Supplementary material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information

Appendix 1. Heat generation of PSi/NaCl suspension upon exposure to NIR light

Figure S1 shows that there is almost no difference in the absorption property between NaCl solution and deionized (D.I.) water, suggesting that NaCl does not affect the optical properties of the PSi suspension. Figure S2 shows that the temperature of NaCl solution is the same as that of D.I. water after 20 min NIR irradiation although the former is slightly higher than the latter for the NIR exposure times less than 17 min. This result suggests that NaCl makes little effect on the photothermal effect of water.

Figure S3 is wide scan XPS spectra of the PSi/NaCl suspension after 20 min NIR irradiation. The details of the main peaks in the XPS spectra are given in Table S1 along with relevant compounds. Table S2 indicates that Na^+ ions form Na compounds such as Na_2SiF_6 by reacting with Si, O and F atoms upon exposure to NIR light. F atoms existing in the PSi suspension seem to originate from the HF/C_2H_5OH solution used for electrochemical anodization of Si to synthesize the PSi. There can be many spontaneous chemical reactions for Na_2SiF_6 formation. As an example, we may hypothesize a chemical reaction for Na_2SiF_6 formation as follows:

$$2Na^+ + 2Cl^- + SiF_4\,(g) + 2HF\,(aq) = Na_2SiF_6\,(c) + 2HCl\,(aq): \Delta H° = -32.33\ \text{kcal/mole} \quad (1)$$

where SiF_4 and HF may originate from the HF/C_2H_5OH anodization solution. SiF_4 represents a chemical reaction product of Si and HF. However, F may exist not as a component of a compound such as SiF_4 but as just impurity atoms adsorbed by PSi or an anodization residue in a state of HF at the surface of PSi in reality. The enthalpy change ($\Delta H°$) for the reaction to form 1 mole of Na_2SiF_6 (c) calculated using the thermodynamic data shown in Table S2 is -32.33 kcal/mole. The negative value of $\Delta H°$ indicates that this reaction is exothermic. From the above discussion we may conclude that the heat generation effect of NaCl in the PSi/NaCl-suspension is not due to the photothermal effect of NaCl itself but due to the chemical reaction of Na^+ ions with Si atoms at the surface of PSi and F atoms existing as impurities in the suspension.

Table S1. Details of the main peaks in the XPS spectra of the PSi/NaCl suspension after 20 min NIR irradiation along with relevant compounds

PSi/NaCl-suspension		Candidates	
Elemental Identification Name	Peak Binding Energy (eV)	Compound Name	Binding Energy[1] (eV)
Si 2P	103.21	SiO_2 Na_2SiF_6	103.6 104.3
F 1S	685.99	Na_2SiF_6	686.0
Na1S	1072.86	Na_2SiF_6	1071.7
O 1S	533.07	SiO_2	533
Cl 2P	200.19	NaCl	198.4
C 1S	286.20	C_2H_5OH	286.3

Table S2. Heat of formation of the substances involved in the chemical reaction for Na_2SiF_6 formation

Substance	Na^+	Cl^-	SiF_4 (g)	HF (aq)	Na_2SiF_6 (c)	HCl (aq)
Heat of formation[2] ($\Delta H_f°$) (kcal/mole)	-57.28	-40.02	-370	-78.66	-677	-40.02

Figure S4 shows a similar result obtained by Moench et al.[3] using ferromagnetic Fe-filled multiwall carbon nanotube (Fe-CNT) and Fe-CNT/NaCl-suspension. The temperature curves were obtained by measuring the temperature of the muscle tissue during alternating current (AC)-heating. This result suggests that NaCl also affects the photothermal property of CNT. The enhancement in the heat generation property of CNT by NaCl solution may be due to the chemical reaction of Na^+ with carbon and other impurity atoms such as oxygen, since NaCl solution itself has no photothermal effect.

