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Host−Guest Complexation: A Convenient Route for the Electroreduction of Diazonium Salts in Aqueous Media and the Formation of Composite Materials

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Abstract: Electrochemical grafting of a water-insoluble diazonium salt in aqueous media onto an electrode surface was achieved by host−guest complexation. 1-(2-Bisthienyl)-4-aminobenzene (BTAB) was solubilized in a water/β-cyclodextrin solution (β-CD). The corresponding diazonium salt was generated in situ then electroreduced. This process leads to the attachment of bithiophene or short oligothiophene groups to the electrode surface. The modified surfaces were analyzed by cyclic voltammetry (CV), scanning electrochemical microscopy (SECM), X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRRAS), and atomic force microscopy (AFM). The electrochemical investigations show that the water-based modified surface is similar to one generated in acetonitrile without β-CD. Thus, the attached organic layer behaves like an electrochemical switch (above some threshold potential, a soluble external probe is oxidized, but the oxidized form cannot be reduced). The modified surfaces consist of grafted bisthienylbenzene (BTB) and cyclodextrins that can be removed from the surface. This procedure may be considered as a new means of creating a surface made of submicrometric holes in an organic semiconducting layer.

1. Introduction

The immobilization of organic molecules on metallic, semiconducting, or carbon-based substrates has been extensively studied. This approach constitutes an interesting field for building novel interfaces for applications ranging from the fabrication of molecular or plastic electronic devices,[1,2] biosensing systems,[3] and anticorrosion coatings[4] to smart surfaces.[5] There are several standard reactions induced by electron transfer (to or from) an organic molecule that allow covalent attachment of organic compounds to the surface.[6] One of the most interesting is the electrochemical reduction of a phenyldiazonium salt to produce the corresponding phenyl radicals (and N_2) in the vicinity of the electrode, followed by reaction of the radicals with the electrode surface leading to the attachment of phenyl groups.[7] This electrografting procedure has been investigated with various materials such as metals,[8] carbon,[9] silicon,[10] and

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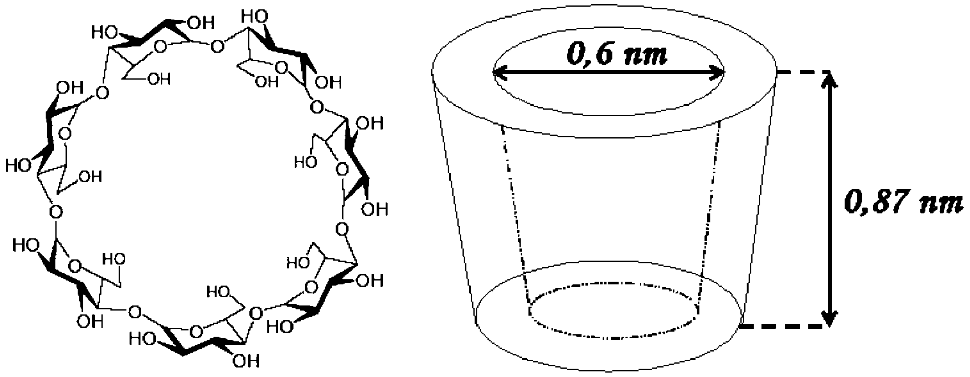

Figure 1. Chemical structure and general form of β-cyclodextrin.

iron[11] in organic (acetonitrile) and aqueous acidic media. Moreover, a wide variety of substituted phenyldiazoniums has been reported. The presence of covalent bonding for many surface materials is highly probable in view of the strong mechanical adhesion of the film, which cannot be explained by weak interactions.[12−14] Furthermore, covalent binding has been demonstrated on carbon[15] and iron surfaces.[16] The modified electrodes have been characterized by several techniques: infrared spectroscopy (IR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), in situ electrochemical atomic force microscopy (EC-AFM), and cyclic voltammetry (CV) when a redox-active species is attached to the surface (e.g., most commonly the nitrophenyl group).[9−17]

This method makes it possible to confer upon the material surface very distinctive properties through the choice of different grafting molecules, maintaining the substrate properties and ensuring an easy and controlable introduction of various surface functionalities.[5,18−22] The layers generated usually are just a few nanometers thick and are covalently attached to the electrode. They have been used as a primary layer for the surface polymerization of various nonconducting polymers[23−25] and more recently for the deposition of a conductive polymer topcoat with enhanced stability.[26]

Electroreduction of diazonium salts was initially performed starting from the salts isolated in acetonitrile. Recently, the electroreduction of a diazonium salt generated in situ from the corresponding amine compound (considered as a precursor) has been reported.[27] This deposition method, which involves simple reagents and does not require the isolation and purification of the diazonium salt, facilitates the grafting of covalently bound layers. Their properties are very similar to those obtained by the classical derivatization method involving an isolated diazonium salt dissolved in acetonitrile or more recently in ionic liquids.[27,28]

Diazonium salts are not always water-soluble, and therefore, they are frequently electroreduced in acetonitrile, which may be a severe drawback for environmentally friendly industrial processes. However, by using surfactants and micellar media, whose amphiphilic properties allow the solubilization of hydrophobic species in aqueous media, it is possible to electroreduce diazonium salts in a water-based medium.[29]

Another widely used technique for solubilizing water-insoluble compounds in water is based on host−guest complexation. β-Cyclodextrin is a naturally occurring molecular tube composed of seven α-1,4-linked glucopyranose units (Figure 1). The rim-to-rim tube length is 0.87 nm, but this dimension varies with the conformation, and cyclodextrins (β-CDs) often pack more closely than this in the solid state through hydrogen-bonding interactions to form channel structures.[30] β-CD has a hydrophilic external surface and a hydrophobic cavity, 0.6 nm in diameter. As a consequence, in aqueous solution, it forms inclusion complexes with a wide variety of organic guests. For instance, bithiophene, terthiophene, 4-aminodiphenylamine, and 1-(2-bisphenyl)amine are easily solubilized in water/β-CD solutions thanks to the hydrophobic part of these molecules that fits the internal dimensions of the β-CD cavity. Such inclusion complexes have been used to generate encapsulated molecular

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wires, usable in molecular electronics[31] and more recently to grow atomic contacts.[32]

