Electrochemically Active Thin Carbon Films with Enhanced Adhesion to Silicon Substrates

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Abstract

Thin carbon films deposited on technologically relevant substrates, such as silicon wafers, can be easily implemented in miniaturized electrochemical devices and used for sensing applications. However, a major issue in most carbon films is the weak film/substrate adhesion that shortens the working device lifetime. This paper describes the facile preparation of robust thin carbon films on silicon/silicon oxide substrates by one-pot sol-gel synthesis. The improved adherence of these carbon films is based on the

incorporation of silica through the controlled synthesis of a resorcinol/formaldehyde gel modified with aminopropyltriethoxysilane. The films demonstrate excellent adhesion to the silicon/silicon oxide substrate, good homogeneity, excellent electrical conductivity and superior electrochemical performance. Moreover, this approach opens the door to the fabrication of thin carbon film electrodes by photolithographic techniques.

Keywords

Carbon/silica film, interfacial adhesion, electrical conductivity, electrochemistry

1. Introduction

Carbon based materials have attracted much attention as electrodes for electrochemical sensors due to its low cost, wide potential window, relatively inert electrochemistry and electrocatalytic activity in a wide range of redox reactions involving inorganic, organic and biological molecules¹. Most carbon electrodes are prepared by processing bulk carbonaceous materials such as graphite and glassy carbon² or carbon nanomaterials³ including nanotubes⁴ or graphene⁵. The introduction of these carbon materials into an electrode varies from sensor to sensor depending on its uses. For instance, to prepare carbon paste electrodes⁶, which are widely used for research purposes, the carbon particles can be easily dispersed in a paste or a liquid vehicle. By contrast, the industrial mass production of screen printed electrodes (SPE), such as the ones used in glucose test strips for diabetes⁷, requires engineering complex carbon-based inks by

incorporating binders and other additives to the liquid carrier. The widely used SPEs⁸ are thick-film electrodes which were developed to meet the needs of disposable miniaturized electrochemical probes to enable on-site analyses⁹. Nowadays, a growing trend towards enabling automated on-site monitoring in real time and for extended periods of time has placed miniaturized robust electrodes in the limelight. SPEs are not tailored to meet these specific needs as the presence of binders and other additives are at the origin of an accelerated deterioration of electrode performance. In this context, miniaturized thin-film carbon electrodes are an attractive alternative offering additional advantages such as improved electrochemical performance, thanks to its nearly pure carbon composition, and the possibility of fabrication using robust and well setup photolithographic based processes.

The deposition of high quality carbon films is critical for the electrochemical sensor application and has met three important requirements¹⁰. Firstly, the deposition procedure should be simple and cost-effective. Secondly, the films have to be robust enough to be patterned by photolithographic techniques, which involve working with reactive solvents and photoresists of different nature. Thirdly, the resulting sensor must be mechanically and chemically robust to withstand exposure to various electrolyte media and multiple electrochemical processes. To fulfill the above-mentioned characteristics, the thin carbon films must demonstrate an excellent interfacial adhesion to the substrate.

A variety of methods have been reported for the preparation of thin carbon films displaying a wide range of structures and properties between those of graphite and

diamond^{1, 10} or even more exotic forms of carbon such as nanotubes¹¹ or graphene¹². Most of these films have been prepared on technologically relevant substrates such as silicon either by depositions in vacuum or by pyrolysis processes of gases¹³ and films prepared from liquid precursors such as polymers¹⁴ or photoresists¹⁵. The pyrolysis approach has the advantages of simplicity and low cost and moreover, the so-called pyrolyzed photoresist films (PPF) are perfectly suited for the film patterning by photolithography before pyrolysis. However, a quite common shortcoming of carbon microelectrodes prepared by photolithography is a weak film/substrate interaction, manifested by film flaking during long term operation and this represents the most hampering limitation for sensor applications of these materials.

