Carbon nanotubes, Conductive Carbon Black and Graphite Powder Based Paste Electrodes

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Carbon nanotubes, conductive carbon black and graphite powder were used to fabricate three kinds of paste electrodes, respectively. The electrochemistry and electroanalytical properties of the electrodes were characterized in parallel by voltammetry, impedance and chronoamperometry. Obviously the surface and bulk structure of the material affect not only the electrode kinetics but also the interactions with analyte in solution. Resulting from the voltammetric response data from a broad species, including ferrocene, potassium ferricyanide, ascorbic acid, dopamine, 2'-deoxyguanosine 5'-triphosphate, malachite green, Cd^{2+} and Pb^{2+}, it highlights that conductive carbon black paste electrode shows the most promising electroanalytical properties in general, owing to the remarkable high signal/noise ratio. Meanwhile, the importance of the components in the paste electrodes also depends on the particular redox system involved.

1. INTRODUCTION

As modern electrochemistry and electroanalytical chemistry continue to develop, the range of working electrode materials continues to expand. Even though, it is undoubtedly that by far carbon and its derivatives still occupy a very important place due to many advantages: wide electrochemical window, good electrical conductivity, long-term stability, low residual current and so on. The best known carbon based electrodes are those involving glassy carbon, carbon paste, carbon fiber, screen-printed carbon strips, carbon films, diamond, pyrolytic graphite, fullerenes, carbon nanotubes (CNTs), reticulated vitreous carbon, etc [1, 2]. Among them, carbon paste is one of the most attractive materials for analyst [1-5] due to added three advantages: easy renewal, easy modification and reproducibility.

Commonly, a carbon paste electrode (CPE) is fabricated by packing a mixture of binder and carbon material into a given holder. Thus, the electrochemical and electroanalytical properties of the electrode are affected on not only the binder but also the carbon materials. The basic requirements for the binder are its practical insolubility in the solution under measurement, a low vapor pressure to ensure both mechanical stability and long lifetime, and further, in the case of applications, its electrochemical inactivity in the potential window of interest [6]. In comparison, carbon materials are more significant. Their structures, physicochemical characteristic and some other specific features are decisive factors for the electrochemical properties of the electrode. So they have been paid much attention. From the early era of CPEs up until now, the most often selected carbon material is graphite powder (GP) with particles in the low micrometric scale [2]. Recently, Rivas et al. reported that CNTs based paste electrodes (CNTPEs) offered a dramatic improvement in the electrochemical behavior of dopamine, ascorbic acid, uric acid, dopac, hydrogen peroxide and DNA [7, 8]. In 2004, Valentini et al. also found that CNTPEs exhibited obvious advantages compared with GP based electrodes (GPPE) [9]. Kachoosangi et al. [10] even advocated that the next step to extend the utility of CPEs was to replace GP with CNTs. Meanwhile, in 1991 Skládal found that the electroanalytical ability of the conductive carbon black (CCB) based electrode (CCBPE) was better than that of the GPPE [11]. More recently, the electrochemical behavior of the CCBPE prepared using a nanostructured commercial CCB (N220) was investigated. The results showed that the CCBPE could be considered to construct biosensors at low cost.

To the best of our knowledge, up to now there are few reports on the difference of electrochemical characterization among the GPPE, the CCBPE and the CNTPE. In this paper the electrochemical and electroanalytical properties of the three kinds of CPEs were investigated in parallel. A rather wide range of electro-active species were used as indicators to evaluate the voltammetric response of the three kinds of paste electrodes. By offering these data, our purpose is to help the analyst on the choice of carbon material for particular analyte.

2. EXPERIMENTAL

2.1 Apparatus and chemical

Cyclic voltammetry (CV), differential pulse voltammetric (DPV), chronoamperometry and electrochemical impedance spectroscopy (EIS) were performed using a CHI 660D Electrochemical Analyzer (CH Instruments, Shanghai, China) with a three-electrode arrangement, consisting of a paste working electrode ($\Phi = 3.8$ mm), a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode. A model pHS-25 digital pH meter (Shanghai Leici Factory, China) was used for pH measurement. Scanning electron microscopic (SEM) measurements were carried out on a JSM-6700F scanning electron microscope (Japan Electron Company).