In the present work, we show that it is possible to electrograft organic molecules through the electroreduction of a water-insoluble diazonium salt in water using host−guest complexation. A water-insoluble amine, namely, 1-(2-bisthienyl)-4-aminobenzene (BTAB), was solubilized in an aqueous solution of β-CD. The corresponding diazonium salt is generated in situ by adding $NaNO_2$ and $HClO_4$ to the amine/β-CD solution. It is then electroreduced on various substrates and yields modified surfaces. These surfaces have been characterized using cyclic voltammetry, scanning electrochemical microscopy (SECM), XPS, infrared reflection absorption spectroscopy (IRRAS), and AFM. Moreover, as the modified electrode contains bisthienylbenzene (BTB) and β-CD, we anticipate the possibility of removing the β-CD specifically. To achieve this, the BTB-modified electrode was immersed in acetonitrile and submitted to several potential scans in the presence of a redox probe. Finally, we attempt to reintroduce the β-CD onto the modified surface in order to check if β-CD ingress and egress are reversible.

2. Materials and Methods

2.1. Chemical and Reagents. Commercially available reagents were used as received without further purification.

1-(2-Bisthienyl)-4-aminobenzene was synthesized and purified according to previously published procedures.[33] Ferrocene was supplied by Alfa Aesar, acetonitrile (HPLC grade) by Prolabo, and $NaNO_2$ by Merck. Hydrated β-cyclodextrin (β-CD), ferrocenemethanol (FcMeOH), and perchloric acid ($HClO_4$, 17 $mol \cdot L^{-1}$) were from Acros Organics, tetrabutylamonium tetrafluoroborate $[(Bu_4N)BF_4]$ and lithium perchlorate ($LiClO_4$) from Aldrich.

2.2. Apparatus and Procedures. 2.2.1. Electrochemical Experiments. Basic electrochemical experiments were carried out in a single-compartment three-electrode cell using a CHI 440A potentiostat (CH Instruments, Austin, TX). The auxiliary electrode was a platinum grid; a saturated calomel electrode (SCE) was used as reference. Working electrodes were homemade glassy carbon (GC) discs (area = 0.2 cm^2) fabricated from carbon rods (Tokai, Japan) embedded in Teflon, and gold disk electrodes (area = 0.1 cm^2) from CH Instrument (Austin, TX). Before use, the carbon and gold electrodes were successively polished with 3 and 1 μm diamond paste (Struers, Denmark), ultrasonicated in analytical grade acetone for 3 min, and rinsed with ultrapure water.

2.2.2. Scanning Electrochemical Microscopy (SECM). SECM measurements were performed using a commercial instrument with close-loop piezoelectric motors, CHI 900B. A three-electrode setup was employed with Ag/AgCl serving as the reference electrode; a platinum wire was used as the counter-electrode, and a carbon electrode (diameter 3 mm) was used as the substrate. The ultramicroelectrodes (UME) were prepared in the laboratory following a general procedure.[34] Disc-shaped UMEs 10 μm in diameter were made by sealing platinum wires (Goodfellow) in a soft glass tube that was subsequently ground at one end. The glass edge was conically shaped with an outer diameter of 100 μm yielding an RG value between 5 and 10. Prior to use, the UME was polished using diamond pastes of decreasing grain size. All aqueous solutions were prepared with Milli-Q water and deoxygenated by N_2 bubbling before use. All SECM experiments were performed in aqueous solution with 0.1 $mol \cdot L^{-1}$ $LiClO_4$ as the supporting electrolyte and 10^{-3} $mol \cdot L^{-1}$ FcMeOH as the redox mediator.

2.2.3. X-ray Photoelectron Spectroscopy (XPS) Experiments. XPS signals were acquired using a VG Scientific ESCALAB 250 system equipped with a microfocused, monochromatic Al Kα X-ray source (1486.6 eV) and a magnetic lens that increases the electron acceptance angle and hence the sensitivity. A 650 μm X-ray beam was used at 20 mA × 15 kV. The spectra were acquired in the constant analyzer energy mode with pass energies of 150 and 40 eV for the survey and narrow regions, respectively. Charge compensation was achieved with an electron flood gun combined with an argon ion gun. The argon partial pressure in the analysis chamber was 2×10^{-8} mbar. Avantage software, version 3.51 (Thermo Electron), was used for digital acquisition and data processing. Spectra were calibrated by setting the main C1s component to 285 eV. Surface compositions (in atomic %) were determined by considering the integrated peak areas of C_{1s}, N_{1s}, S_{2p}, and O_{1s} with the corresponding sensitivity factors corrected for the analyzer transmission.

2.2.4. Infrared Reflection Absorption Spectroscopy (IRRAS) Experiments. IR spectra of a gold working electrode were recorded on a Nicolet Magna-IR 860 spectrometer with Fourier transform, equipped in order to measure the reflectivity with polarized light and under grazing incidence. IR spectra were referenced to that of a freshly cleaned gold surface.

2.2.5. Atomic Force Microscopy (AFM). All atomic force microscopy experiments were carried out in the tapping mode with a Pico plus (Molecular Imaging). All the data shown here were recorded with Si cantilevers (NCH Scientec) with average stiffness, as given by the manufacturer, of about 50 $N \cdot m^{-1}$; resonance frequency was around 300 kHz.