Chemical bonding between the film and the substrate is essential to ensure a robust construct. Thus, considering the well-known fact that silica films on Si substrates show strong film/substrate adhesion due to the formation of siloxane chemical bonds (-Si-O-Si-)¹⁶, one route to improve the adherence of carbon film on Si substrates is by the incorporation of silica into the carbon matrix. Interestingly, we reported that pyrolyzed organic gels are appealing materials to fabricate electrodes for electrochemical sensors¹⁷ and moreover sol-gel chemistry offers the possibility of mixing the different precursors from carbon and silica at molecular level resulting in homogeneous composite (carbon/silica) hybrid materials¹⁸. In particular, Song *et al.* have reported on porous carbon/silica films on Si substrates fabricated by spin coating a sol composed of both silica and phenol/formaldehyde, followed by a pyrolysis step^{18b}, pointing out that the addition of silica into the carbon matrix significantly improved the

adhesion of the film on the substrate. Moreover, conductivity of these carbon/silica films up to 40 wt% silica content remained comparable to that of carbon inks commonly used for the preparation of screen printed electrodes. In their approach the carbonaceous and silica sols were synthesized separately and then mixed together. Such approach is time-consuming, requiring a multiple-step process carried out over several days.

Here, we report on the fabrication of hybrid carbon/silica thin films with enhanced interfacial adhesion to silicon/silicon oxide substrates by a one-step sol-gel route. Resorcinol and formaldehyde are used as the carbon source whilst aminopropyltriethoxysilane (APTES) was selected as the silica source. A homogeneously mixed solution of these three components formed a gel that is spin-coated onto the substrate and converted into a carbon/silica film by controlled pyrolysis. The synthetic conditions to prepare uniform films on silicon/silicon oxide substrates are then optimized. Surface morphology, electrical conductivity as well as electrochemical performance of these films are systematically investigated. The films display remarkable enhanced interfacial adhesion to silicon wafers and superior electrochemical properties. In addition, the films could be photolithographically patterned for the fabrication of robust carbon films electrodes.

2. Experimental Section

2.1. Reagents and Materials

The following chemicals were purchased from Sigma-Aldrich and used as received: resorcinol ($m\text{-C}_6\text{H}_4(\text{OH})_2$, 99% pure), formaldehyde water solution (CH_2O , 37wt.%, methanol stabilized), (3-aminopropyl)trimethoxysilane (APTES $\geq 98\%$), ethanol (96% pure), acetic acid (CH_3COOH , 99.7% pure), Potassium ferricyanide and potassium ferrocyanide 99% pure and potassium nitrate (purity $>99.0\%$), also from Sigma-Aldrich were employed for the electrochemical characterization .

500 μm thick 4-inch silicon wafers were thermally oxidized at 1000°C to get a 1 μm thick silica layer, labeled as silicon/silicon oxide wafer. The oxide-terminated silicon wafer was diced into $2 \times 2 \text{ cm}^2$ substrates. Prior to use, the substrate was thoroughly cleaned in hot piranha solution and rinsed in distilled water.

2.2. Preparation of Carbon/Silica films

The preparation of carbon/silica films involves three steps, namely: 1) sol preparation, 2) spin-coating an organic/silica film and 3) carbonization. The nature of the sol is critical for the successful deposition of the films by spin-coating. The influence of the sol in the final thickness of the film is presented in detail in section 2.3. Table 1 lists the composition of the sols employed for producing the carbon films. In step 1), APTES was first dissolved in ethanol or an ethanol/acetic acid mixture in a glass container, and

then resorcinol and formaldehyde were added successively. The mixture was stirred continuously at room temperature until a clear homogeneous solution was formed. The resorcinol/APTES molar ratio was varied between 1 and 4. The relative molar content of resorcinol and APTES are indicated in the sample labeling by the two digits following carbon silica, respectively. The labeling of the films shown in Table 1 also takes into account if relatively high (A_H) (785 μ L) or low quantities (A_L) (50 μ L) of acetic acid were used in the preparation of the sol, adding A_H and A_L respectively in the label. For comparison, a carbon film, labeled C-A, was also prepared using a sol containing only carbon precursor.

Table 1. Sol compositions, details of the gelation process and resulting film thickness.

