doi:10.1246/cl.2011.87

Hybridization of Carbon Nanotubes with Si–π Polymers and Attachment of Resulting Hybrids to TiO_2 Surface

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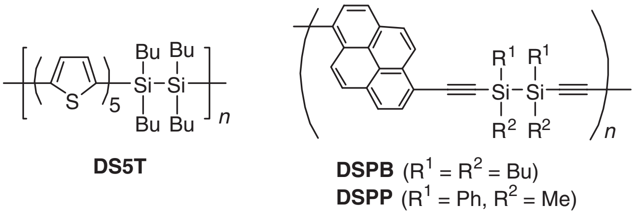
(Received October 26, 2010; CL-100911; E-mail: jo@hiroshima-u.ac.jp)

The Sonogashira coupling of diethynyldisilanes with dibromopyrene in the presence of single-walled carbon nanotubes (SWNTs) produced soluble hybrid materials of poly(disilanylenediethynylpyrene)s and SWNTs. Ball milling of poly(disilanylenediethynylpyrene)s or poly(disilanylenequinquethienylene) with SWNTs also afforded the polymer–SWNT hybrids. Irradiation of TiO_2 electrodes in chloroform solutions of the hybrids led to the attachment of the hybrids to the TiO_2 surface via Si–O–Ti bonding. Applications of the hybrid-attached TiO_2 electrodes to dye-sensitized solar cells were studied.

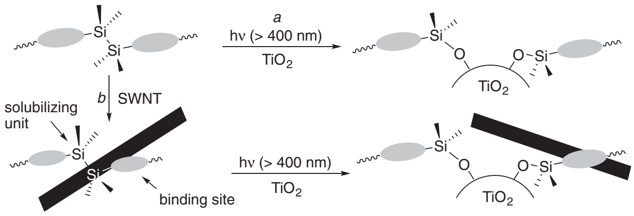
Carbon nanotubes (CNTs) are of current interest because they possess unique electrical, mechanical, and thermal properties. However, CNTs are essentially insoluble in common organic solvents due to their strong tendency to form aggregates, and much effort has been made to solubilize them.[1] The introduction of carboxy groups on the surface and edge of CNTs and the conversion of the carboxy groups into amide and ester units are often employed.[2] Other chemical modifications of the CNT surface with organic groups have been reported to enhance solubility and/or dispersibility.[3] However, such chemical modifications may change the properties of the CNTs and therefore, recent attention is focused on the nonbonding interaction of CNTs with solubilizing organic compounds.[4] Here, we report the solubilization of single-walled CNTs (SWNTs) by hybridization with polymers having π-conjugated units that serve as the binding sites to SWNTs, which are linked by solubilizing organodisilanylene units (Chart 1). Disilanylene units are also anticipated to undergo numerous chemical transformations for the further functionalization of the polymer–SWNT hybrids.[5] We recently reported that UV irradiation (>400 nm) of a TiO_2 electrode in a solution of poly(disilanylenequinquethienylene) (**DS5T**) led to the attachment of the polymer to the TiO_2 surface through Si–O–Ti anchoring bonds, as a new method for the preparation of organic–inorganic hybrids (Scheme 1, *a*).[6] We demonstrated also that the polymer-attached TiO_2 electrodes could be used for dye-sensitized solar cells (DSSCs). As an example of the potential applications of the present polymer–SWNT hybrids bearing Si–Si bonds, we examined the attachment of the hybrids to TiO_2 (Scheme 1, *b*) by photoreactions and applications of the resulting hybrid-attached TiO_2 to DSSCs.



DS5T

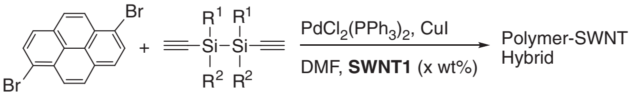
DSPB ($R^1 = R^2 = Bu$)
DSPP ($R^1 = Ph$, $R^2 = Me$)

Chart 1. Si–π polymers.



Scheme 1. Preparation of organic–inorganic hybrids using Si–π polymers.