3. Results and Discussion

3.1. Electroreduction of BTAB Diazonium Salt. As already stated, the rim-to-rim tube length of β-CD is 0.87 nm, and its hydrophobic cavity has a diameter of 0.6 nm (Figure 1). As a consequence, terthiophene and other aromatic compounds that fit the internal dimension of the cavity are easily solubilized in water/β-CD solutions. 1-(2-Bisthienyl)-4-aminobenzene (BTAB) is 1.3 nm long and 0.45 nm wide, which is close to the dimensions of terthiophene. BTAB is thus another water-insoluble molecule that is easily solubilized when β-CD is added in water. Such behavior reveals that an inclusion complex is formed between BTAB and cyclodextrin. Note that the hydrophilic part of BTAB, that is, the amino group, is likely to remain outside the cavity in a chemical environment close to that of an aniline molecule solubilized in water, as demonstrated in our study of aminodiphenylamine/β-CD inclusion complexes.[35] As a consequence, BTAB solubilized in water/β-CD can be transformed in situ into the corresponding diazonium salt. When the stoichiometric amount of $NaNO_2$ and a small excess of $HClO_4$ are used, the solution turns dark green and is stable

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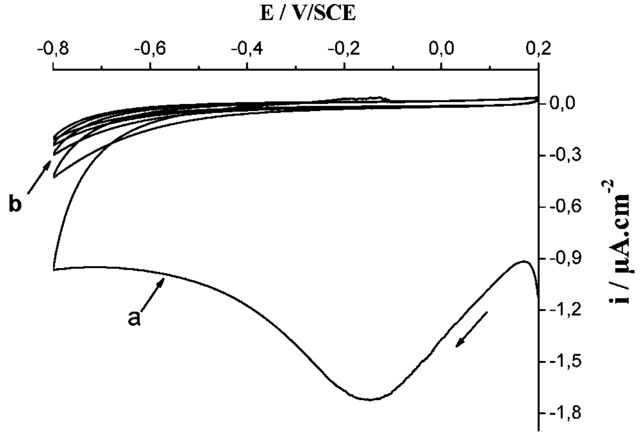

Figure 2. Electroreduction of the BTB diazonium on a carbon disk electrode in aqueous solution of 2×10^{-3} mol•L^{-1} BTAB, 2×10^{-3} mol•L^{-1} $NaNO_2$, 0.1 mol•L^{-1} $HClO_4$, and 4×10^{-2} mol•L^{-1} β-CD: (a) first scan; (b) second to fifth scan. Sweep rate: 0.05 V•s^{-1}.

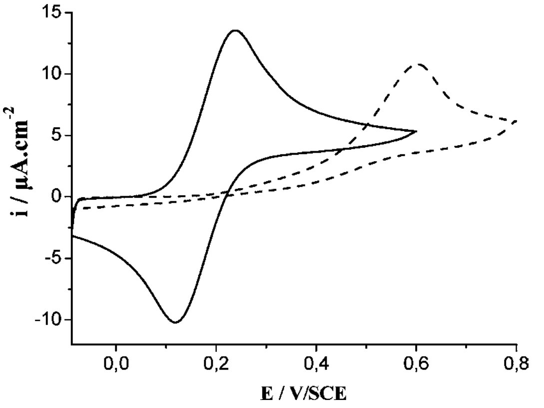

Figure 3. Cyclic voltammetry in 10^{-3} mol•L^{-1} FcMeOH + 0.1 mol•L^{-1} $LiClO_4$ solution of (-) a bare carbon electrode and (--) a [BTB/CD-GC] electrode (BTB film generated using five electroreduction cycles between 0.2 and −0.8 V/SCE). Sweep rate: 0.1 V.s^{-1}.

enough for the salt to be electrochemically reduced. If there is no β-CD, the suspension of BTAB in water mixed with $NaNO_2$ and $HClO_4$ does not turn green, and the diazonium salt cannot be generated.

Figure 2 shows the reduction at a carbon electrode of BTB diazonium generated using 2×10^{-3} mol•L^{-1} BTAB, 2×10^{-3} mol•L^{-1} $NaNO_2$, and 0.1 mol•L^{-1} $HClO_4$ in a 4×10^{-2} mol•L^{-1} solution of β-CD in water.

The CV shows an irreversible wave with a peak potential around −150 mV (Figure 2a), indicating that an irreversible reaction (i.e., the cleavage of the C−N bond and elimination of dinitrogen) is associated with the electron transfer. Following this, upon a second scan (Figure 2b), the wave disappears almost completely and cannot be seen upon further scans. This behavior indicates the blocking of the surface by the organic groups that become attached to the surface. It is now widely accepted that such a reaction leads to the covalent grafting of monomers or oligomers.[36] In the following, this electrode will be labeled [BTB/CD-GC] for BTB modified glassy carbon electrode in the presence of β-CD.

3.2. Characterization of BTB-Modified Electrodes. Several techniques were used to investigate the modified surfaces.

3.2.1. Electrochemical Behavior. As a preliminary experiment, freshly prepared [BTB/CD-GC] electrodes were immersed in an aqueous solution of ferrocenemethanol (FcMeOH) to probe their electrochemical behavior toward reversible outer-sphere redox species. Figure 3 compares the FcMeOH electrochemical response on bare carbon and [BTB/CD-GC] electrodes. As expected, on the carbon electrode, FcMeOH exhibits reversible redox behavior at a standard potential $E° = 0.24$ V/SCE while the CV recorded on [BTB/CD-GC] appears unusual: no current is observed in the potential range where FcMeOH redox reactions usually occur. The organic layer totally blocks the electrode in this potential window. However, when scanning is continued to more positive potentials, the current increases dramatically, and an "irreversible" wave is observed with an oxidation peak at 0.6 V. To test the stability of the layer, the modified electrode was ultrasonicated for 10 min; then, it was immersed into the same FcMeOH solution, and its behavior was recorded in the same potential range. There is no significant difference between the voltammograms recorded before and after the electrode was sonicated. This is a clear indication that the BTB organic layer is strongly attached to the carbon surface and suggests covalent grafting on carbon.

It is important to note that, contrary to the case where the modifications are generated by the reduction of other diazonium salts such as those derived from aniline, nitroaniline, aminobiphenyl, or para-aminobenzoic acid,[36] the layer obtained through the electroreduction of the BTB diazonium salt has diode-like behavior. Above some potential threshold, a soluble external probe is oxidized, but the oxidized form cannot be reduced. This behavior is similar to that obtained when BTB diazonium electroreduction is performed in acetonitrile.[37] Such behavior is related to the electroactivity of the grafted layer that acts as a dopable organic semiconductive material and switches from an insulating state to a conductive state above a potential threshold.[37−39]

The electrochemical investigations described above indicate that host−guest complexation of a water-insoluble diazonium salt followed by its electroreduction is a convenient route for grafting surfaces. This procedure is an alternative to the recently developed electroreduction of water-insoluble diazonium salts using a micellar medium.[26]

3.2.2. AFM Analysis of the Surfaces. BTB was deposited on ITO surfaces under conditions similar to the previous ones (the modified electrodes are now labeled [BTB/CD-ITO]), and the surfaces were investigated using AFM. Figure 4 shows AFM images of (a) BTB-ITO generated in acetonitrile and (b) [BTB/CD-ITO] generated in water/β-CD. The thickness of the the [BTB/CD-ITO] layers was measured by scratching the surface with the AFM tip. Figure 4c shows the cross-section through the hole.