CNTs (main range of diameter < 10 nm; length: 1-2 μm; ash ≤ 0.2 wt%; special surface area: 400-650 m^2/g) were purchased from Shenzhen Nanotech Port Ltd. Co. (China). CCB (HG-1P, density: 1.7-1.9 g/cm³; particle size: 35-50 nm; BET surface area: 110-130 m^2/g; ash: 1.75%) was purchased

from Guanghua Chemical Plant (Zibo, China). GP (purity > 99.85; granularity: 30 μm; surface area: 10-14 m^2/g) was made in Shanghai Colloid Chemical Plant (Shanghai, China). Ascorbic acid (AA) and dopamine (DA) were purchased from Sigma (USA). The other usual reagents were purchased from Shanghai Chemical Reagent Co. (Shanghai, China) and were all of analytical reagent grade. Solutions were all prepared with sterilized ultrapure water (Resistivity: 18.2 MΩ cm^{-1}) from Poseidon-R70 water purification system (Research Scientific Instruments Co. Ltd, Xiamen, China).

2.2. Fabrication of paste electrodes

Before the fabrication of the CNTPE, the CNTs material was pretreated with a protocol reported [12]. All paste electrodes were fabricated by conventional method described in previous reports [8, 13, 14] with minor modification. In brief, carbon materials (CNTs, CCB or GP) and paraffine were hand-mixed carefully in a mortar in an appropriate ratio, followed by being packed tightly into a glass tube (3.8 mm, i.d.). The paste electrodes were kept at room temperature before used. Their surfaces were smoothed on a weighing paper prior to use.

2.3. Electrochemical measurements

Unless otherwise indicated, CV experiments were performed at a scan rate of 0.100 V/s; DPV experiments were performed at a pulse amplitude of 0.05 V, a pulse width of 0.05 s and a pulse period of 0.2 s. The volume of solutions was 10 mL and the mixtures were stirred with a Teflon coated magnetic stirring bar at about 500 rpm for chronoamperometry. The EIS measurements were carried out in a 1.0 mM K$_3$[Fe(CN)$_6$] solution containing 0.5 M KCl. The AC voltage amplitude was 0.005 V and the voltage frequencies were ranged from 10 KHz to 1 Hz. The applied potential was selected as 0.182 V from the formal potential of the redox probe [Fe(CN)$_6$]$^{3-/4-}$. The electrochemical analysis of Pb^{2+} and Cd^{2+} included two steps: accumulation and stripping. Firstly, metallic cations were preconcentrated onto the electrode surface and then reduced to Pb^0 and Cd^0 under -1.2 V (*vs*. SCE) for a desired time under stir. Secondly, reduced Pb^0 and Cd^0 were oxidized to metallic cations during the anodic potential sweep at the pulse amplitude of 0.05 V, the pulse width of 0.05 s and the pulse period of 0.2 s. All experiments were conducted at room temperature (25 ± 0.5 °C).

3. RESULTS AND DISCUSSION

3.1. Paste composition ratio

An ideal paste electrode should exhibit good electroanalytical ability. At the same time, it is mechanical robustness in electroanalytical applications. Thus, the amount of binder required to produce a CPE that is easy to manipulate and possesses good working stability is, in fact, also strictly correlated to the available surface of the type of carbon utilized [13]. Namely, the carbon material/paraffine ratio is of importance. For the CPE system, the lower amount of binder allows the

better electrochemical communication between carbon particles. Accordingly, a series of CPEs were prepared by mixing different percentages of carbon materials and binder to optimize the composition ratio [13, 14]. In our experiment, to fabricate stable electrodes the percentage composition of paraffine in the CNTPE, the CCBPE and the GPPE should be 50%, 47% and 20%, respectively. As expected, the percentage of CNTs in the paste composite is the highest due to the considerable special surface area of this material (400-650 m^2/g). In the case of CCB, which has larger surface area (110-130 m^2/g) than GP (10-14 m^2/g), an amount of paraffine of 47% is also required. This rule is in good agreement with previous reports [13].

