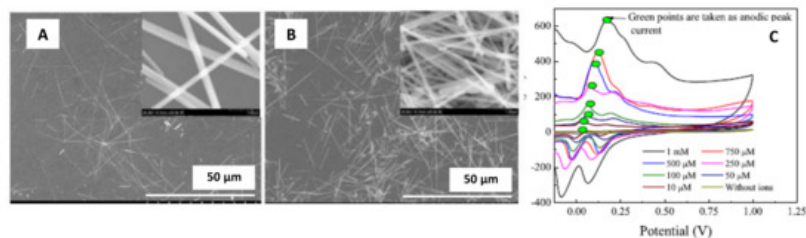
DPV measurements were performed in 0.1 M phosphate buffer saline (PBS) containing different concentrations of HCT, in a range from 1.0 to 600.0  $\mu\text{M}$ . The limit of detection was 0.6  $\mu\text{M}$ . Finally, the  $\text{La}^{3+}/\text{ZnO}/\text{SPE}$  was used to evaluate the proposed method's applicability to determine HCT in tablets and urine samples. The results showed that recoveries ranged from 98% to 103%, with excellent reproducibility.

### 3.5. Nanowires

Usually, SPE are modified with nanowires for different purposes: biomedical, environmental, and food industry. In particular, nanowires are capable of interfacing with other nano-micro scale systems. Due to the long axial morphology, nanowires have a higher surface-to-volume ratio making them similar to biological macromolecules to create excellent nano-bio devices [65]. Kabir et al. [66] developed an electrochemical sensor to detect phosphate using novel ammonium molybdate tetrahydrate/silver nanowires (AMT/AgNWs) modified SPE.

The authors prepared the AgNWs following the procedure developed by Korte et al. [67]. AgNWs were synthesized using silver nitrate as a precursor and polyol as a reducing agent. Additionally,  $\text{CuCl}$  or  $\text{CuCl}_2$  were added to reduce the remaining free  $\text{Ag}^+$  ions during the initial phase of AgNWs formation.

After the synthesis, the investigators modified a screen-printed electrode with the AgNWs and AMT using the drop-casting method [5]. The modified electrode surface was characterized using SEM; the AgNWs exhibited a 100 nm diameter approximately for a reaction time of 10 min. In comparison, a reaction time of 16 min generated AgNWs with a larger diameter of 125 nm (Figure 10A,B).



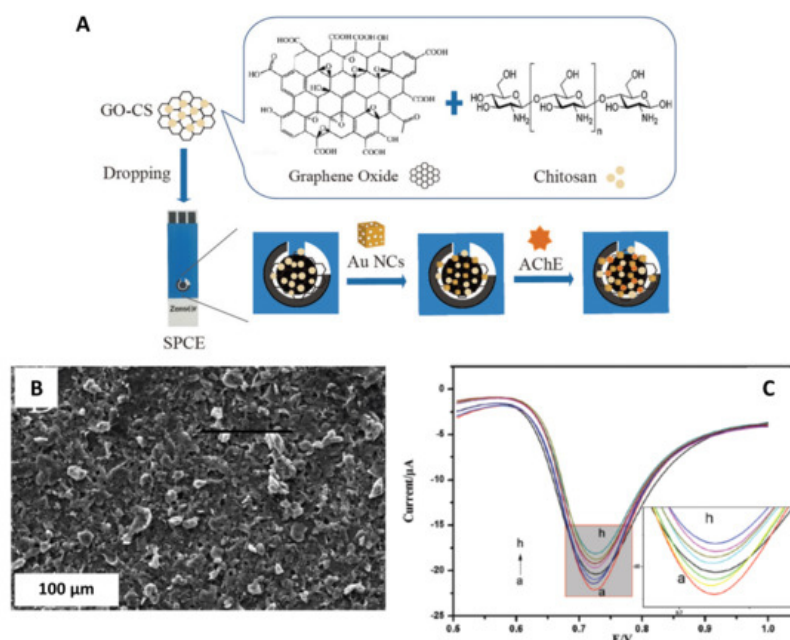
**Figure 10.** (A) SEM micrograph of ammonium molybdate tetrahydrate (AMT)/silver nanowires (AgNWs) for a reaction time of 10 min. (B) (AMT)/silver nanowires (AgNWs) for a reaction time of 16 min. (C) Cyclic voltammograms obtained for the AMT/AgNWs modified screen-printed electrodes for phosphate detection using 0.1 M  $\text{H}_2\text{SO}_4/\text{KCl}$  electrolyte. Reproduced with permission of Kabir et al., IEEE Sensors Journal; published by IEEE, 2018 [66].