For [BTB/CD-ITO] and BTB-ITO electrodes, a dense layer is observed over the whole area, and the average root-mean-square (rms) roughness measured using AFM is about 1.2 and 1.7 nm, respectively. This value has to be compared to a rms of 0.8 nm for the initial bare ITO electrode. The roughness of the electrode increases upon BTB/β-CD deposition, and the surface morphology changes, indicating that a thin layer is

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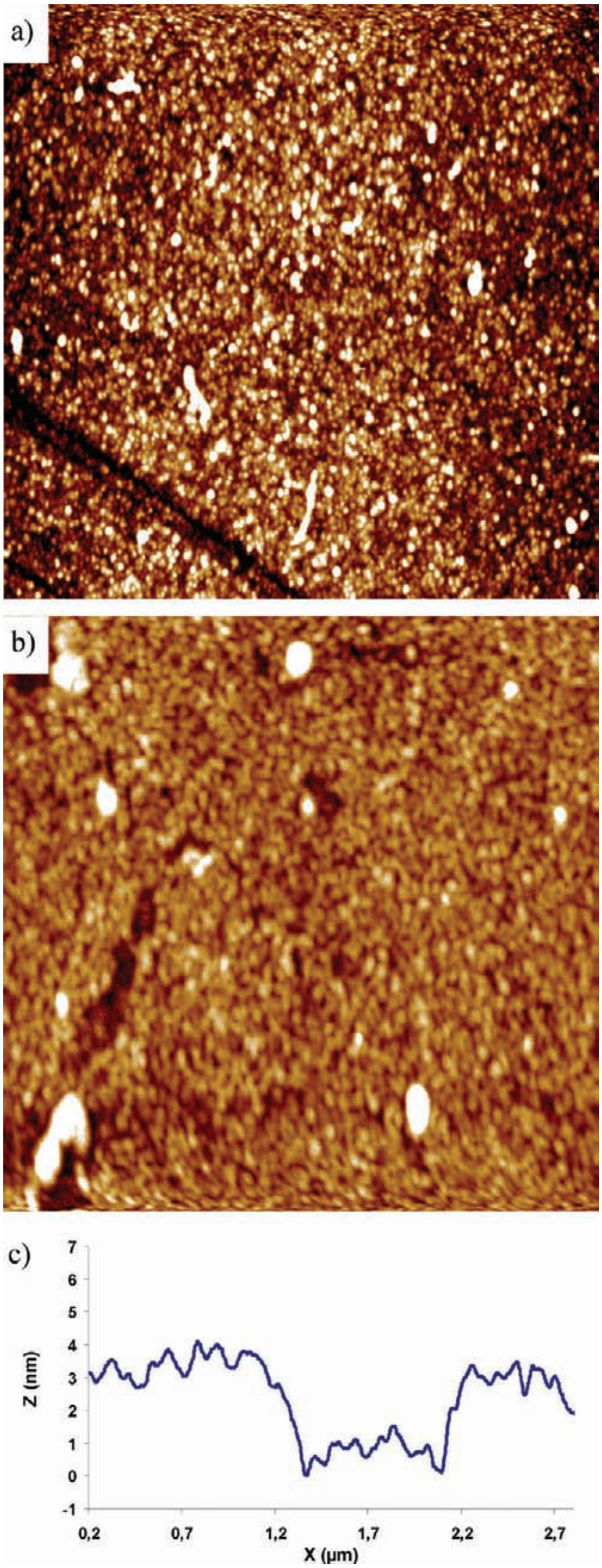


Figure 4. AFM images: (a) BTB-ITO surface generated in acetonitrile; (b) [BTB/CD-ITO] surface generated in water/ β-CD. (c) Cross-section through the hole made by AFM scratch experiment in contact mode. Scan size 3 × 3 μm^2. The height contrast is 8 nm for all images.

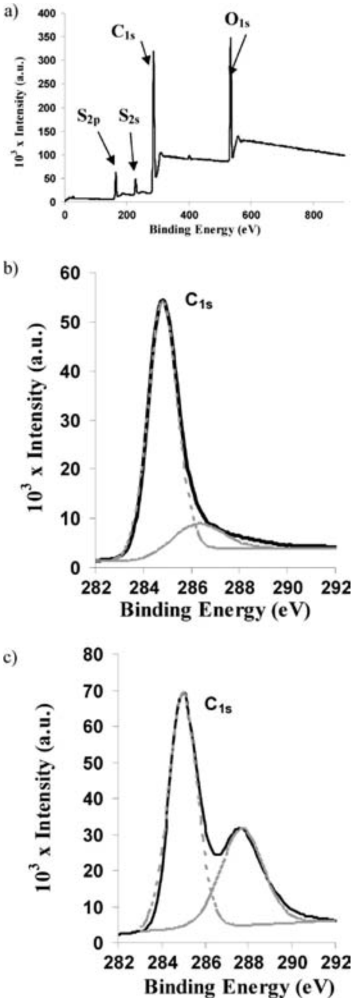
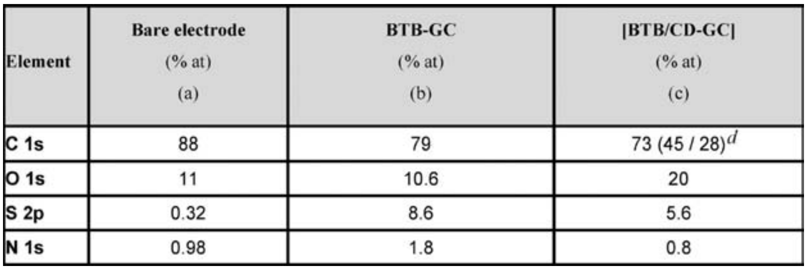