3.2. Morphological characterizations of the CPEs

Since electrochemistry is based fundamentally on interfacial phenomena, the nature of the electrode surface is of obvious importance. In Fig. 1, A, B and C are the typical morphological features of the CNTPE, the CCBPE and the GPPE, respectively. It's clear that the roughness of the electrodes is associated with the granularity of the conductive materials. The GPPE is characterized by a surface formed by irregularly shaped micrometer-sized flakes of graphite. This is in good agreement with previous reports [9, 13]. By contrast, the CCBPE shows a more uniform and rough surface topography. In accordance with Ref. [9], the CNTPE also shows a uniform surface topography, formed by the assembling of rather large smooth regions. In addition, on the surfaces of the CNTPE and the CCBPE there are few large cavities and cracks.
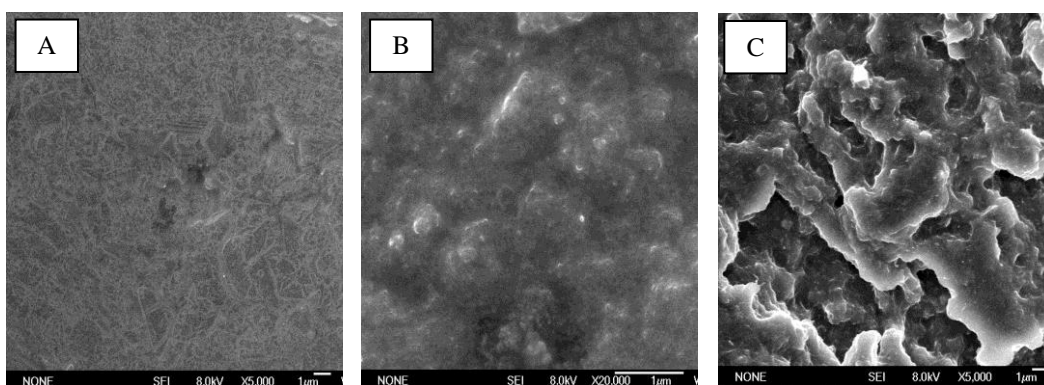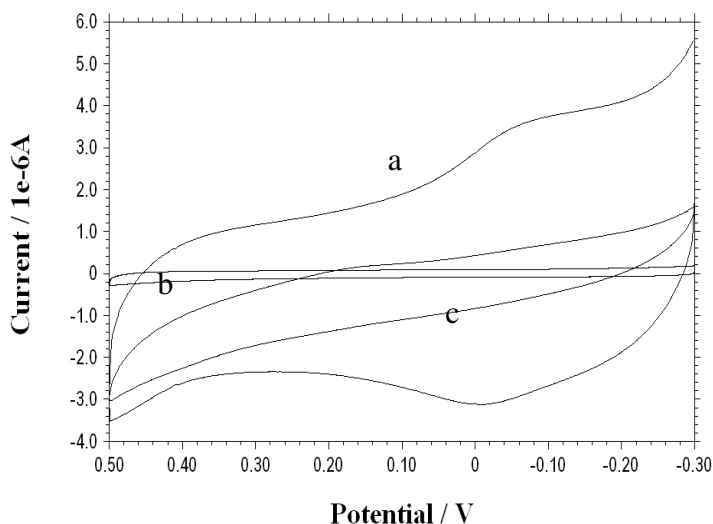

Figure 1. SEM images of the CNTPE (A), the CCBPE (B) and the GPPE (C). CNTs/paraffine ratio: 50/50 (w/w) %; CCB/paraffine ratio: 53/47 (w/w) %; GP/paraffine ratio: 80/20 (w/w) %. Accelerating voltage, 8.0 kV.

