# Preparation, characterization and photoelectrochemical study of mixed $C_{60}$–Starburst® PAMAM G0.0 dendrimer films anchored on the surface of nanocrystalline $TiO_2$ semiconductor electrodes

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**Nanocrystalline $TiO_2$ silanized electrodes were prepared and further modified in a sequential fashion with $C_{60}$ and Starburst® PAMAM G0.0 dendrimers, resulting in a novel photoelectrochemical sensitization film that showed particularly high photocurrent (IPCE) and global photoconversion efficiencies ($\eta$).**

The conversion of solar light into useful chemical or electrical energy with semiconductors using liquid junction cells has motivated considerable research work in recent decades. Wide band gap semiconductor materials are chemically stable under energy photoconversion conditions, but their absorption is maximum in the UV region of the spectrum and therefore, their use in solar energy conversion devices is seriously limited.[1a] To solve this problem, the surface of a semiconductor material can be covered with a monolayer of a carefully chosen visible light harvesting compound which promotes selective injection of the photogenerated electrons directly into the conduction band of the semiconductor substrate and, at the same time, the coupled oxidation of a redox carrier in the electrolytic solution. Thus, sensitized nanocrystalline semiconductor (NSc) electrodes, which have very large roughness factors, can be used to construct devices that work in a regenerative continuous fashion with visible light and with efficiencies comparable to those obtained using solid state silicon based solar cells.[1b] Among the compounds that have been explored as sensitizers of NSc $TiO_2$ electrodes, buckminsterfullerene (**$C_{60}$**) has been shown to be an attractive candidate either by itself or combined with other light absorbing compounds such as Ru(II)-polypyridyl. Using this approach, incident photon to current conversion efficiencies (IPCE)† close to 65%,[2a] and global conversion efficiencies ($\eta$)† of 0.1%[2b] have been measured. On the other hand, dendrimer molecules are hyperbranched species similar to covalent micelles that, by virtue of their molecular arrangement, have been successfully used to modify electrode surfaces and to control the structure as well as some processes that take place at the electrode-solution interface.[4] In this work, we describe the preparation and photoelectrochemical behaviour of a multilayered $C_{60}$–**PAMAM G0.0** (a commercially available poly(amidoamine) dendrimer, $(((NH_2(CH_2)_2NHCO(CH_2)_2)_2NCH_2)_2)$ film prepared on top of a previously silanized NSc $TiO_2$ electrode.

NSc $TiO_2$ electrodes were prepared by applying a 4 V potential difference[5] between a steel sheet and an ITO conducting glass substrate immersed in a 10 mL (0.5 g $TiO_2$ in 5% 2-propanol in water (v/v)) colloidal suspension for 60 s. Following previous reports in the literature,[6] the electrodes were then taken out from the electrophoretic apparatus, sintered at 723 K in air for 30 min, and characterized by AFM, XRD, Raman spectroscopy, cyclic voltammetry (CV) and perfilometry. From these characterization studies, it was found that the electrodes thus prepared consisted of nanoparticulated $TiO_2$ in anatase phase, with roughness factors of 540, an average thickness value of 15 μm and a flat band potential, $E_{FB}$, of $-0.2$ V *vs.* NHE which is a value that agrees well with previous reports.[7] The NSc $TiO_2$ electrodes were then exposed to 5% HCl solutions for 15 min with gentle stirring, rinsed with EtOH for 60 s, and further silanized by exposing the substrates to 3% $(CH_3O)_3Si(CH_2)_3NH_2$ ethanolic solutions for 24 h. After this chemical treatment, the electrodes were rinsed with EtOH and placed in an oven at 388 K for 15 min to promote the formation of the corresponding polysiloxane species.[8a] Polysiloxination of the relevant substrates was verified with FT-IR spectroscopy, since the –Si–O–Si– and the $–CH_2–$ stretching bands were observed at 1130–1140 $cm^{-1}$ and 2930 $cm^{-1}$, respectively.[8b]

Polysiloxaned NSc $TiO_2$ electrodes, bearing amine functional groups, were then refluxed in a 1.0 mM $C_{60}$ solution in toluene for 9 h at 363 K in order to covalently attach a fullerene layer as previously reported by Mirkin and co-workers.[9] A G0.0 PAMAM dendrimer layer was incorporated in the sensitizer film in the following stage, using the same amine addition reaction by exposing the modified electrode to a 0.1 mM dendrimer solution in $CH_2Cl_2$ at 323 K for 9 h. The same procedure was employed in three sequential steps of fullerene addition until the electrode represented schematically in Fig. 1 was obtained.