Samples	R (g)	F (ml)	APTES (ml)	Ethanol (ml)	HAc (μ L)	Reaction time (h)	Gelation time (h)	Film thickness (nm)	Cracks on films
CS11- A_{H-1}	0.4	0.54	0.84	2	785	x	0.15	x	x
CS11- A_H	0.4	0.54	0.84	4	785	1	10	~400	No
CS21- A_H	0.4	0.54	0.42	2	785	1	24	~400	No
CS41- A_H	0.4	0.54	0.21	2	785	24	72	~400	No
CS41- A_L	0.4	0.54	0.21	2	50	1	10	~400	No
CS41	0.4	0.54	0.21	2		0.15	0.5	~800	No
C-A	0.4	0.54		2	785	120	168	~350	No

x: unprocessable; CS: carbon silica; R: resorcinol; F: formaldehyde; HAc: acetic acid; Reaction time: the time before spin-coating the sol

In step 2) the sols were spin-coated onto 2 x 2 cm² silica/silica oxide substrate. Then, gels were deposited by spin coating using rotation speeds from 1000 rpm to 4000 rpm.

We observed that the average film thickness before pyrolysis decreased when increasing the rotation speed, tending to level off above 3000 rpm. In order to obtain reproducible resorcinol/formaldehyde/SiO₂ films, the spin-coating with the sols was

always performed at 4000 rpm for 45 s.

The viscosity of the sols, which is closely related with its composition, dramatically increases with reaction time and plays a decisive role in the quality of the coated film and its final thickness. In order to obtain continuous and crack-free films, the viscosity of the sols at different reaction times was measured with a HAAKE RheoStress RS600 rheometer in velocity control mode with a shear rate of 2880 s^{-1} during 30 seconds at 20°C . Sols with viscosities ranging from 6 to 10 mPa·s resulted in good quality crack-free films with thicknesses between 400 and 800 nm. However, spinning sols with viscosities higher than 11 mPa·s produced after pyrolysis cracked films thicker than 1000 nm (see figure S1). The viscosities were adjusted to suitable values by carefully controlling reaction times at room temperature before spinning. The suitable reaction times that were used to obtain crack-free C/SiO₂ films of around 400 nm thick are included in Table 1 for all the sol compositions.

In step 3), immediately after spin-coating, the gels were placed in an oven at 60°C for more than 4 hours for gel aging. Afterwards, they were placed in a quartz tube and pyrolyzed under Ar+H₂ (95%+5%) atmosphere to convert them into C/SiO₂ films. For carbonization, the furnace temperature was raised to 1000°C at a rate of 200°C/h , maintaining it at this temperature for 2 hours and then switching the power off to let the furnace cool down to room temperature. During the pyrolysis process, the gas flow rate was $100\text{ cm}^3/\text{min}$.

2.3. Film characterization

The chemical compositions and the nature of the C and Si bonds of the surface of C/SiO₂ films were analyzed by X-ray photoelectron spectroscopy (XPS) employing AlK α radiation. Scanning electron microscopy was used to study the chemical homogeneity of the films. The surface morphology of the C/SiO₂ films was observed by optical microscopy and atomic force microscopy (AFM) using an Agilent 5100 equipment and a KLA profilometer. The thickness of the spin-coated films before and after carbonization was measured with the profilometer on a zone of the film that had been intentionally scratched with a razor blade (see Figure S1 for a representative 3D profilometric image of a measured film after pyrolysis). The microstructure of the films was studied by Scanning Electron Microscopy at 10 kV (Carl Zeiss Auriga-40 and FEI Quanta 200). A cross section of the film and the substrate was obtained with Focussed Ion Beam equipment (Zeiss 1560XB Cross Beam) at 30 KV and 50 pA using Ga ions.

The interfacial adhesion of carbon-based and carbon-silica films to Si substrates was assessed by observing the eventual detachment of the films from the substrate after submitting them to an ultrasonic treatment of 3 minutes in an acetone bath. The interfacial adhesion was also characterized by additional peeling test. Before performing the test the substrates were glued on a microscope glass slide using silver paste. A piece of a transparent tape (MagicTM from 3M) was scotched onto the film and then peeled off while holding the glass slide.