3.3. Electrochemical behaviors of the CPEs

The electrochemical behaviors of as-prepared CPEs were examined in a 0.2 M B-R buffer solution of pH 7.0. In Fig. 2, curve *a*, curve *b* and curve *c* are the CV responses of the CNTPE, the CCBPE and the GPPE, respectively. From curve *a* there is a pair of stable redox peaks due to the electroactive of the carboxylic acid groups on the CNTs treated with oxidizing acid [15]. On a certain

degree, it is not a negligible negative factor when the CNTPE is used as working electrode in voltammetric experiments. Meanwhile, there is no visible peak from curve *b* and curve *c*. Remarkably, it can be seen easily that the background current from the curve *b* is the smallest one among that from the three kinds of CPEs, though the they have the same geometric areas. This indicates that the background current is not proportional to the exposed total electrode area. The background current of carbon materials has practical importance in designing electrode geometries to reduce ohmic potential losses. Seen in this light, CCB has the most attractive prospect for fabricating paste electrode.

Figure 2. Cyclic voltammograms of the CNTPE (a), the CCBPE (b) and the GPPE (c) scanned in a 0.2 M B-R buffer solution of pH 7.0. Scan rate: 0.100 V/s. Accumulation time: 2 s.

The electrochemical areas of the three kinds of CPEs were evaluated using chronoamperometry in a 1.0 mM ferrocene monocarboxylic acid solution. The slope of the linear region of the I–$t^{-1/2}$ plot in the short time region provides the product $nFAC_0D^{1/2}\pi^{-1/2}$ using the Cottrell equation:

$$i_d = nFAC_0D^{1/2}(\pi\tau)^{-1/2}$$

where $C_0=1.0$ mM, $D=7.96\times10^{-10}$ cm^2/s [16], are respectively, the concentration and diffusion coefficient of ferrocene monocarboxylic acid, and the other parameters have their usual meanings. Then, 0.197 cm^2, 0.137 cm^2 and 0.105 cm^2 were obtained for the electrochemical areas of the CNTPE, the CCBPE and the GPPE, respectively. The apparent geometric areas of the three kinds of paste electrodes were all 0.113 cm^2. As expected, the electrochemical area of the GPPE exposed to the solution is smaller than the geometric area, with the remainder occupied by the insulating "host" [17]. However, the electrochemical area of the CNTPE is notable larger than its geometric area. This is probably due to the roughness factor of the CNTs [9]. Unfortunately, at the same time it leads the highest capacitance [18]. For the case of the CCBPE, the electrochemical area is about 21% larger than its geometric area.

The relative difference between the electrochemical area and the geometric area is obvious different for the three kinds of CPEs. In other words, these indicate that the paste composition strongly affects the electrochemical behavior of the paste electrodes.

