Electronic Supplementary Materials for

Carbon nanotube-silicon heterojunction solar cells with surface-textured Si and solution-processed carbon nanotube films

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The reflectivity of the flat (without texture) and textured Si surfaces without and with CNT films was measured using a UV-Vis spectrophotometer (Jasco V-650, Tokyo, Japan). The same Si substrates utilized in the fabrication of CNT–Si solar cells were used for this measurement. The thermal oxide layer was fully removed by hydrofluoric acid. Two substrates were then textured by the method described in the Experimental section. The CNT films (T = 90% at 550 nm) washed for 70 min with hot water before drying were attached to one flat Si substrate and one textured Si substrate.

Texturing effectively decreased the reflectivity of the Si surface with CNT films; from 39.5% without texture to 14.9% with texture at a wavelength of 550 nm.



Fig. S1 UV-Vis reflection spectra of flat and textured Si surfaces without and with CNT films.

Photovoltaic performances of four cells without Si surface texture and four cells with Si surface texture were evaluated. Compared with the cells without texture, the cells with texture showed ~1.3-times improvements in the average J_{sc} and PCE to 32.1 mA/cm² and 9.87%, respectively, with small variations.



Fig. S2 *J-V* curves of the CNT–Si solar cells without and with texture. No anti-reflective coatings nor doping of the CNTs were applied to the cells.

The CNT–Si solar cells were assembled by attaching as-filtrated CNT films (T = 90%) to the Si substrates with texture. The V_{oc} , FF, and PCE values (0.450 V, 0.438, 6.32%) are significantly lower than those with the CNT films washed before drying (0.536 V, 0.575, 9.87%, shown in Fig. S2). The impurities in the CNT films, SDBS or particularly Na contained in the SDBS molecules, possibly trap carriers and promote the carrier recombination.



Fig. S3. *J-V* curves of the CNT-Si solar cells with texture made using as-filtrated CNT films.

The hydrophobicity of three differently treated CNT films were estimated by contact angle measurement of water droplets. Three differently treated CNT films (T = 90%) were prepared on HF-treated Si wafers and contact angles were measured for 10–12 water droplets of 1 µL for each film (blue open circles). The mean contact angles (black closed circles) were 86.9°, 100.9°, and 118.0° with standard deviations (shown with red error bars) of 5.9°, 6.5°, and 7.6° for the film as-filtrated, that dried on Si, washed, and that washed before drying, respectively. This result suggests that the SDBS and/or its residue are removed from the CNT film surface by washing with hot water and it becomes more difficult to remove them once the film is dried.



Fig. S4. Contact angles of water droplets with differently treated CNT films.

Two CNT films (T = 90%) were analyzed using FT-IR (Thermo Fischer Nicolet6700, Kanagawa, Japan) spectrometry. One film was dried on a Si substrate without post-treatment and the other film was washed by hot water before drying and transferring onto the Si substrate. For reference, SDBS aqueous solution was coated on a Si substrate, dried and analyzed.

Some absorption peaks indicated by red arrows appeared for the SDBS layer coated on the Si substrate (red line). Characteristic peaks were observed for the C–H stretching vibration at ~2950 cm⁻¹ and for the sulfonate group at ~1200 and 1000–1050 cm⁻¹.³⁷ None of such peaks were present on the spectra of the CNT films (blue and green lines). The amount of SDBS in both of the films was presumably too small for detection.



Fig. S5 FT-IR spectra of SDBS, as-filtrated CNT film and CNT film washed before drying.

³⁷ H. Zaghouane-Boudiaf, M. Boutahala, C. Tiar, L. Arab and F. Garin, *Chem. Eng. J.*, 2011, **173**, 36–41.

Five samples prepared by the following procedures were observed with Raman spectroscopy (HR-800, Horiba, Kyoto, Japan). An as-filtrated CNT film ($T \sim 50\%$) and a CNT film washed before drying were attached to Si wafers and dried at 100 °C for 3 min. Non-dispersed CNT agglomerates were placed on a Si wafer, wetted with an ethanol drop, and dried at 100 °C for 10 min. The SDBS was dissolved in purified water, dropped on a Si wafer, and dried at 100 °C for 3 min. No peak characteristic for SDBS was detected from the CNT films.



Fig. S6 Raman spectra of CNT agglomerates, CNT films, SDBS, and Si wafer.

Three CNT films (T = 80%) were analyzed using XPS (JEOL JPS-9010TR, Tokyo, Japan). Note that Fe and S are used as catalysts in CNT synthesis.³⁴



Fig. S7 XPS spectra and elemental composition of as-filtrated and washed CNT films on Si substrates.

The optical transmittance at 550 nm was measured using UV-Vis spectrophotometer (JASCO V-630, Tokyo, Japan). The data were fitted by the following equation, where T, a, ρ , and R_{sheet} represent optical transmittance, optical absorption coefficient, electric resistivity and sheet resistance, respectively.

 $T = \exp(-a\rho/R_{\text{sheet}})$

 R_{sheet} was measured by the 4-probe method.



Fig. S8 Relationship between the optical transmittance and sheet resistance of the CNT films prepared on slide glass substrates.