Four-point probe measurements were carried out to ~~get~~ determine the sheet resistance of the C/SiO₂ films. Three measurements were performed on different areas of each sample and the film thickness determined on an area of 200 μm x 200 μm by profilometry. From the profilometric measurement, the maximum, the minimum and the average value were considered to calculate the resistivity values from the sheet resistance. The resistivity value was determined from the average of those nine values and its standard deviation was considered its error. The electrochemical properties of these C/SiO₂ films were investigated by assessing the cyclic voltammetric behavior of the ferricyanide/ferrocyanide redox couple using a Autolab unit with GPES software (Metrohm-Autolab B.V., The Netherlands). In order to carry out these measurements, the film area to be used as the working electrode was defined by gluing a 3 mm diameter cylindrical plastic cuvette to the film surface using thermoplastic silicone. Electrical contact was done by fixing an Al wire on one corner of the film with silver paste (see Figure S2 for a schematic drawing of the set-up). When carrying out the measurements, a silver wire pseudo-reference electrode and a stainless steel wire counter electrode were immersed in the cuvette to complete the electrochemical cell.

3. Results and Discussion

3.1. Sol-gel synthesis of C/SiO₂ films on Si substrates

As can be seen from Table 1, the incorporation of APTES into resorcinol/formaldehyde system accelerates gelation. Keeping constant the acetic acid content, the gelation time

decreased significantly by increasing the relative content of APTES from 0.2 to 0.5. For instance, CS11-A_{H-1} gelled after only ~0.15 h when it was synthesized in 2 mL ethanol as the samples CS21-A_H, CS41-A_H and C-A, but crack-free films could not be obtained with this sol. To facilitate sol handling and processing into a film by spin coating, gelation rate was thus slowed down by doubling the volume of solvent. Acids are catalysts for both resorcinol/formaldehyde and silica sol-gel processes. However, the gelation rate of resorcinol/formaldehyde/APTES system was observed to ~~speed-up~~ increase dramatically by decreasing the acetic acid content. For instance, in the case of the C/SiO₂ CS41 film series, the gelation time decreased from 72 h to 30 min with the absence of 785 μ L acetic acid. This paradoxical behavior can be understood if one takes into account that gels are also base-catalyzed and that the presence of an amino group in APTES provides base characteristics to the compound. The amino group catalyzes inter- or intra-molecular reactions between silane molecules and silanol groups to form siloxane bonds, one of the necessary steps of the resorcinol/formaldehyde/APTES gelation process. The slowing down in the gelation rate induced by the addition of acetic acid occurs because it neutralizes the basic character of the amino group weakening its catalytic effect.

The carbonization processes involved a large reduction of the vertical film dimensions. Taking sample CS21-A_H as an example, the average thickness of the film decreased from ~900 nm to ~400 nm, *i.e.* ~55% reduction in thickness. Taking into account the fact that the SiO₂ xerogel shrinks less than the resorcinol/formaldehyde xerogel during pyrolysis, it was expected that shrinkage decreases for samples containing more SiO₂. Indeed, in the case of sample CS11-A_H, which contains the largest amount of SiO₂, a ~50% reduction in thickness was observed. Even though the presence of acetic acid in the CS41 sample series significantly slowed down the gelation rate, we did not observe any influence of this parameter on the film shrinkage. Interestingly, thanks to the strong interfacial adhesion between C/SiO₂ film and the silicon/silicon oxide substrate, none of the studied C/SiO₂ films showed shrinkage of the lateral dimensions regardless the dimensions of the used substrates. In spite of the important shrinkage resulting from pyrolysis the C/SiO₂ films are expected to present a substantial porosity. Even though this could not be characterized by standard methods due to the small mass of the films, we investigated the porosity of bulk C/SiO₂ materials by nitrogen adsorption porosimetry. For instance, in the case of the bulk CS41 monoliths the porosity is characterized by the presence of pores below 3 nm (micropores) and a surface area of XX m²/g (see Figure S4).

3.2. Interfacial adhesion between the films and the Si substrate

In order to test the adhesion of the films to the substrate we established a test providing though conditions for the material in the context of its final application as

electrochemical sensor in liquid solution. Two films (with and without SiO_2) were immersed in acetone and placed in an ultrasonic bath for 3 min. Figure 1 shows the images of the films after the test. It can be clearly observed that the pure carbon film (C-A), peels off from the Si substrate, demonstrating a very poor interfacial adhesion. By contrast, the carbon-silica film (C41-A_L) shows no flaws after the ultrasonic treatment, indicating that addition of SiO_2 significantly enhances the film interfacial adhesion. We hypothesize that this fact is directly related to the formation of Si-O-Si covalent bonds between the SiO_2 xerogel and the SiO_2 layer on the silicon substrate. Moreover, it can also be concluded from Figure 1 that a molar concentration of 25% of APTES with respect to resorcinol creates a C/ SiO_2 thin film with a strong enough interfacial adhesion to ensure robust films. In fact, except for C-A film, no film detachment was observed in any of the hybrid C/ SiO_2 film samples listed in Table 1.