Appendix 2. In vivo cell test results

Table S3. MTT Assay Test Results

Sample	Treatment	NIR exposure time (min)	Cell viability (%) *			
			Test 1	Test 2	Test 3	Average
A	Control	20	94.7	108.3	96.4	99.8
B1	PSi/NaCl suspension	10	103.3	95.8	97.8	98.9
C1	Control + NIR	10	93.0	100.5	97.1	96.9
D1	PSi/NaCl suspension + NIR	10	4.7	3.7	5.4	4.6
B2	PSi/NaCl suspension	20	90.6	97.1	106.5	98.1
C2	Control + NIR	20	99.2	95.7	90.6	95.2
D2	PSi/NaCl suspension + NIR	20	3.2	2.1	2.5	2.6

* MTT assay is a laboratory test and a standard colorimetric assay (an assay which measures charges in color) for measuring the activity of enzymes that reduce MTT to formazan, giving a purple color. Yellow MTT is reduced to a purple formazan in the mitochondria of living cells. A solubilization solution is added to dissolve the insoluble purple formazan product into a colored solution. The absorbance of this colored solution can be quantified by measuring at a certain wavelength by a spectrophotometer. Some suspension may remain even after media is removed and may affect the color of the formazan, resulting in the cell viability. Although cell viability cannot exceed 100 % theoretically, cell viability values higher than 100 % are commonly obtained experimentally. The cell viability data in Table S3 is just the raw data obtained experimentally. The cell viability values higher than 100 % may be regarded as 100 %.

References

1 J. F. Moulder, W. F. Stickle, P. E. Sobol and K. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy*, Physical Electronics, Inc., Minnesota, USA, 1995.

2 *CRC Handbook of Chemistry and Physics*, ed. R. C. Weast, 58th edn, CRC Press, Inc., Florida, USA, 1978.

3 I. Moench, A. Meye, and A. Leonhardt, Chapter 9 in *Nanomaterials for Cancer Therapy*,

ed. C. Kumar, Wiley-VCH Verlag GmbH & Co. KGaA, Weinbeim, 2006.

Figure Captions

Figure S1. The absorption spectra of D. I. water, 0.9 % NaCl solution, and 17 % NaCl solution after 300 mW/cm^2 NIR irradiation for 20 min.

Figure S2. Comparison of the heat generation abilities of 0.9 % NaCl solution and D. I. water.

Figure S3. XPS spectra of the PSi / NaCl suspension after 20 min NIR irradiation.

Figure S4. Temperature development in the muscle tissue into which Fe-CNTs or Fe-CNT / NaCl-suspension was injected.[3]