3.4 Electrochemical impedance spectroscopic studies

Since the resistance for an electrode is one of the most important factors which affect electrochemical behavior, the three kinds of CPEs were characterized by EIS. Curve *a* in Fig. 3 is the Nyquist diagram of 1.0 mM $[Fe(CN)_6]^{3-/4-}$ at the CNTPE. The high-frequency section of the curve shows an arc, the diameter of which displays a rather low surface electron-transfer resistance (R_{et}) owing to the attractive electrical conductivity of CNTs, even though the negative charge of carboxylic acid groups at the tip of the CNTs can produce repulsion to $[Fe(CN)_6]^{3-/4-}$ [12]. Curve *b* is the Nyquist diagram at the CCBPE. From this curve a lower R_{et} is found. By contrast, from curve *c*, which is the response of the GPPE, a high value of the R_{et} is obtained (about 2, 000 Ω). These results indicate that the order of the conductive ability of the paste electrodes is: the CCBPE > the CNTPE > the GPPE.
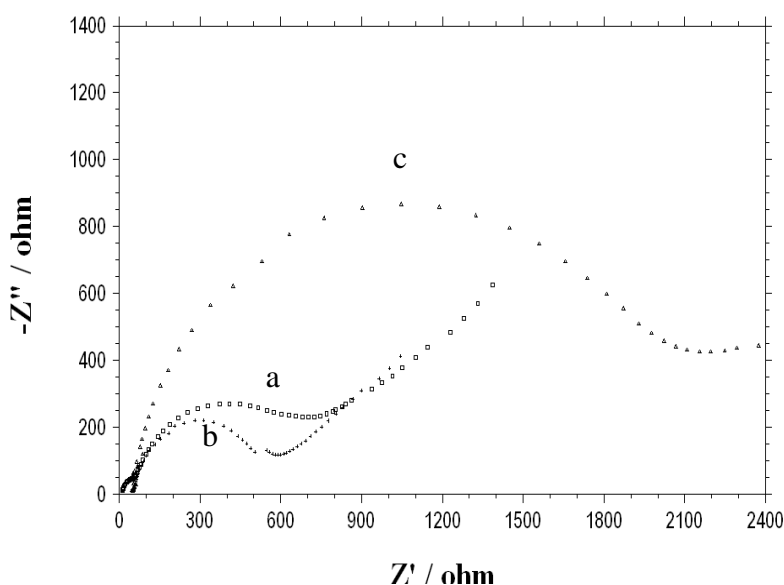
Figure 3. Nyquist plots of the CNTPE (a), the CCBPE (b) and the GPPE (c). Supporting electrolyte solution: 1.0 mM $K_3[Fe(CN)_6]$ containing 0.5 M KCl.

3.5 Electroanalytical performance

To evaluate the electroanalytical performance of the three kinds of CPEs, a group of typical species were employed for measurements in parallel.

Fig. 4(A) shows the CV behaviors of 0.1 mM ferrocene in 0.6% nitric acid solution at the CNTPE (curve *a*), the CCBPE (curve *b*) and the GPPE (curve *c*). From the figure and the voltammetric parameters summarized in Table 1, we can see that the anodic peak current (i_{pa}) : cathodic peak current (i_{pa}) at the CNTPE is nearly 1:1 with a large background current. Meanwhile, at the CCBPE the current

response is the largest with the lowest potential separation (ΔE_p). In the case of GPPE, the electrode kinetics is the poorest. But at it the current response is almost as sensitive as that at the CCBPE. In general, an ideal working electrode for voltammetric application shows good electrode kinetics, accompanying with high sensitive current response. However, the behaviors of the three kinds of CPEs are complex towards ferrocene. It's interesting but not easy to explain now.

Table 1. CV parameters for 0.1 mM ferrocene in 0.6% nitric acid solution at the three kinds of CPEs. Quiet time: 2 s. Scan rate, 0.100 V/s.

Electrode	E_{pa}(mV)	E_{pc}(mV)	ΔE_p(mV)	i_{pa}(μA)	i_{pc}(μA)	i_{pa} / i_{pc}
CNTPE	348	249	94	-1.936	1.817	1.07
CCBPE	296	234	62	-3.064	2.516	1.22
GPPE	257	179	78	-3.001	2.201	1.36

Potassium ferricyanide is another kind of species which are often used to characterize the electrochemical properties of working electrodes [14]. Fig. 4(B) shows the CV behaviors of 1 mM potassium ferricyanide in 0.1 M KCl solution at the CNTPE (curve *a*), the CCBPE (curve *b*) and the GPPE (curve *c*). Curve *b* is the sharpest with the largest current response, indicating the most attractive electroanalytical property of the CCBPE towards this species.