Figure 5. High-resolution XPS C_{1s} spectra: (a) survey spectrum; (b) BTB-GC; (c) [BTB/CD-GC] electrodes. Gray lines represent the deconvolution curves.

deposited. The BTB/β-CD layer homogeneity may be good locally, but nevertheless, small nodules remain. Their sizes and shapes are different from one area to another, and their heights are sometimes close to that of one layer, that is, 1.2 nm. Thus, it seems possible that they correspond to nucleation points for the growth of a new layer above the first one. Moreover, film growth seems to be inhomogeneous, and there are some holes that appear to be relatively dispersed. The average hole depth is close to 5 nm, which corresponds to a thickness of approximately four BTB layers (cross-section not shown). Scratching experiments performed on [BTB/CD-ITO] using an already published procedure[37] confirmed an average thickness of 4(±1) nm (see Figure 4c), which is similar to the value for BTB films grafted in acetonitrile.

3.2.3. XPS Analysis of [BTB/CD-GC] Surfaces. A bare carbon electrode, a carbon surface BTB-grafted in acetonitrile (BTB-GC), and a carbon surface BTB-grafted in water/β-CD ([BTB/CD-GC]) were analyzed. Prior to each experiment, the sample was thoroughly rinsed in the solvent used for electroreduction (i.e., water or acetonitrile for [BTB/CD-GC] or BTB-GC, respectively), ultrasonicated for 10 min, and dried in air. The wide-scale energy spectrum of a [BTB/CD-GC] (Figure 5a) shows strong C_{1s} and O_{1s} peaks at 285 and 532.7 eV, respectively, together with a small N_{1s} peak at 400 eV and a S_{2p} sulfur signal as a doublet ($2p_{3/2}$ and $2p_{1/2}$ with a relative ratio

Table 1. XPS Analysis of Bare Carbon and BTB-Modified Carbon Electrodes



Element	Bare electrode (% at) (a)	BTB-GC (% at) (b)	[BTB/CD-GC] (% at) (c)
C 1s	88	79	73 (45 / 28)[d]
O 1s	11	10.6	20
S 2p	0.32	8.6	5.6
N 1s	0.98	1.8	0.8

[a] Bare carbon electrode.[b] BTB-GC generated in acetonitrile (usual procedure).[c] [BTB/CD-GC] (aqueous solution).[d] The two values of C_{1s} for [BTB/CD-GC] correspond to atomic ratios of carbon atoms bonded to C and O (285 and 287.7 eV, respectively).

of 1/2) at 164–165.1 eV.[40] These peaks confirm the presence of grafted BTB molecules at the surface. Two separate C_{1s} peaks were observed at 285 and 287.7 eV corresponding to two carbons with a different chemical environment (Figure 5c). In contrast, the spectrum of a BTB-GC electrode (Figure 5b) shows one major peak at 285 eV with a small shoulder corresponding to oxidized carbons at 286.1 eV.

Atomic surface concentrations of the three electrodes, computed from the integration of the XPS core level peaks, are compared in Table 1.

The C_{1s}/S_{2p} ratio changes from 275 on bare carbon to 9 for the BTB-GC surface (grafting in acetonitrile) (Table 1, columns a and b), reaching a value compatible with the expected value of 7 for BTB or oligo(BTB) grafted layers. This result confirms that a BTB layer has been successfully grafted onto the carbon electrode, even though the O/C ratio remains unexpectedly high.

In the case of a [BTB/CD-GC] surface (Table 1, column c), the C_{1s}/S_{2p} ratio and the C_{1s}/O_{1s} ratio are 13 and 3.6, respectively, two values significantly different from those for BTB layers generated in acetonitrile (9 and 7.4). These results clearly indicate that the surface is not a compact BTB layer and that there is an excess of carbon and oxygen. This excess could be assigned to residual β-CD, despite rinsing and ultrasonication. Indeed, the C_{1s} spectrum displays two peaks at 285 and 287.7 eV that can be attributed to carbon atoms engaged in C–C bonds from grafted BTB and to carbon atoms bonded to O atoms in cyclodextrin, respectively. Deconvolution of the C_{1s} signal indicates an atomic composition of 45% and 28% for the carbon 285 and 287.7 eV peaks, respectively. The C_{1s}(285 eV)/S_{2p} ratio is 6.8, in good agreement with that expected for BTB, whereas the C_{1s}(287.7 eV) over O_{1s} ratio is 1.4, a value compatible with that expected for β-CD (carbon/oxygen ratio equal to 1). It can therefore be concluded that the [BTB/CD-GC] surface does not consist only of grafted BTB but also incorporates some β-CD that is not readily removed. The C_{1s}(285 eV)/C_{1s}(287.7 eV) ratio can be used to roughly estimate the relative amount of grafted BTB and incorporated β-CD. The value of 1.6 suggests an average composition close to one β-CD molecule for four to five grafted BTB molecules and/or one β-CD molecule encapsulating an oligomer consisting of four to five BTB molecules.

3.2.4. IRRAS Analysis. Further experiments were performed to confirm the presence of cyclodextrin and BTB on the electrode. BTB films were deposited on gold electrodes, and the modified surfaces are now labeled [BTB/CD-Gold]. Note that, since the film is thin, IRRAS spectroscopy is only used here to confirm β-CD insertion in the organic layer (full IR characterization of the coating requires PM-IRRAS and is not within the scope of this study). The IR spectrum of [BTB/CD-Gold] exhibits the signature of β-CD at 2926 and 3400 cm^{-1} (ν_{CH2} and ν_{OH}, respectively) along with bands in the 1100 cm^{-1} region attributed to C–O stretching (despite rinsing and ultrasonication). These bands are not seen in the spectrum of the BTB-Gold electrode generated in acetonitrile. Some IR bands attributed to the BTB thiophenes can also be identified: δ_{C-H} out-of-plane deformations (at 800 cm^{-1} and 702 cm^{-1}) and C–H bending above 3000 cm^{-1}. These bands are not seen in the β-CD spectrum.