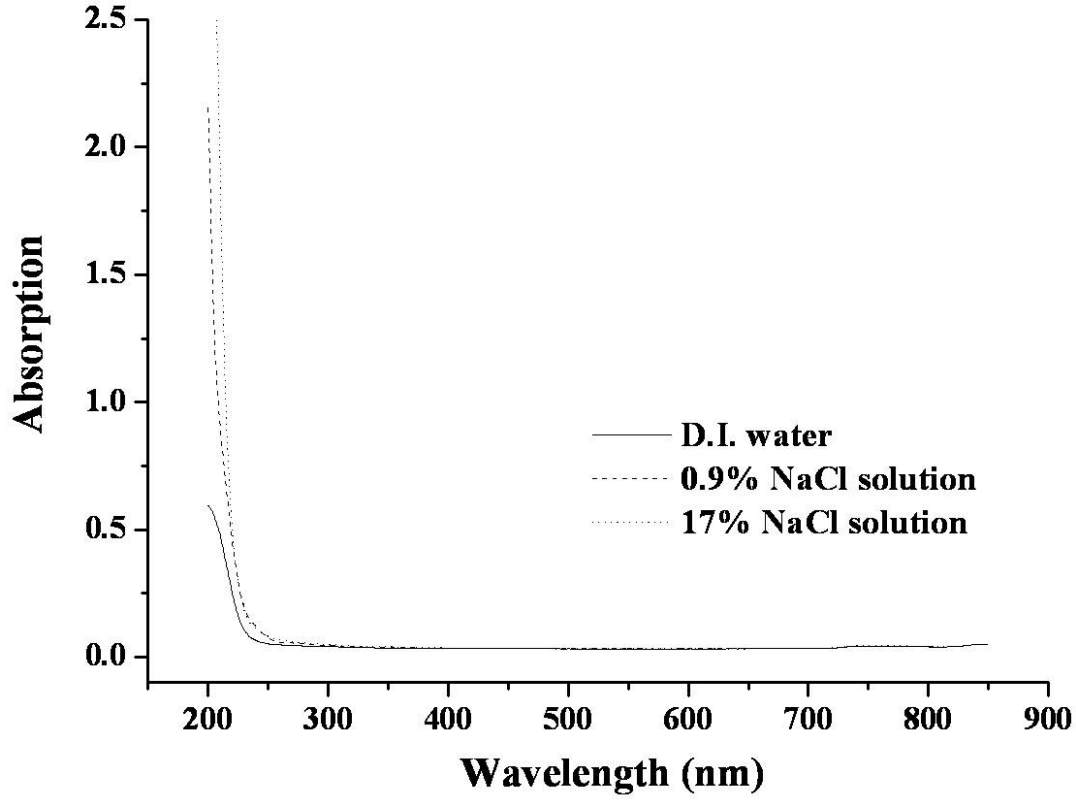

Fig. S1

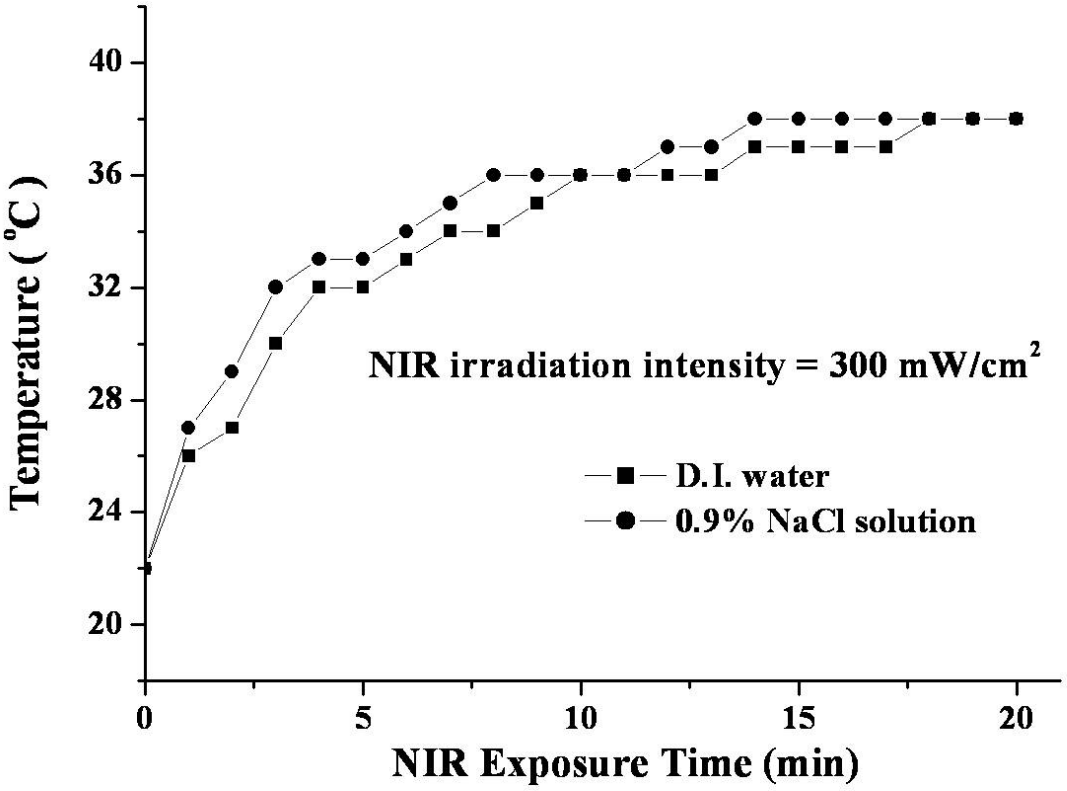

Fig. S2