AA is a water-soluble vitamin that is widely required in metabolism. It has prophylactic function to many kinds of diseases [19]. DA is one of the most significant catecholamine, functioning as a neuro-transmitter in the central nervous system [20]. It is of significant importance to detect their percent in medicament and some other conditions. By far there are a few reports on determining the two with CPEs [21, 22]. Fig. 4(C) and (D) show the CV behaviors of 0.2 mM AA and 50 μM DA in 0.4 M PBS buffer solution of pH 3.1 at the CNTPE (curve *a*), the CCBPE (curve *b*) and the GPPE (curve *c*), respectively. From the figures and the voltammetric parameters summarized in Table 2, we can see that the CNTPE shows obvious sharper and larger voltammetric peaks as well as lower overvoltages for the two redox systems in comparison with the GPPE, indicating the improved electron-transfer kinetics and good accumulation ability [7]. However, in the case of AA, the sensitivity of the current response at the CCBPE is even higher than that at the CNTPE, in despite of a higher E_{pa}. In particular, the small background is of worthy to pay attention.

Table 2. CV parameters for 0.2 mM AA and 50 μM DA in 0.4 M PBS buffer solution of pH 3.1 at the CNTPE, the CCBPE and the GPPE. Quiet time: 60 s. Scan rate, 0.100 V/s.

Electrode	AA		DA				
	E_{pa}(mV)	i_{pa}(μA)	E_{pa}(mV)	E_{pc}(mV)	ΔE_p(mV)	i_{pa}(μA)	i_{pc}(μA)
CNTPE	245	-9.259	376	321	55	-4.423	4.128
CCBPE	264	-9.523	437	284	153	-2.170	1.834
GPPE	486	-4.181	524	189	335	-1.844	1.072

Unlike other three kinds of reactive substrates for DNA synthesis, 2'-deoxyguanosine 5'-triphosphate (dGTP) exhibits sensitive voltammetric response. So it can be used to monitor the process of polymer chain reaction [23] or loop-mediated isothermal amplification [24]. Fig. 4(E) is the CV behaviors of 10 μM dGTP in 0.4 M B-R buffer of pH 6.0 at the three kinds of CPEs. The E_{pa}s at the CNTPE (curve *a*), the CCBPE (curve *b*) and the GPPE (curve *c)* are 936 mV, 1016 mV and 994 mV. And the corresponding i_{pa}s are -5.759 μA, -16.70 μA and -2.818 μA, respectively. It can be seen that the CCBPE shows the most sensitive current response towards dGTP, though the overvoltage is higher than that from curve *a*.

Malachite green (MG) is a cationic triphenylmethane dye. Recently some methods based on electrochemical technique are established to determine trace amount MG [25, 26]. The electroanalytical ability of the three kinds of CPEs towards MG was evaluated, too. Fig. 4(F) is the CV behaviors of 0.5 mg/L MG in 0.4 M PBS buffer of pH 6.5. The E_{pa}s at the CNTPE (curve *a*), the CCBPE (curve *b*) and the GPPE (curve *c*) are 526 mV, 871 mV and 816 mV. And the corresponding i_{pa}s are -0.542 μA, -2.580 μA and -0.535 μA, respectively. Resulting from these data two practical aspects are available. One is that the CNTPE shows obvious electro-catalysis, leading to a lower E_{pa}. The other is that we can obtain a rather sensitive current response by using the CCBPE.

Heavy metals cause environmental and health problems because of their stability in contaminated sites and complexity of mechanism in biological toxicity [27]. It is well known that the method based on anodic stripping voltammetry is approved to be attractive for detecting trace amount heavy metals [4, 28]. As shown Fig. 4(G) and (H), curve *a*, curve *b* and curve *c* are the anodic stripping voltammetric behaviors of 60 μg/L Cd^{2+} and 50.0 μg/L Pb^{2+} at the CNTPE, the CCBPE and the GPPE, respectively. After a 120 s accumulation under -1.2 V, there are only little humps at the GPPE. However, during the DPSV scan, obvious and well-shaped anodic stripping peaks appeared at the CNTPE and the CCBPE. The current values of the Cd^{2+} at the CNTPE and the CCBPE are -1.323 μA and -1.744 μA, respectively. In the case of Pb^{2+}, the current values are -0.577 μA and -1.377 μA. These indicate that the CCBPE enables a more significantly enhancement of the sensitivity of the determination of these heavy metals. In addition, the low background current from the CCBPE makes it an especial advantage in experimental performance.