Overall, these experiments confirm that the modified electrode generated by the electroreduction of BTB diazonium salts in water/β-CD is a hybrid material consisting of grafted BTB or oligo(BTB) molecules and β-CD. A ratio of one β-CD molecule for four to five BTB moieties is measured using XPS. AFM indicates that the layer thickness is close to 5 nm, which corresponds to four BTB layers. β-CD incorporation is confirmed using IRRAS. However, the way β-CD is attached or incorporated into the film is still unknown and must be discussed. At this point, one can only state that simple rinsing in water followed by ultrasonication is not capable of removing all the β-CD incorporated during the electrodeposition process. Despite the mixed composition of the BTB-CD layer, it must be stressed that the electrochemical behavior of the electrode is similar to that observed on a modified electrode generated in acetonitrile without β-CD. In both cases, for a redox probe with a redox potential lower than the threshold potential of the conjugated film, we observe a diode-like behavior induced by an electrochemical switch from an insulating to a conducting state of the grafted BTB or oligo-BTB molecules.

3.3. Post-Treatment of BTB-Modified Electrodes: β-CD Removal. In order to determine the nature of the β-CD interaction in the BTB/CD-modified electrodes, various procedures were used to remove it (ultrasonication, rinsing in various solvents, and electrochemical cycling in different electrolytes). Electrochemical cycling of a [BTB/CD-GC] electrode in a solution of 10^{-3} mol·L^{-1} ferrocene (Fc) and 0.1 mol·L^{-1} $LiClO_4$ in acetonitrile gave the best results. Indeed, the electrochemical response of the electrode in the FcMeOH/water solution after several cycles in the Fc/acetonitrile solution (Figure 6) shows that the diode-like behavior observed toward FcMeOH in water is rapidly lost. The electrode now behaves almost as a bare carbon electrode with oxidation and reduction peaks of FcMeOH in their usual potential range. However, the peak-to-peak separation ΔE_p of the electrochemical waves increases to 150 mV, and the peak currents are significantly reduced compared to that observed with the bare electrode. This ΔE_p increase can be compared with the electrochemical response of Fc over a

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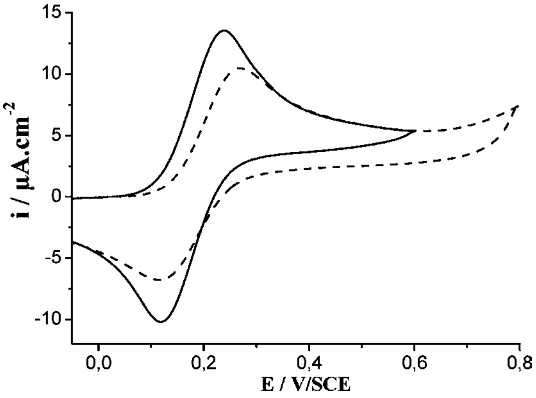

Figure 6. Cyclic voltammetry in an aqueous solution of 10^{-3} mol•L^{-1} FcMeOH and 0.1 mol•L^{-1} $LiClO_4$ of (-) a bare carbon electrode and (--) a [BTB/CD-GC] electrode (obtained after cycling the modified electrode in 10^{-3} mol•L^{-1} ferrocene/acetonitrile). Sweep rate: 0.1 V/s.

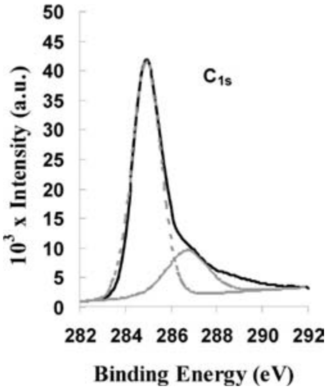

Figure 7. High-resolution XPS C_{1s} spectra of a [BTB/CD-GC]-CD surface after electrochemical cycling in ferrocene/acetonitrile.

partially blocked electrode in a case of low coverage,[41] and this might suggest that some BTB is still attached to the surface. This new modified electrode will be labeled [BTB/CD-GC]-CD in the following, indicating that β-CD has been desorbed.

Such behavior could also be interpreted as a sign that the layer initially deposited on the electrode has been peeled off. This might imply that the BTB molecules deposited in the hybrid layer are not covalently grafted and are removed by cycling in acetonitrile. This interpretation has to be ruled out for several reasons. First, the IR spectra of the [BTB/CD-GC]-CD electrode still exhibit features characteristic of grafted BTB. Second, XPS experiments on the [BTB/CD-GC]-CD electrode indicate that the atomic surface composition remains distinctly different from that of bare carbon, even though there are marked differences compared to [BTB/CD-GC] surfaces (Figure 7). The atomic surface composition is now closer to that of a BTB-GC generated in acetonitrile. Indeed, the C_{1s}/S_{1s} ratio is close to 11 (compared to 9 for BTB-GC and 13 for BTB-CD-GC), suggesting that some of the carbon and oxygen excess has been removed by electrochemical cycling.

More importantly, Figure 7 shows that the C_{1s} spectrum displays only one clear peak at 285 eV and almost no peak at 288 eV (careful examination of the 288 eV region reveals a small shoulder corresponding to a C_{1s}(285)/C_{1s}(288 eV) ratio of 4 compared to 1.6 for [BTB/CD-GC]. This last peak was attributed to β-CD incorporation, and its decrease indicates that β-CD has been (partially) removed from the hybrid material. This completely changes the electrochemical response of the electrode toward FcMeOH in water, as depicted in Figure 6. Note that electrochemical cycling in FcMeOH/water completely failed to remove β-CD from the electrode. Note also that the C_{1S}(285)/C_{1s}(288 eV) ratio of 4 for the [BTB/CD-GC]-CD electrode corresponds to an approximate layer composition of 12 BTB molecules for 1 β-CD compared to 4 BTB molecules for 1 β-CD in [BTB/CD-GC] film.