The AMT/AgNWs/SPE were electrochemically characterized using cyclic voltammetry, with a sweep potential from  $-0.4$  to  $+0.4$  V and a scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$  (see Figure 10C). The results allowed the authors to conclude that AgNWs contributed in increasing the anodic peak current. The calibration curves exhibited linearity between the anodic peak current and the phosphate concentration. Therefore, the use of AgNWs increased the sensitivity of the modified SPE, reaching a sensitivity of  $0.71 \mu\text{A}\cdot\mu\text{M}^{-1}$ . Additionally, the LOD value was found to be  $3 \mu\text{M}$ .

### 3.6. Nanocages

Nobel-metal nanocages represent a novel type of nanostructures with hollow interiors and porous walls [68]. These structures are produced by galvanic replacement reaction, resulting in assemblies with unique and tunable properties. Compared to the solid nanoparticles, both inner and outer surfaces of gold nanocages (AuNCs) provide good electron transfer from the aptamers's (short DNA or RNA fragments) redox center to the surface electrode [69].

Yao et al. [69] developed a new biosensor to detect chlorpyrifos, an extensively used organophosphate pesticide in agriculture [70]. Firstly, a nanocomposite was constructed of graphene oxide (GO), chitosan (CS), and the AuNCs. Secondly, the acetylcholinesterase (AChE) enzyme was immobilized in the previous matrix and was used to modify a screen-printed electrode. Finally, the constructed biosensor AuNCs/GO-CS/AChE/SPCE (Figure 11A) had good sensitivity towards detecting acetylthiocholine chloride (ATCI) and pesticides.



**Figure 11.** (A) Schematic process to construct AChE sensor. (B) SEM micrograph of the AuNCs/GO-CS nanocomposite. (C) DPV obtained for AChE/AuNCs/GO-CS/SPCE in PBS buffer pH 8.0 with 1.0 mM ATCI after inhibition with chlorpyrifos ( $0.01, 0.1, 1, 5, 10, 50, 100,$  and  $500 \mu\text{g}\cdot\text{L}^{-1}$ ) for 12 min. Reproduced with permission of Yao et al., New Journal of Chemistry; published by The Royal Society of Chemistry, 2019 [69].

Several characterization techniques such as SEM, TEM, high-resolution scanning transmission electron microscopy (HR-STEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), among others, were used to characterize the nanocomposite and the AuNCs (see Figure 11B).



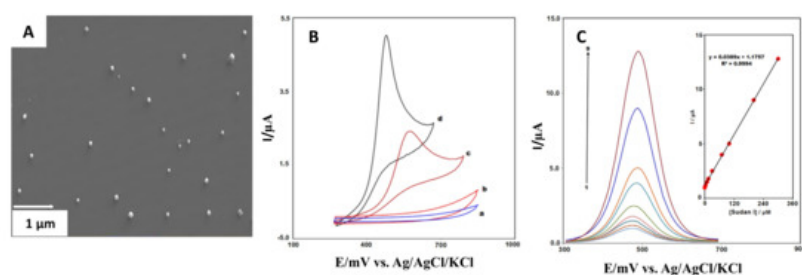
The electrochemical response of the AuNCs/GO-CS/ACH/SPCE was studied by cyclic voltammetry in phosphate buffer containing 0.1 M KCl and 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  (see Figure 11C). The cyclic voltammograms exhibited that the peak current signal increased with the AuNCs, promoting the electron transfer. Additionally, electrochemical impedance spectroscopy (EIS) studies were performed on the modified biosensor. These results exhibited that after immobilization of the AChE, the impedance was significantly reduced compared to bare SPCE.

### 3.7. Nanocubes

Among the variety of shaped nanoparticles, cubic nanoparticles have received particular interest because of their intrinsic size-dependent properties and resulting applications [74], i.e., silver nanocubes have been used for several applications, including plasmonic sensing surface-enhanced Raman scattering, metamaterials, catalysis, and bionanotechnology [72].

Sudan I (1-phenylazo-2-naphthol) is an industrial dye used to color oils, waxes, and polishes, but also it is added to food and cosmetics for color enhancement [73]. This dye can have a genotoxic effect and also can be a potential carcinogen. Food adulteration with this substance is considered a significant risk for public health [74].

Mahmoudi-Moghaddam et al. [75] developed a screen-printed electrochemical sensor based on  $\text{La}^{3+}$ -doped  $\text{Co}_3\text{O}_4$  nanocubes to determine the Sudan I dye. The  $\text{La}^{3+}$ -doped  $\text{Co}_3\text{O}_4$  nanocubes (Figure 12A) were synthesized using cobalt(II) nitrate hexahydrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , lanthanum(III) nitrate hexahydrate  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and polyvinylpyrrolidone (PVP). After the synthesis, the screen-printed electrodes were modified following a drop-casting method.