Figure 1. Representative images of pure carbon and C/ SiO_2 films on Si substrates after ultrasonic treatment in acetone bath for 3 min.

More evidence on the enhanced adhesion of the C/SiO₂ films compared to C films was obtained with a peeling tests using scotch tape (see Movies S1 and S2) The Movies clearly show that the C film is peeled off from the substrate with the tape while this is not the case for the C/SiO₂ film.

3.3. Topography of the carbon thin-films

Figure 2(A) shows a representative optical image of a C/SiO₂ thin film and the corresponding surface profile recorded with a profilometer. It shows that the film surface is not flat as it presents roughness at two scales. A wave-like roughness morphology with an amplitude of about 50 nm and a periodicity of about 50 μ m onto which a surface roughness of smaller vertical and lateral dimensions could be detected. This is a common feature of spin coated films and has been related to the rapid drying of the deposited film during the spin-coating process, especially when a volatile solvent with low boiling point such as ethanol is used.¹⁹ In addition, we found that the wave-like roughness becomes more pronounced for thicker films. For instance, the wave amplitude increased from 40 to 70 nm as the thickness of the CS21-A_H C/SiO₂ film increased from 400 to 800 nm. It was also found that in films of different composition but comparable thicknesses, the SiO₂ content had little effect on the wave amplitude. At this point, it should be emphasized that the motivation of our work was ~~the development of~~ developing C/SiO₂ films ~~that can~~ to be further patterned by photolithographic techniques into microelectrodes for electrochemical sensing. The

~50 nm wavelike roughness is expected to have a negligible influence on the patterning process considering the overall C/SiO₂ film thickness (between 400-800 nm) and the usual thickness of the photoresists required to produce patterns in the micron range (between 1-5 μ m).

Figure 2. Representative optical (A), SEM (B) and AFM (C) images of the C/SiO₂ thin films. The inset of (A) is the extracted surface profile scanned by profilometer. The inset of (B) is the SEM image of a cross-section of the film created by intentionally scratching the film from top to bottom (see yellow dotted arrows) and a cross-section of the film and the substrate along the left-right direction performed using a FIB (yellow arrow).

Figure 2(B) shows a characteristic SEM image of a film in planar view which displays the already mentioned wave-like roughness and the absence of cracks. The inset of Figure 2(B) shows a cross section of the film in the vertical direction, obtained by intentionally scratching it (see yellow dotted arrows) and a cross-section of the film and the Si substrate along the horizontal direction, created using a focused ion beam equipment (see yellow arrow). It is important to stress that the creation of these cross-sectional features did not result in crack formation at the interface or the surface of the film, providing further evidence of its robustness.

Atomic force microscopy (AFM) was used to analyze the surface roughness of the

C/SiO₂ films with an increased lateral resolution. Figure 2 (BC) shows a typical AFM image recorded on the CS41 sample, for which a surface roughness value of around 0.2 nm was obtained. The surface roughness measured by AFM became larger in the films with higher SiO₂ content. For instance, the roughness value increases up to ca. 1 nm for the sample CS11-A_H with the largest SiO₂ content. Nevertheless, for the targeted application, the roughness of these C/SiO₂ films can be considered small and its homogeneity excellent as any phase separation between carbon and SiO₂ components was not observed at the macro and microscales by scanning electron microscopy analysis using the backscattered electrons mode, which reveals an intensity contrast when changes in the average atomic number exist in the studied materials. However, one can get further insight into the microstructure of the C/SiO₂ films thanks to the selective etching of SiO₂ in a 2M NaOH aqueous solution. After immersing the films for 2 hours in the solution, the SEM images reveal a highly branched dendritic-like structure with the voids between the branches, formerly occupied by SiO₂, with lateral dimensions below the micron range (See Fig. S3). Extending the immersion time results in the complete detachment of the film and makes the solution acquire a dark tone as a result of the C debris in suspension. These observations indicate that the film consists of two independent intermixed networks of C and SiO₂, resulting from the polymerization of resorcinol and formaldehyde and the hydrolysis and condensation of APTES, respectively. Such interwoven C and SiO₂ networks are responsible for the increased robustness of the films thanks to the strong attachment of SiO₂ to the substrate through silanol bonds. Regarding the nature of the intermixed networks, we