Based on all the performances above we can see that the chemical, physical and structure property of the carbon materials play an important role on the electrode behaviors. This is just in good agreement with McCreery et al. [17]: "The diversity of carbon as an electrode material stems largely from its structural polymorphism, chemical stability, rich surface chemistry, and strong carbon-carbon bonds present both internally and often between the carbon materials." The broad investigation towards several species with applications in voltommetric measurement demonstrates that better electroanalytical properties are obtained by using nanostructure carbon materials (i.e. CNTs and CCB) than that by common GP. This maybe ascribe to not only the sufficient surface area but also the defects of the structure and higher density of edge planes on the nanostructured carbon materials, which are believed to strongly affect the population of sites available for catalysis [17].

Certainly, functional groups on the nanostructured carbon materials can be another important factor [29]. It is to be noted that CNTs results should be viewed with some cautions, due to variations in the level of edge sites and the possibility of trace metal contamination [30].
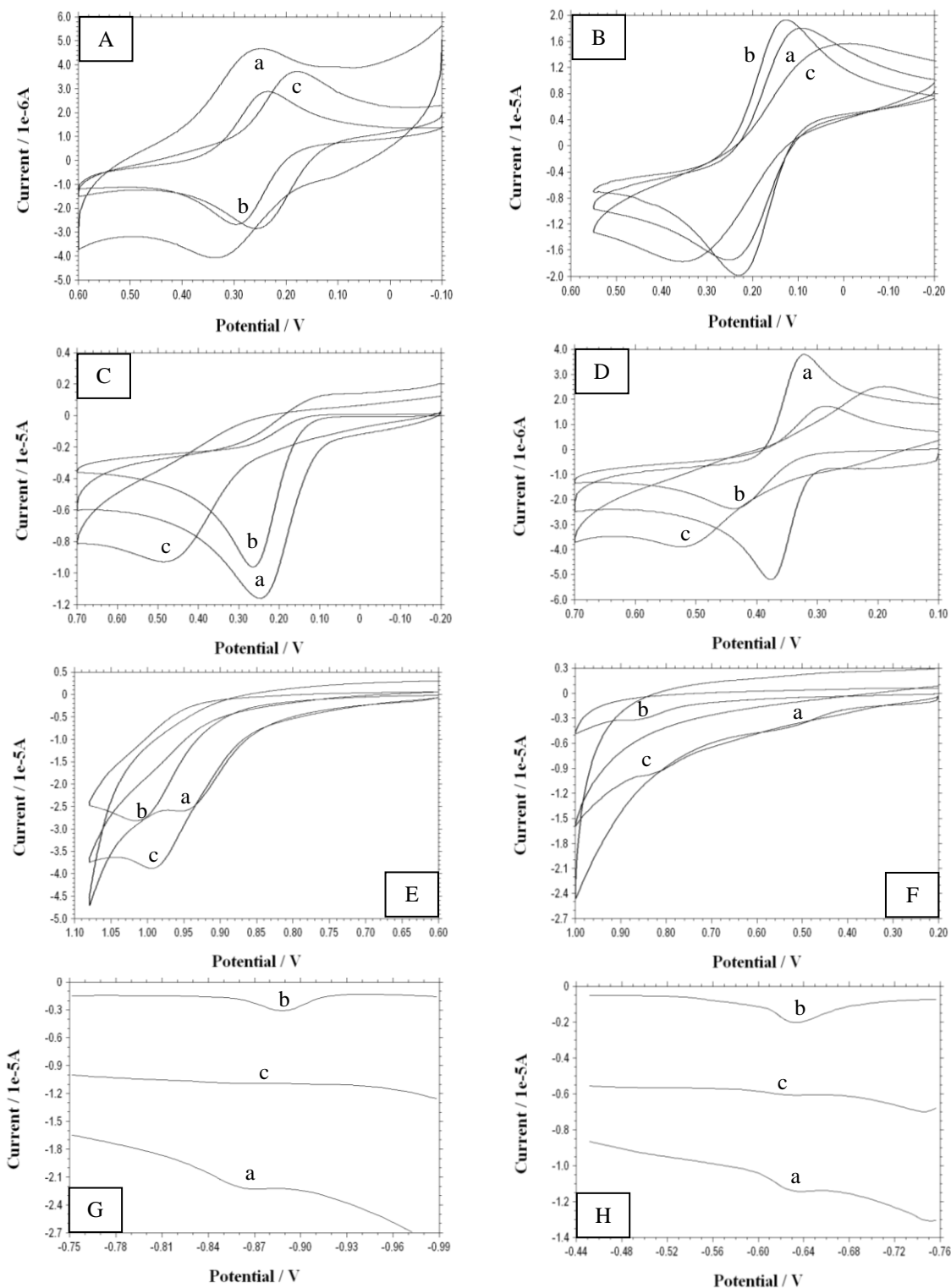
Figure 4. Voltammograms of 0.1 mM ferrocene (A), 1 mM potassium ferricyanide (B), 0.2 mM AA (C), 50 μM DA (D), 10 μM dGTP (E), 0.5 mg/L MG (F), 60 μg/L Cd^{2+} (G) and 50 μg/L Pb^{2+} (H) at the CNTPE (a), the CCBPE (b) and the GPPE (c). (A) Electrolyte: 0.6% nitric acid solution , quiet time: 2 s; (B) Electrolyte: 0.1 M KCl, quiet time: 2 s; (C) and (D) Electrolyte: 0.4 M PBS buffer of pH 3.1, quiet time: 60 s; (E) Electrolyte: 0.4 M B-R buffer of pH 6.0, quiet time: 120 s; (F) Electrolyte: 0.4 M PBS buffer of pH 6.5, quiet time: 240 s; (G) and (H) Electrolyte: 0.4 M PBS buffer of pH 3.1, accumulation at -1.2 V for 120 s with stir, quiet time: 10 s. CV scan rate, 0.100 V/s. DPV parameters: pulse amplitude 0.05 V, pulse width 0.05 s, pulse period 0.2 s.