Table 1. Preparation of **DSPB**– and **DSPP**–SWNT hybrids by in situ hybridization



Run	Polymer /mmol[a]	SWNT /wt %[b]	Hybrid /mg	Emission Φ[c]
1	**DSPB** (0.875)	**SWNT1**[d] (5)	**PB1I-5** (148)	0.22
2	**DSPB** (0.875)	**SWNT1**[d] (10)	**PB1I-10** (152)	0.11
3	**DSPB** (0.875)	**SWNT1**[d] (15)	**PB1I-15** (160)	0.18
4	**DSPP** (0.583)	**SWNT1**[d] (5)	**PP1I-5** (154)	0.15
5	**DSPP** (0.583)	**SWNT1**[d] (10)	**PP1I-10** (211)	0.07
6	**DSPP** (0.583)	**SWNT1**[d] (15)	**PP1I-15** (202)	0.08
7	**DSPB** (0.875)	**SWNT2**[e] (15)	**PB2I-10** (137)	0.24

[a] Each monomer amount used for the preparation. [b] wt % of SWNT based on dibromopyrene. [c] Absolute emission quantum efficiency in $CHCl_3$ as determined by an integral sphere. [d] **SWNT1**: 1.2–1.5 nmϕ. [e] **SWNT2**: 0.7–1.3 nmϕ.

Polymer–SWNT hybrids **PB1I** and **PP1I** were prepared as brownish black solids by the Sonogashira coupling of dibromopyrene with diethynyldisilane in the presence of SWNTs (**SWNT1**: 1.2–1.5 nmϕ and **SWNT2**: 0.7–1.3 nmϕ), followed by reprecipitation of the soluble products from $CHCl_3$/EtOH (Table 1).[12] The absorption and emission spectral shapes were not evidently affected by the hybridization, but the emission quantum efficiencies were clearly decreased (cf. $\Phi = 0.30$ and 0.15 for polymers **DSPB** and **DSPP**, respectively), suggesting quenching of the emission by energy or electron transfer from the photoexcited polymers to SWNTs.[12] In contrast, the introduction of large amounts of SWNTs resulted in increases in the quantum efficiencies to some extent (Runs 3 and 6 in Table 1). It is possible that the aggregation of SWNTs may

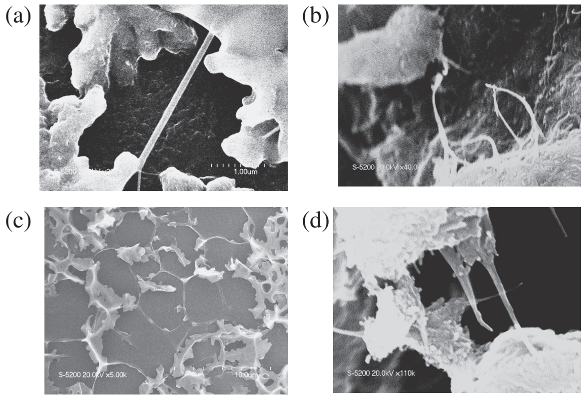


Figure 1. SEM images of drop-cast films of (a) **PB1I-15**, (b) **PP1I-15**, and (c) **PB2M-10**, and (d) TiO_2 attached to **PB1I-15**.

Table 2. Preparation of polymer–SWNT hybrids by ball milling

$$\text{Si-}\pi\text{ polymer} \xrightarrow[\text{SWNT1 or 2 (x wt\%)}]{\text{Ball Milling}} \text{Polymer-SWNT Hybrid}$$

Run	Polymer /mg	SWNT /wt %[a]	Hybrid /mg	Emission Φ[b]
1	**DSPB** (22)	**SWNT1**[c] (5)	**PB1M-5** (19)[d]	0.20
2	**DSPB** (26)	**SWNT2**[c] (5)	**PB2M-5** (21)[d]	0.23
3	**DSPB** (25)	**SWNT2**[c] (10)	**PB2M-10** (14)[d]	0.18
4	**DS5T**[e] (26)	**SWNT2**[c] (5)	**TB2M-5** (17)[d]	0.15

[a]wt % of SWNT based on polymer weight. [b]Absolute emission quantum efficiency in $CHCl_3$ as determined by an integral sphere. [c]**SWNT1**: 1.2–1.5 nmϕ, **SWNT2**: 0.7–1.3 nmϕ. [d]Yield was determined by evaporation of a portion of the hybrid solution. [e]Φ in $CHCl_3 = 0.21$.

affect the quenching process. Hybrid **PB2I-10** prepared from **SWNT2** showed weak absorption bands due to SWNTs (Run 7 in Table 1). Figures 1a and 1b illustrate SEM images of the drop-cast films of **PB1I-15** and **PP1I-15**, showing tube and string-like structures with diameters of 50–100 nm, ascribed to bundled SWNTs that are probably covered by the polymer substances. No such structures were observed at all in **DSPB** and **DSPP**.[12] The molecular weights of the hybrids were measured by GPC to be approximately $M_w = 10000$ ($M_w/M_n = 1.4$) for **PB1I** and $M_w = 3000$ ($M_w/M_n = 1.4$) for **PP1I**. However, presumably, SWNTs were detached from the polymers by GPC and these values reflect the molecular weights of the SWNT-free Si–π polymers only.