considered the possibility of the amine moiety present in APTES participating in the enhanced robustness of the films by creating a chemically bonded C/SiO₂ interface, as it has been reported that alkyl amines can be bonded to glassy carbon (cite here: Deinhammer, R. S., Ho, M., Anderegg, J. W. & Porter, M. D. Electrochemical oxidation of amine-containing compounds: a route to the surface modification of glassy carbon electrodes. *Langmuir* **10**, 1306-1313 (1994); Nasir, T., Zhang, L., Vila, N., Herzog, G. & Walcarius, A. Electrografting of 3-Aminopropyltriethoxysilane on a Glassy Carbon Electrode for the Improved Adhesion of Vertically Oriented Mesoporous Silica Thin Films. *Langmuir* **32**, 4323-4332 (2016)). We could not find evidence of C-N-Si bonding from XPS measurements. These measurements revealed that N was not present in the C-SiO₂ films, even though it was detected in the gel films before pyrolysis (see Figure S4), indicating a thermal decomposition of the amine moieties.

3.4. Sheet Resistance of the C/SiO₂ Thin-Films

The addition of APTES made the deposition of C/SiO₂ thin films much easier and more efficient in terms of reaction time than that of pure carbon films and also strongly improved their interfacial adhesion to silicon/silicon oxide substrate. However, the presence of SiO₂ hinders the charge transport through carbon, resulting in a higher electrical resistivity of C/SiO₂ compared to that of the pure carbon film. Figure 3 presents the electrical conductivity of the different C/SiO₂ thin films. The electrical conductivities reported in the literature for carbon xerogel and aerogel materials pyrolyzed at 1000°C vary from 1 to 40 S·cm⁻¹.²⁰ Here, the electrical conductivity for the

pure carbon xerogel film is $\sim 30 \text{ S}\cdot\text{cm}^{-1}$. The electrical conductivity decreases with the increase of the SiO_2 content. For instance, the conductivities measured for the films CS41- A_H and CS11- A_H that, which contain the lowest and highest amount of SiO_2 in the CS- A_H series, are around 5 and $18 \text{ S}\cdot\text{cm}^{-1}$, respectively. Nevertheless, the conductivity of these C/ SiO_2 films are quite comparable to or even more conductive than that of typical screen printed carbon inks used in electrochemical sensing whose reported values are between $1\text{-}10 \text{ S}\cdot\text{cm}^{-1}$.²¹ One can expect that the conductivity measurements are affected by the existence of the 50 nm wavelike roughness. An estimation of the relative error related to such variations for a typical thickness of 400 nm results in a relative error of about 12%, in agreement with the larger errors experimentally determined, except for CS41 films.

Figure 3. Electrical conductivities of C/ SiO_2 films containing different of SiO_2 content or prepared from sols with different concentrations of acetic acid.

Figure 3 also shows that the film prepared from a sol without acetic acid (CS41) shows a somewhat higher electrical conductivity than those with the same C/ SiO_2 composition but prepared from sols containing acetic acid (CS41- A_H and CS41- A_L). This

conductivity change is due to differences in the surface chemical composition of the films, which were revealed by a comparative XPS analysis of the CS41 and CS41-A_H films. Figure 4 presents the normalized XPS spectra corresponding to the C 1s, O 1s and Si 2p of these two films. The CS41-A_H film shows higher relative intensities of the Si 2p and O 1s peaks and correspondingly a lower relative intensity of the C 1s peak. In Figure 4c one can also note that the shapes of the Si 2p spectra of the two films are quite different. Using Gaussian curve fitting, the Si 2p spectrum of both films can be decomposed into two peaks ascribed to oxidized silicon and centered at around 103.4 eV and 101.9 eV (see inset of Figure 4c) corresponding to sample CS41. The 103.4 eV peak corresponds to SiO₂ whereas the 101.9 eV peak falls in the binding energy range of the suboxides (SiO_x, with $x < 2$). Interestingly, the relative SiO_x content is much higher in CS41 film than in CS41-A_H film. This supports our hypothesis that the presence of acetic acid alters the gelation process of APTES by blocking the catalytic effect of amino group making the gelation slower.