On one hand, the electroanalytical behavior of the CCBPE is similar to that of microelectrode based on carbon nanoparticle [31], which exhibits excellent performance towards some organic and inorganic analytes. In comparison, the comprehensive electroanalytial ability of the CCBPE is a little better than that of the CNTPE owing to the remarkable higher signal/noise ratio, saying nothing of the GPPE. Taking the cost of the materials into consideration, the superiority of the conductive carbon black will be more prominent. On the other hand, as noted in the examples, the importance of the components in the paste electrodes depends on the particular redox system involved, although some useful generalizations are available.

4. CONCLUSIONS

The diversity of CPEs stems largely from the geometrical and physicochemical properties of the carbon materials. Both the nature of the electrode surface and the electrochemical behaviors depend strongly on the components. E.g.: the CNTPE and CCBPE have a more uniform and rough surface topography in comparison with the GPPE. The surface and bulk structure of the materials affect not only the electrode kinetics but also the interactions with analyte in solution. In general, the CPEs made from nanostructure carbon materials show more desired electroanalytical ability by voltammetric techniques towards a broad species. In particular, the economical CCBPE is a promising working electrode for a few important applications due to the attractive high signal/noise ratio, which results from the low background current. Meanwhile, we cannot ignore that the importance of the components in the CPEs also depends on the particular redox system involved, e.g. to determine DA by CV the CNTPE is more appropriate.

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