Surface confinement of $C_{60}$ on the electrode surface at each modification stage, was verified by CV experiments in 0.1 M $Bu_4NPF_6$ solutions in $CH_2Cl_2$ at 298 K. As expected, the CV responses were characterized by a quasi-reversible redox wave whose size is clearly related to the amount of $C_{60}$ present at each modification step (data not shown). Since direct electrochemical quantification of the covalently bound fullerene from these data was difficult due to the quasi-reversible character of the CV response, UV-Vis spectroscopy was utilized by taking advantage of the transparent character of the NSc $TiO_2$ modified electrodes. In this way, the absorbance ($A$) of the modified electrodes bearing 1, 2 and 3 fullerene layers was recorded at $\lambda = 594$ nm since at this wavelength the absorbance of the films is always smaller than one. Considering an approximate absorption coefficient of 2678 $M^{-1}$ at $\lambda = 594$ nm (which was obtained from a linear relationship of $A$ *vs.* $C_{60}$ concentration in 3 : 1 dendrimer/fullerene solutions in $CH_2Cl_2$/toluene (2 : 1 v/v) previously refluxed for 9 h at 323 K), it was observed that the concentration of $C_{60}$ in the film increased

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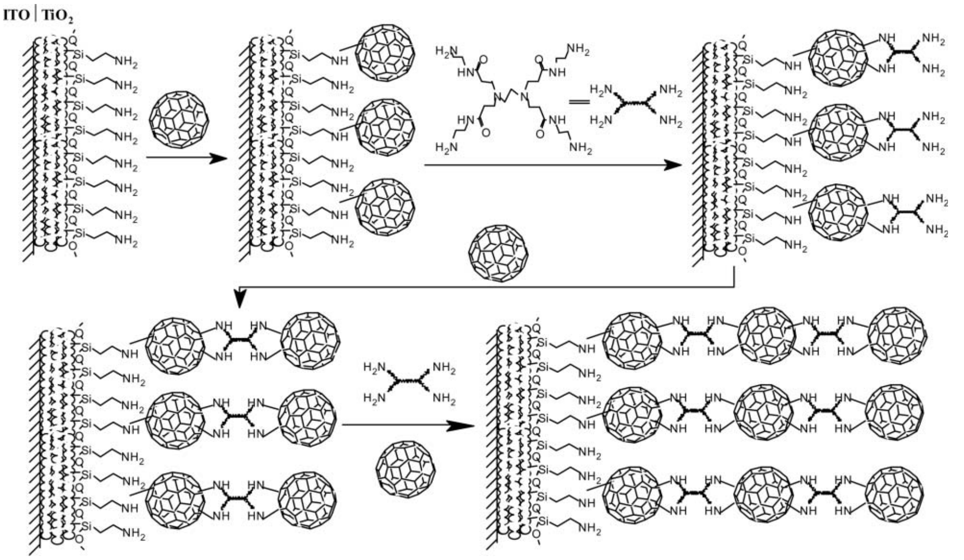

**Fig. 1** Scheme showing the electrode surface modification protocol.

linearly with the number of $C_{60}$ layers in the organic film ($r^2 = 0.999$).

Following the report by Bonhôte and co-workers,[10] it was also possible to calculate the surface coverage of fullerene molecules using the absorbance data for the NSc $TiO_2$ modified electrodes. The values obtained were $4.39 \times 10^{-10}$, $7.65 \times 10^{-10}$ and $1.28 \times 10^{-9}$ mol cm$^{-2}$ for NSc electrodes subjected to one, two and three fullerene sequential modification steps, respectively. Assuming a single monolayer surface coverage value[11] of $3.4 \times 10^{-10}$ mol cm$^{-2}$, the calculated number of $C_{60}$ layers corresponds to 1.29, 2.25 and 3.76 for each one of the three sequentially modified semiconductor substrates prepared.

Photocurrent action spectra were also obtained for the three electrodes using the photoelectrochemical cell presented in Fig. 2, which was constructed using a Ti substrate covered with a film of colloidal graphite as a counter electrode, a deoxygenated 0.3 M KI + 0.015 M $I_2$ aqueous electrolytic solution,[12] and a Teflon tape that was used to maintain a 0.5 mm gap between the two electrodes.

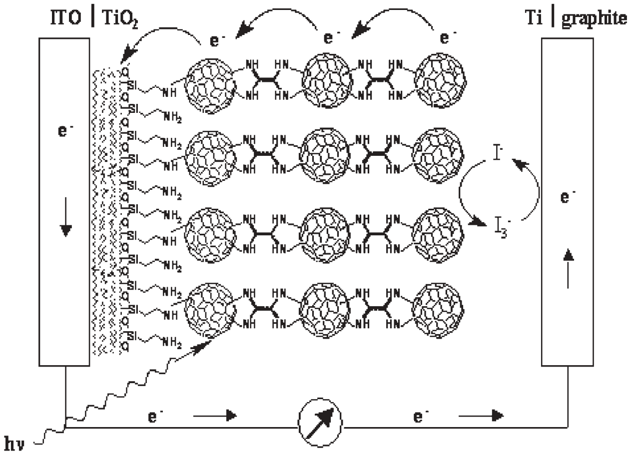

**Fig. 2** Schematic diagram of the cell employed in the photoelectrochemical experiments. Studies were carried out using one, two and three fullerene layer modified NSc electrodes at 298 K.