Figure 4. XPS spectra of showing the binding energies of C 1s (A), O 1s (B) and Si 2p (C) for the CS41 and CS41-A_H films.

Why does the system without acetic acid result in a C/SiO₂ film (CS41) with somewhat lower content of SiO₂ on the surface? We believe that it has to do with the above the presence of acetic acid which slows the gelation of APTES network.

In order to get a better insight into this mechanism and avoiding the complexity of

gelation studies in films we investigated the formation of bulk monolithic gels from the CS41 and CS41-A_H sols. The monitoring of the resorcinol/formaldehyde/APTES sols without and with acetic acid at different stages of the gelation process gave valuable information to understand the differences observed in the films (see images of different stages of the process in Figure S3). On one hand, at a given reaction time the color of the CS41 sol was darker than that of CS41-A_H sol, confirming the faster gelation of CS41 system. On the other hand, during the ageing stage following the gelation process, we observed that the gel of CS41-A_H showed a homogeneous appearance whereas the color of the CS41 gel was lighter at the bottom and darker at the top. As we know, SiO₂ gels are normally white and resorcinol/formaldehyde gels are red in color. The homogeneous color of the CS41-A_H system during the whole process reveals a simultaneous formation of resorcinol/formaldehyde and APTES networks. By contrast, for the CS41 system the gel was first white and then gradually turned to red but showing a color gradient from the top to the bottom of the gel, evidencing the initial gelation of APTES later followed by the formation of resorcinol/formaldehyde gel. Thus, in the CS41 system, the initially formed SiO₂ network tends to form clusters (cite: J. D. Wright and N. A. J. M. Sommerdijk, *Sol Gel Materials Chemistry and Applications* CRC Press, London 2001, page 20.) because it is base-catalyzed, and those are dragged towards the bottom of the container due to its higher density and the resulting gel is not homogeneous. If this phenomenon is extrapolated to the formation of gel films by spin coating, one can understand the higher relative SiO₂ content at the surface of the CS41-A_H film and its lower conductivity.

3.5. Electrochemical Performance of the C/SiO₂ Thin-Films

Figure 5 displays typical voltammograms recorded with the C/SiO₂ films. Quasi-reversible electrochemical responses were recorded, showing an anodic to cathodic peak current ratio of around 1. It was also observed that the peak to peak potential separation (ΔE_p) appreciably decreases from ca. 167 mV to 137 mV when the molar fraction of APTES in the films decreased from 0.5 to 0.2 while, by contrast, the faradic peak currents increased from 10/-11 μ A to 26/-29 μ A, respectively. The higher peak current and lower ΔE_p indicate a larger active surface area and a faster electron transfer at the electrolyte C/SiO₂ film interface. This is the expected behavior taking into account the lower sheet resistance of the films with lower silica content. Surprisingly, pure carbon films showed a similar peak current but larger ΔE_p compared to those recorded with CS41 films. This might be related to the differences in the surface chemistry and the interaction of the redox probes with the surface, which is known to greatly influence the electron transfer and so the resulting electrochemical performance²².

Figure 5. Cyclic voltammograms recorded with C/SiO₂ films with different silica content, in a 0.1 M KNO₃ solution containing 1 mM ferri/ferrocyanide redox couple. Scan rate: 50mV/s.

The influence of the scan rate on the peak currents was studied with the CS41 film. The recorded peak currents (see Figure S4) are proportional to the square-root of the scan rate in the range of 10-100 mV/s, which is the usual behavior of a diffusion-controlled electrode process.