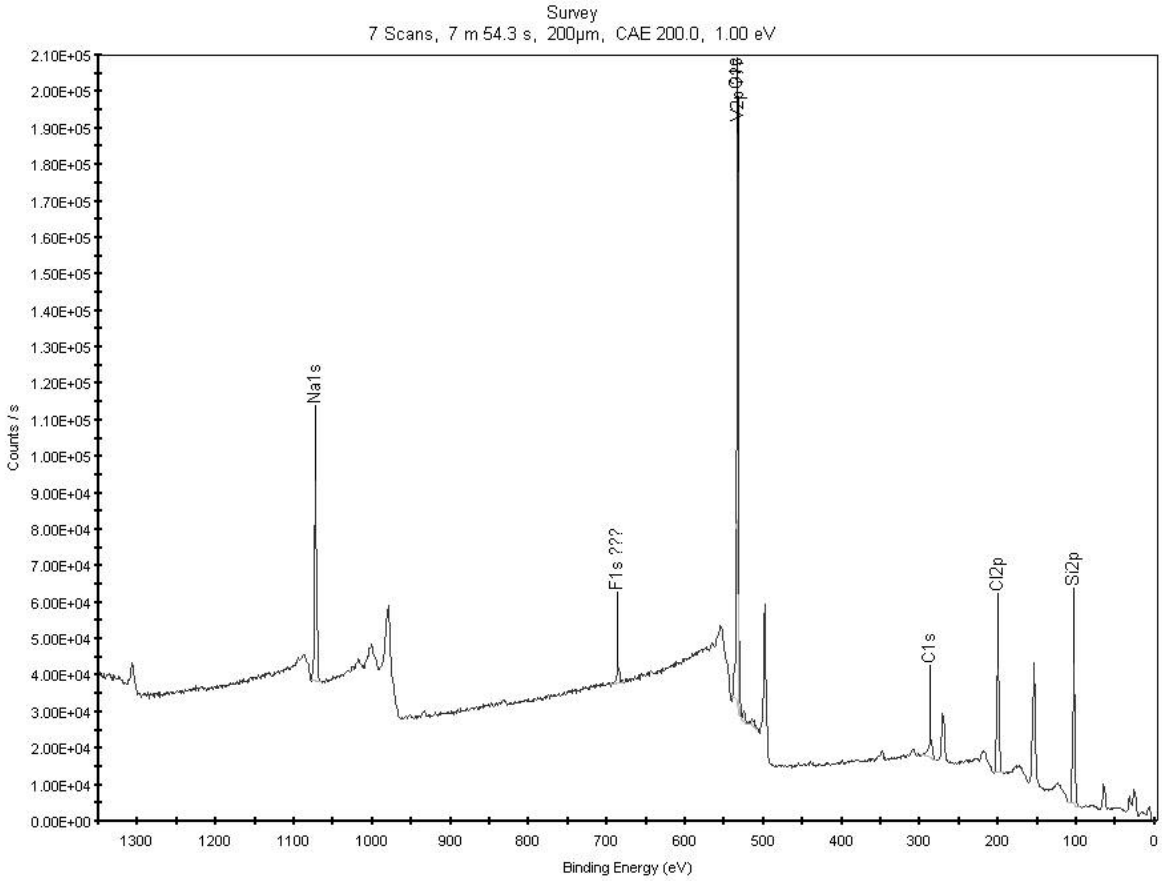

Fig. S3

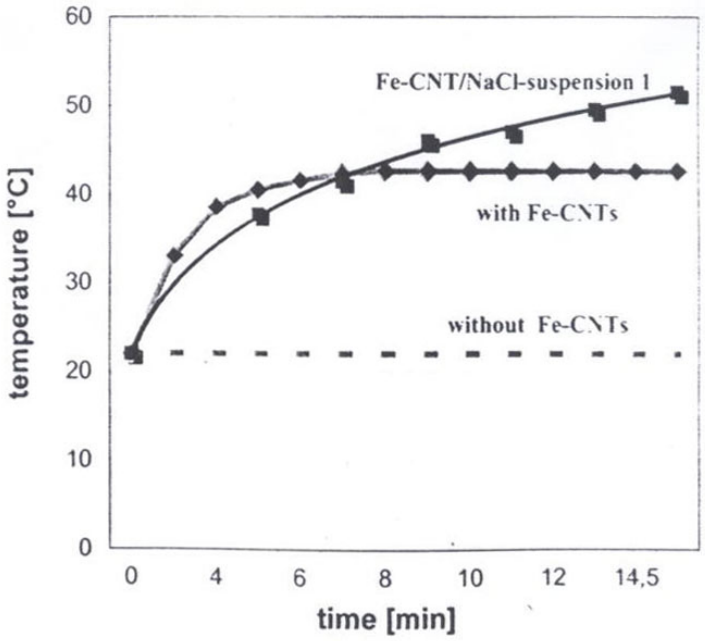

Fig. S4