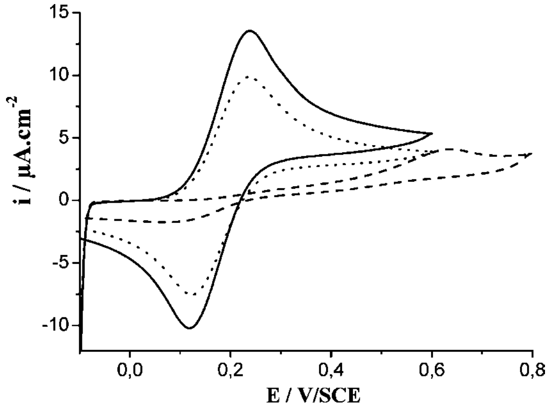

Figure 8. Cyclic voltammetry in a solution of 10^{-3} mol•L^{-1} FcMeOH and 0.1 mol•L^{-1} $LiClO_4$ of (-) a bare carbon electrode, (••••) a [BTB/CD-GC-CD] modified carbon electrode obtained after cycling the [BTB/CDGC] electrode in an acetonitrile solution of 10^{-3} mol•L^{-1} ferrocene, and (--) a [BTB/CD-GC-CD] +CD electrode obtained after 1 h exposure to an aqueous solution of β-CD. Sweep rate: 0.1 V/s.

This removal of β-CD appears to be partially reversible. If the electrode is immersed in water/β-CD for 1 h (labeled now [BTB/CD-GC-CD]+CD), the electrochemical behavior observed for the original electrode ([BTB/CD-GC]), lost because of β-CD removal, is partially restored, as can be seen in Figure 8. The FcMeOH oxidation signal is strongly shifted toward positive potential (0.65 V) as in the case of the [BTB/CD-GC] electrode but with a much weaker peak current (the reduction signal of the generated ferrocinium methanol (Fc^+MeOH) remains visible in the reverse cycle). This behavior is fully reproducible and is not observed when a bare electrode without grafted BTB or a BTB-GC electrode generated in acetonitrile is immersed in water/β-CD. Furthermore, XPS analysis reveals that the C and O atomic surface concentration increases back to a level close to that of the initial [BTB/CD-GC] (Table 1) with a C/O ratio close to 1.2 and a C/S ratio of about 23. Finally, IRRAS spectra (not shown) of the [BTB/CD-GC-CD]+CD electrode exhibit an additional increase in the IR bands of β-CD.

These observations demonstrate that the BTB-modified electrodes generated in water/β-CD consist of grafted BTB molecules or grafted nodules of several BTB molecules covering part of the bare electrode. These grafted BTB molecules are separated by β-CD molecules or domains of β-CD, incorporated in the layer. Cyclodextrin can be removed from the electrode using an adequate procedure. This process appears to be partially reversible and can be used to control the electrochemical response of the electrode toward FcMeOH in water.

3.3.1. SCEM and AFM Experiments. The modified [BTB/CD-GC], [BTB/CD-GC]-CD, and [BTB/CD-GC-CD]+CD electrodes were analyzed using SECM in the feedback mode.[42]

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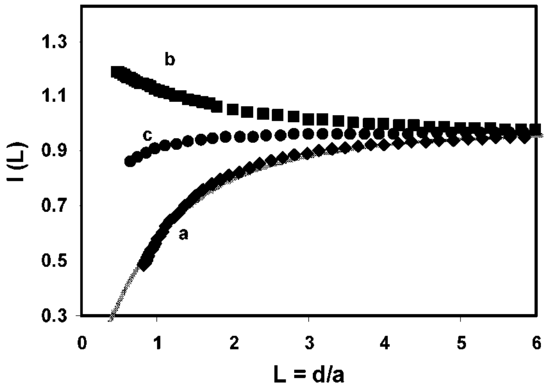

Figure 9. Experimental approach curves of Pt UME in aqueous solution containing 10^{-3} mol·L^{-1} FcMeOH and 0.1 mol·L^{-1} LiClO$_4$ above (a) [BTB/CD-GC], (b) [BTB/CD-GC]-CD, and (c) [BTB/CD-GC-CD]+CD electrodes. The substrate potential is 0.1 V/SCE; solid line (-) represents the theoretical approach curve for an insulating substrate.

Figure 9 shows the experimental approach curves obtained using FcMeOH as a redox mediator. For the normalized distance $L > 3$, $I(L)$ is close to 1; this value reflects the absence of interaction between the Fc$^+$MeOH electrogenerated at the UME and the substrate (at 0.1 V), for this distance. For the modified [BTB/CD-GC] electrode (Figure 9a), when the separation distance L decreases, the normalized current falls, which indicates that the mediator is not regenerated. This behavior corresponds to negative feedback. Moreover, the experimental approach curve is in good agreement with the theoretical variation expected for an insulating substrate, demonstrating the insulating properties of the surface under these conditions. The approach curve was recorded in different areas of the surface, and the same behavior was observed. It is worth noting that the approach curve carried out above a carbon substrate exhibits total positive feedback. These results demonstrate that the [BTB/CD-GC] electrode is homogeneous toward the reduction of Fc$^+$MeOH generated on the UME and diffusing toward the layer, despite its mixed composition. It is worth noting that the insulating behavior deduced from SECM is in perfect agreement with the absence of Fc$^+$MeOH reduction at [BTB/CD-GC] surfaces, seen in the earlier CV experiments (see Figure 3). SECM confirms the result obtained using CV and demonstrates that the oxidation of FcMeOH above [BTB/CD-GC] electrodes is irreversible.

The SECM response of the [BTB/CD-GC]-CD electrode (after β-CD removal in acetonitrile) using FcMeOH as a reversible mediator is presented in Figure 9b. The approach curve exhibits an enhancement of the tip current when the separation distance decreases and positive feedback is observed. This means that the substrate permeability has changed, and as a consequence, the modified electrode is seen to be partially conductive in SECM. It fully reproduces the results observed using CV (see Figure 6) with the [BTB/CD-GC]-CD electrode and demonstrates that β-CD removal makes it possible to recover a large fraction of the bare electrode. However, the approach curve does not match the theoretical curve expected for a totally conducting substrate when the regeneration of the mediator is under diffusion control. This deviation from the theoretical curve could be attributed to BTB remaining on the surface, which slows the reverse reaction. Simulation of the experimental approach curve gives an electron transfer rate around 4×10^{-3} cm·s^{-1}. In contrast, after reintroducing β-CD on the surface, the SECM response (Figure 9c), which clearly indicates a decrease in the tip current when the separation distance diminishes, leads after simulation to a rate constant of about 2×10^{-4} cm·s^{-1}. This value, which is 20 times smaller than that obtained after removing β-CD, confirms that some β-CD has been readsorbed onto the surface.