Consistent with previous reports,[2a,b] the largest IPCE measured for the three modified electrodes studied was obtained at $\lambda$ = 430 nm. Inspection of the data presented in Table 1 and Fig. 3a shows, contrary to the linear increase observed for the concentration of $C_{60}$ molecules with the number of layers, that the increase in IPCE values follows a logarithmic relationship with the number of fullerene layers, reaching values as high as 82% for the three fullerene layered electrode. This efficiency is comparable to the one reported by Kamat and co-workers for a $C_{60}$–Ru(II)-polypyridyl sensitized NSc electrode which is, to the best of our knowledge, the largest value reported for this type of system.[2a]

Since $E(C_{60}/C_{60}^{-})$ has been reported as −0.23 V *vs.* NHE,[2b] it is also important to point out that photogenerated electron injection from the sensitized film to the conduction band of the NSc $TiO_2$ electrode is possible because the flat band potential of the electrophoretically prepared NSc electrodes is −0.20 V *vs.* NHE, *i.e.*, about 0.30 V more positive than that corresponding to a typically prepared NSc $TiO_2$ sintered electrode.[7]

Discharge experiments carried out using a 42.5 mW cm$^{-2}$ incident light source, as described by Cherepy and co-workers,[13] allowed the calculation of some of the values in Table 1. It is interesting to note that whereas the fill factor of the three electrodes studied here remains approximately the same, the short circuit current as well as the open circuit photopotential changes with the number of layers in a non-linear fashion.

In fact, as can be appreciated in Fig. 3b, the total photoconversion efficiency of the cell ($\eta$) using electromagnetic radiation that spans the visible region of the spectrum, also increases logarithmically with the number of fullerene layers. For the three layered

**Table 1** Photoelectrochemical data for one, two and three $C_{60}$ layered NSc $TiO_2$ modified electrodes at 298 K

| Step | $A$/a. u.[a] | IPCE[a,]/% | $i_{sc}$/mA cm$^{-2}$ | $E_{oc}$/V | *ff* | $\eta$/% |
|---|---|---|---|---|---|---|
| 1 | 0.94 | 1.84 | 0.015 | 0.022 | 0.31 | 0.0002 |
| 2 | 1.14 | 10.23 | 0.073 | 0.120 | 0.37 | 0.0076 |
| 3 | 1.35 | 81.97 | 0.263 | 0.600 | 0.36 | 0.1351 |

[a] at $\lambda_{\text{máx}}$ = 430 nm.

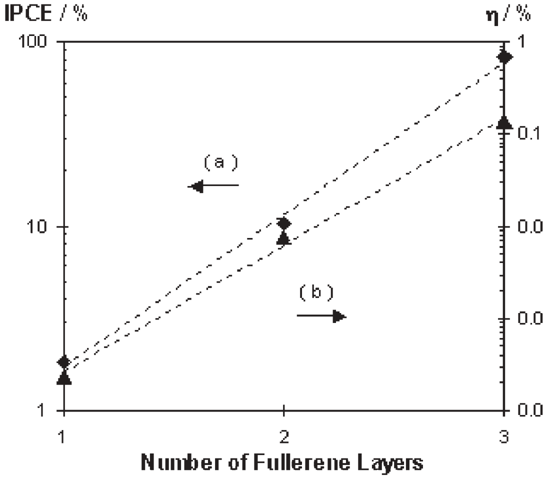

**Fig. 3** Logarithmic relationship between the percentage of (a) IPCE at 430 nm and (b) photoconversion current efficiencies, $\eta$, and the number of fullerene layers anchored on the surface of NSc $TiO_2$ electrodes at 298 K.

electrode a value of 0.13% is reached which, in close analogy to the IPCE case, is not only similar to the value reported by Kamat and co-workers for an NSc electrode modified with electrodeposited $C_{60}$ cluster aggregates,[2b] but also, to the best of our knowledge, the largest one reported for a fullerene sensitized electrode.

In summary, in this work we report preliminary studies of a new family of fullerene–dendrimer modified electrodes characterized by a photoelectrochemical performance that makes them attractive for solar cell technology development. The preparation of similar photoactive films with different sized dendrimers arranged in a dendritic architecture is currently being investigated in our laboratory.

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## Notes and references

† IPCE/% = $((i_{sc}\cdot 1240)/(I_{inc}\cdot\lambda))\cdot 100$; $\eta$/% = $((ff\cdot i_{sc}\cdot E_{oc})/I_{inc})\cdot 100$. Where $i_{sc}$, $I_{inc}$, $E_{oc}$, and $ff$ correspond to short circuit photocurrent density (A $cm^{-2}$), incident light intensity (W $cm^{-2}$), open circuit photopotential (V) and fill factor, respectively.[3]

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