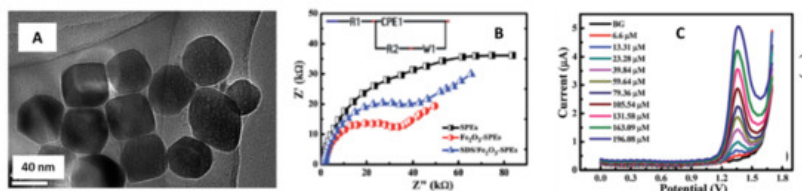
**Figure 12.** (A)  $\text{La}^{3+}$ -doped  $\text{Co}_3\text{O}_4$  nanocubes SEM micrograph. (B) Cyclic voltammograms obtained for the bare (a, c) and modified (b, d) SPE in presence and absence of Sudan I dye. (C) Differential pulse voltammograms of  $\text{La}^{3+}$ -doped  $\text{Co}_3\text{O}_4$  nanocubes/SPE for different Sudan I concentrations (0.3–300  $\mu\text{M}$ ). Reproduced with permission of Mahmoudi-Moghaddam et al., Food Chemistry Journal; published by Elsevier, 2019 [75].

Previous sample preparation was performed to study Sudan I electrochemical response. First, a cyclic voltammetry study was completed. As Figure 12B shows, the analyses conducted with the  $\text{La}^{3+}$ -doped  $\text{Co}_3\text{O}_4$  nanocubes/SPE significantly increased the electrode's electrochemical activity for analyzing Sudan I.

Figure 12C exhibited the differential pulse response corresponding for  $\text{La}^{3+}$ -doped  $\text{Co}_3\text{O}_4$  nanocubes/SPE. The calibration curve shows a linear correlation between the modified electrode's peak current and the different Sudan I concentrations. These results showed an excellent analytical performance with a LOD and LOQ of 0.05 and 0.15  $\mu\text{M}$ , respectively.

Another investigation used iron oxide nanocubes ( $\text{Fe}_2\text{O}_3$ -NCs) to modify screen printed electrodes ( $\text{Fe}_2\text{O}_3$ -NCs-SPE) and determine Meclizine electrochemically [76]. Meclizine is an antihistamine drug commonly used to help with motion sickness and dizziness [77]. The authors synthesized iron oxide nanocubes using a hydrothermal approach with ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) as a precursor. Once the nanocubes were obtained, the drop-casting technique was used to modify the screen-printed electrodes with SDS molecules' addition. SDS is an anionic surfactant that forms a monolayer on the SPE surface with a high density of negatively charged ends. This effect can probably enhance the voltammetric signal of MEC in highly acidic media [76].

In Figure 13A, a high-resolution transmission electron microscopy (HR-TEM) micrograph of the synthesized  $\text{Fe}_2\text{O}_3$ -NCs is observed, an average particle size of 37 nm was obtained.



**Figure 13.** (A)  $\text{Fe}_2\text{O}_3$  nanocubes HR-TEM micrograph. (B) Nyquist plots obtained for the non-modified SPEs,  $\text{Fe}_2\text{O}_3$ -NCs-SPEs and SDS/ $\text{Fe}_2\text{O}_3$ -NCs-SPEs. (C) Differential pulse voltammograms of  $\text{Fe}_2\text{O}_3$  nanocubes/SPE for different meclizine concentrations (6.6–196.08  $\mu\text{M}$ ). Reproduced with permission of Khorshed et al., Analytical Methods Journal; published by The Royal Society of Chemistry, 2019 [76].

The modified SPE's electrochemical behavior was studied using several electrochemical techniques, impedance spectroscopy, cyclic voltammetry, and differential pulse voltammetry.

The Nyquist plots (Figure 13B) exhibited a successful attachment of the  $\text{Fe}_2\text{O}_3$ -NCs onto the SPE surface, decreasing the charge transfer resistance significantly compared to the non-modified electrode.

The differential pulse voltammograms (Figure 13C) were obtained in 0.05 M  $\text{H}_2\text{SO}_4$  and increasing MEC concentration ranging from 6.66–196.08  $\mu\text{M}$ . The calibration plot confirmed the linearity between the oxidation peak heights and the MEC concentration, with a limit of detection of 1.69  $\mu\text{M}$ .

Finally, the modified SPEs were used to analyze real samples (pharmaceutical formulation and urine), showing recoveries of 99.28% and over 100%, respectively. This reveals the potential applicability of  $\text{Fe}_2\text{O}_3$ -NCs-SPE for the meclizine determination.

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