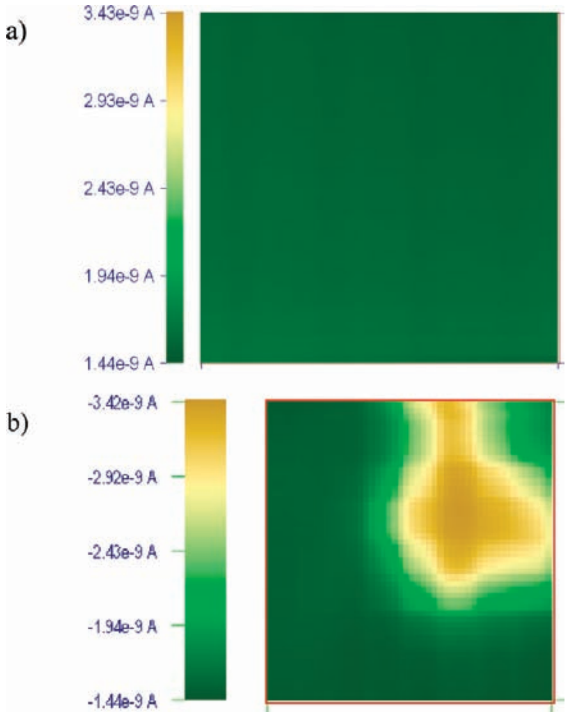

Figure 10. SECM images (size 50 × 50 μm^2) over the same BTB/CD-modified carbon electrode: (a) after grafting; (b) after grafting and after β-CD removal in acetonitrile. 5 μm radius tips and 1 μm·s^{-1} are used. The substrate was polarized at 0.1 V.

Finally, on the basis of these observations, the electrode was investigated using SECM in the image mode[42] with Fc as the mediator in acetonitrile. Figure 10 shows the successive images recorded at a fixed distance. The initial scan of the [BTB/CD-GC] electrode shows a homogeneous surface (Figure 10a). The tip current value is around 1.4 nA, which under our experimental conditions corresponds to half the steady state current obtained when the tip is located far away from the substrate. This value indicates that the mediator is not regenerated at the surface, suggesting that the imaged surface behaves as an insulator. However, the image presented in Figure 10b (after β-CD removal) reveals conductive areas with a current twice the steady-state value. The observed images are to some extent similar to those published by Nijhuis et al.[43] on redox active ferrocenyl dendrimers immobilized at monolayers of β-CD on glass via multiple host–guest interactions. In this study, local oxidation of the Fc-dendrimers by the microelectrode generated mediator resulted in an effective removal of the Fc-dendrimers from the host surface. In the present case, the conductive area could be attributed to the local desorption of physically adsorbed β-CD on the initial [BTB/CD-GC] electrode. Consequently, this desorption produces areas (several square micrometers) observed in the SECM as conducting surfaces. After several scans of the Fc probe on the surface, the electrode is gradually completely switched from an insulator to a permeable substrate toward ferrocinium reduction. Note that the same experiment performed

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in water using FcMeOH as the mediator does not show any gradual evolution of the BTB-modified surface, which remains insulating.

Therefore, the SECM investigations demonstrate the possibility of creating holes on the [BTB/CD-GC] electrode by removing β-CD. Nevertheless, the tip size used, 5 μm, gives only an overall view of the holes. It is therefore difficult to estimate the real hole size (depth and diameter) and their distribution on the surface (distance between adjacent holes). Figure 6 shows that, after β-CD removal, the electrochemical response of FcMeOH exhibits a clear semi-infinite diffusion peak with no evidence of a plateau that would be expected if the electrode were to behave as an ultramicroelectrode or an array of independent ultramicroelectrodes.[43] This result means either that macroscopic holes have been created in the layer or that microscopic or nanoscopic holes with a distance between two adjacent holes smaller than the diffusion layer have been obtained. Indeed in these two situations, the electrode behaves as a macroelectrode and does not exhibit spherical diffusion with a plateau current.[41] AFM in the tapping mode confirms that holes with micrometric or macroscopic lateral size are not obtained in the BTB layer after β-CD removal. Indeed, the topography of the [BTB/CD-ITO]-CD electrode is close from that of a [BTB/CD-ITO] electrode. Well-defined holes are not seen easily in the modified surface, and none of them has a diameter over 50 nm, which clearly shows that β-CD removal does not cause micrometric holes and confirms the findings deduced from the semi-infinite diffusion peak shown in Figure 6. Further work using STM and AFM on better defined substrates, such as HOPG or PPF carbon surfaces, is in progress in the laboratory in order to characterize this electrode at a smaller scale.

4. Conclusion

In this work, we have shown that 1-(2-bisthienyl)-4-aminobenzene can be solubilized in water/β-CD using host−guest complexation. The electroreduction of the corresponding diazonium salt generated in situ yields modified surfaces. These surfaces formed in aqueous media have an electrochemical behavior similar to that observed when the electroreduction is performed in acetonitrile in the absence of β-CD. Host−guest complexation of water-insoluble diazonium salts followed by their electroreduction is thus a convenient route for grafting surfaces. From a practical point of view, this strategy makes it possible to use diazonium electroreduction for surface modification in environmentally friendly industrial processes. From a more fundamental viewpoint, XPS and IRRAS analyses show that the surfaces generated consist of grafted bisthienylbenzene (BTB) and cyclodextrin with an approximate BTB/β-CD ratio of 4 to 5. The cyclodextrin can be removed from the surface and yields a modified surface that is only partially modified by BTB with submicrometric holes and has an electrochemical response close to that of a bare electrode with a clear semi-infinite diffusion peak (at the scan rates investigated), indicating that the distance between two adjacent holes is smaller than the diffusion layer. Even though regular spacing of the grafted BTB is not obtained, these electrodes, in which a fraction of the surface is not modified (holes obtained through cyclodextrin desorption), may be used for postfunctionalization and may allow the construction of various tunable hybrid materials.

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