Figure 6 compares the cyclic voltammetric responses of a porous carbon xerogel paste electrode (C_pPE) as prepared in our previous publication¹⁷, a commercial screen printed graphite electrode (DRP 110 from DropSens S.L, Spain; SPGE), a commercial glassy carbon electrode (CH Instruments Inc., US; GCE) and the CS41 C/SiO₂ film electrode. At a scan rate of 50 mV/s, ΔE_p values of around 210, 181, 107 and 137 mV were obtained, respectively. Compared to C_pPE and SPGE, a much smaller ΔE_p value was recorded with CS41 C/SiO₂ film electrode, indicating a relatively faster electron transfer at the CS41 film electrolyte interface. The heterogeneous electrochemical rate constant k^0 was also calculated for the four electrodes tested using the Nicholson method (eq.1)²³.

$$\varphi = k^0 [\pi D n \nu F / (RT)]^{-1/2} \quad (\text{eq.1})$$

where D is the diffusion coefficient of potassium ferricyanide in 0.1 KNO₃ (ca. 7.01 x 10⁻⁶ cm²·s⁻¹)²⁴, n is the number of electrons involved in the electrochemical reaction, which in this case is equal to one, ν is the scan rate in V/s, F is the faraday constant, R is the universal gas constant and T the absolute temperature. The dimensionless kinetic parameter, φ , is first determined using the following analytical equation:

$$\varphi = (-0.6288 + 0.0021 * \Delta E_p) / (1 - 0.017 * \Delta E_p) \quad (\text{eq.2})$$

The electrochemical performance of the different types of electrodes, described by the ΔE_p and k^0 values evaluated in a 1 mM potassium ferricyanide solution, is reported in Table 2. The k^0 for CS41 film, 0.0017 cm/s; displays quite favorable electron transfer rate compared to SPGE and C_PPE, whose estimated k^0 values were 0.0008 cm/s and 0.0005 cm/s, respectively. In addition, the calculated k^0 values for CS21-A_H and CS11-A_H films were estimated to be 0.0012 cm/s and 0.0010 cm/s, respectively. These values indicate slower transfer kinetics of films with larger SiO₂ contents, but these are still significantly higher than those calculated for SPGE and C_PPE. Additionally, it is known that the electron transfer rate k^0 value typically ranges from 10⁻⁴ to 10⁻² cm/s at carbon based electrodes²⁵, depending on the structure and morphology of carbon materials. The CS41 film electrode underperforms the electrochemical behavior of the commercial GCE, which is as manifested by its smaller ΔE_p and a larger k^0 value of 0.0032 cm/s. Both the GCE and the CS41 film electrodes have in common that they do not incorporate any extra additives to the functional materials and show an enhanced performance compared to that of C_PPE and SPGE, which by contrast contain additives

such as paraffin and curing binders, respectively.

Figure 6. Cyclic voltammograms recorded in a 0.1 M KNO₃ solution containing 1 mM ferri/ferrocyanide redox couple at C_pPE, SPGE, GC and CS41 at a scan rate of 50 mV/s.

Table 2. Peak separation and electron transfer rate k^0 value for different electrodes in a 0.1 M KNO₃ solution containing 1 mM ferri/ferrocyanide redox couple

Electrode type	ΔE_p (mV)	k_0 (cm/s)
CS41 C/SiO ₂	137	0.0017
CS21-A _H C/SiO ₂	155	0.0012
CS11-A _H C/SiO ₂	167	0.0010
SPGE	181	0.0008
C _p PE	210	0.0005
GCE	107	0.0032

4. Conclusions

This study describes the deposition of carbon thin films on silicon/silicon oxide substrates by a one-pot resorcinol/formaldehyde/APTES sol-gel spin coating approach. The inclusion of acid in the sol influences the deposition and the final properties of the films. The interfacial adhesion between carbon films and silicon/silicon oxide substrate ~~was~~ can be significantly enhanced by the addition of a SiO₂ precursor to the sol formulation. Then-carbon/silica films display a uniform appearance but below the micron range present a phase segregation between carbon and silica in the form of interwoven dendritic-like networks. Compared to pure carbon xerogel films, the addition of SiO₂ was not detrimental to the functional properties of the films, showing conductivities larger than those reported for typical screen printed inks. Cyclic voltammetry studies demonstrate the great potential of this material in electroanalytical chemistry, with the additional advantage of its prospective application in the fabrication of carbon/silica thin-film microelectrodes by photolithographic processes. For such application, CS41 appears as the most suitable among the materials studied herein, as it presents the highest conductivity and a short reaction time that allows obtaining films only 10 minutes after preparing the sol.

Supporting information

Profilometry of C-SiO₂ film; electrochemical testing setup; influence of acetic acid in the gelation of Resorcinol-Formaldehyde/APTES sols; XPS spectra; cyclic voltammetries at different scan rates.

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