Similar hybrid materials were prepared also by ball milling the polymers with SWNTs in the solid state.[7,12] The milled mixtures were dissolved in chloroform and filtered (Table 2, Figure 1c). The hybrids prepared by ball milling became insoluble when evaporated and thus they could not be purified by reprecipitation and must be stored in solution. This is probably due to the higher contents of SWNT in the hybrids prepared by ball milling than those by the in situ method. The absorption spectra of the hybrids with **SWNT2** clearly showed multiple bands in the NIR region, which are characteristic of nonaggregated SWNTs (Figure 2),[8] in contrast to the hybrids with **SWNT1** that showed no clear bands in the NIR region, probably due to the low concentration of SWNTs and/or band broadening by aggregation. A hybrid material of **DS5T** with **SWNT2** (Run 4) could be also prepared by this method.

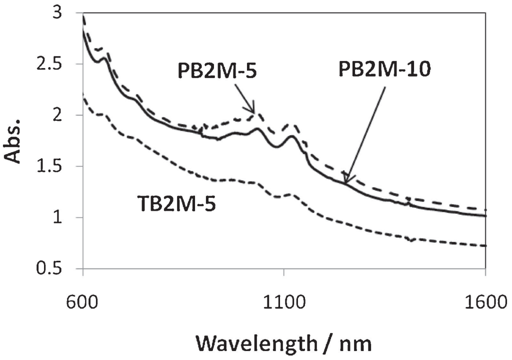


Figure 2. NIR spectra of the polymer–SWNT hybrids.

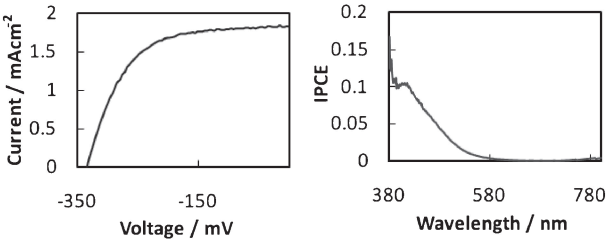


Figure 3. *I–V* plots (left) and an IPCE spectrum (right) of the DSSC based on **TB2M-5**–TiO_2.

Table 3. Performance of DSSCs based on modified TiO_2

Electrode	I_{sc}/mA cm^{-2}	V_{oc}/mV	FF	η/%
DS5T–TiO_2[a]	0.76	−292	0.52	0.11
TB2M-5–TiO_2	1.84	−340	0.62	0.39

[a]See ref. 6.

When TiO_2 electrodes were irradiated with a UV lamp through a filter (>400 nm) in chloroform solutions containing the polymer–SWNT hybrids in an argon atmosphere and the resulting electrodes were washed with chloroform, dark brown hybrid-attached TiO_2 electrodes were obtained (Figure 1d). We then fabricated a DSSC with the structure of FTO (fluorine-doped SnO_2)/**TB2M-5**-attached $TiO_2/I_2{\cdot}I^-$/Pt and examined its performance (Figure 3).[12] The maximum IPCE (incident photon-to-current conversion efficiency) was found at 417 nm, nearly consistent with the absorption maximum of **DS5T** (436 nm), indicating that the photoexcitation occurred in **DS5T**. As can be seen in Table 3, the cell with **TB2M-5**-modified TiO_2 electrode showed energy conversion efficiency η of 0.39%, which was approximately 3.5 times higher than that with the **DS5T**-attached TiO_2 electrode reported previously.[6] The increased current (I_{sc}) is primarily responsible for the improved efficiency of the present device,[9] and it is likely that the introduction of SWNTs facilitated the carrier transport from photoexcited **DS5T**. We examined also applications of **DSPB** and **PB2M-5** to DSSCs. However, both the DSSCs based on these materials showed only very low activity with $\eta = 0.06$–0.07%.

In conclusion, we demonstrated the hybrid formation between Si–π alternate polymers and SWNTs. The attachment of the hybrids to the TiO_2 surface was also studied. Although methods to attach CNTs to silicon metal surfaces have been reported,[10] the present work provides a unique and convenient methodology to attach SWNTs to the TiO_2 surface by a solution process with π-conjugated chromophores, using readily accessible organosilicon polymers.[11] This seems applicable to a variety of new SWNT-containing organic devices. Studies to prepare hybrids using other Si–π polymers as well as to attach the polymer–SWNT hybrids to inorganic oxides other than TiO_2 are underway.

This work was supported by a Grant-in-Aid for Scientific Research (No. 22655065) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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