Supplementary Information for:

Hierarchical Mesoporous Silica Nanoparticles as Superb Light Scattering Materials

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Experimental

Materials : Cetylpyridinium bromide (CPB) (98 %), tetraethyl orthosilicate (TEOS, 98%), cyclohexane, and *iso*-propanol were purchased from Aldrich Chemical Co. and used without further purification. Urea was purchased from Samchun Chemical. TiO_2 NPs (Ti-nanoxide T/SP), N-719, and an iodide-based redox electrolyte (AN50) were purchased from Solaronix (Aubonne, Switzerland) and used as received. FTO glass (15 Ω /cm^2, thickness of 2.2 mm) was obtained from Pilkington (Toledo, USA)

Fabrication of mesoporous silica nanoparticles with radial wrinkle structure : 0.5 g (1.3 mmol) of cetylpyridinium bromide and 0.3 g (5.0 mmol) of urea were dissolved in 15 mL of water. And then, 7.5 mL of cyclohexane and 0.46 mL (6 mmol) of iso-propanol were added to the solution. With vigorous stirring, 1.25 g (6 mmol) of TEOS was dropwised to the mixed solution. After vigorous stirring for 30 min at room temperature, the reaction mixture was heated up to 70 °C, and this state was maintained for 8 h. The reaction mixture washed with acetone and water 3 times through centrifugation. The isolated WSNs by centrifugation were dried in the 70 °C. Finally, the dried WSNs were calcined at 550 °C for six hours in air.

Assembly of dye-sensitized solar cells (DSSCs) : A double-layered structure of the TiO_2 film was composed of the TiO_2-NP (Solaronix, Ti-Nanoxide T/sp) underlayer and the WSNs with TiO_2 NPs overlayer as a scattering layer. To prepare a mixture of WSNs and paste, the WSNs were added to the paste which mixture of lauric acid, ethyl cellulose, and terpineol containing TiO_2 NPs (size = 15 - 20 nm). Fluorine-doped tin dioxide (FTO) glass substrates were cleaned by successive sonication in deionized water, acetone, and 2-propanol for 60 min

each, and then treated with oxygen plasma for 30 s. The FTO glass substrate was pretreated with an aqueous solution of $TiCl_4$ (40 mm) and heated at 450 °C for 30 min. The double-layered structure of the TiO_2 film which composed of TiO2-NP under-layer and WSNs with TiO_2 NPs over-layer was prepared by using a screen print onto the FTO substrate. The TiO_2 films were sintered at 450 °C for 30 min, and then treated with $TiCl_4$ and sintered again as above. The resulting TiO_2 films were immersed in absolute ethanol containing N719 dye (5 × 10-4 M) and kept at room temperature for 24 h. Pt counter electrodes were prepared on the FTO glasses using a 2-propanol solution of H_2PtCl_6 (5 mM), followed by heating at 400 °C for 30 min in air. The electrolyte in the sealed cell was an I^- / I^{3-} redox couple containing BMII (0.60 M), LiI (0.1 M), I2 (0.05 M), and tert-butylpyridine (0.5 M) in acetonitrile.

Characterization : Images of transmission electron microscopy (TEM) were obtained from JEOL JEM-200CX, which are installed at the National Center for Inter-university Research Facilities (NCIRF) at Seoul National University. FE-SEM images were obtain from 6700; JEOL (Tokyo, Japan). Brunauer−Emmett−Teller (BET) surface areas of HNPs were determined using a Micromeritics analyzer (ASAP 2000; Micromeritics Co., Norcross, GA). Diffuse reflectance spectroscopy (DRS) was investigated from A Lambda 35 spectrophotometer (PerkinElmer). The photocurrent–voltage (I–V) characteristics of the assembled DSSCs were evaluated using a 500 W xenon lamp (XIL model 05A50KS source units). The incident photon-to-current efficiency (IPCE; PV Measurements, Inc., Boulder, CO) was measured from 300 to 800 nm under the global AM 1.5 solar emission spectrum.

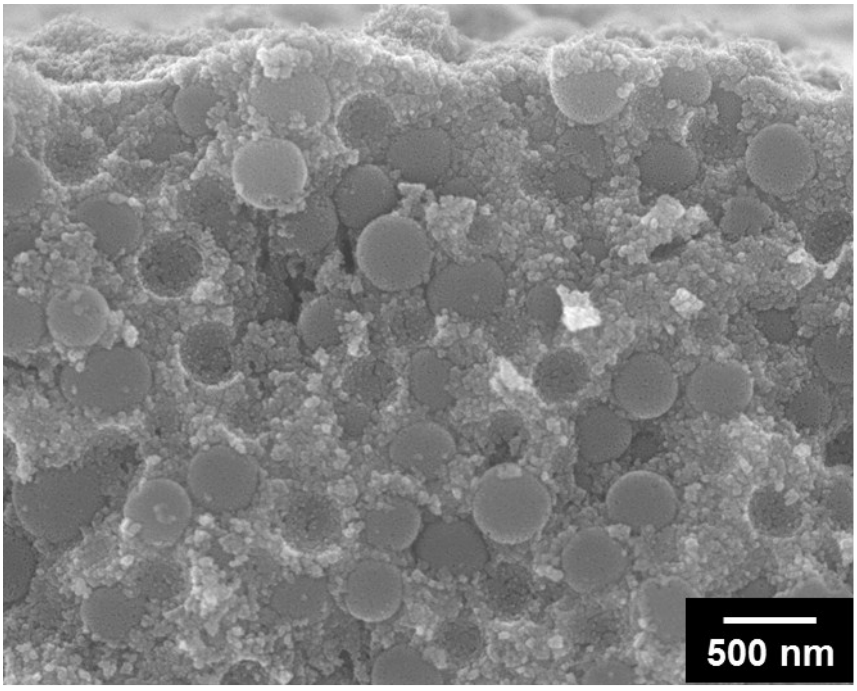

Fig. S1. SEM image of WSNs over-layer as a scattering layer of working electrode in the DSSCs device.

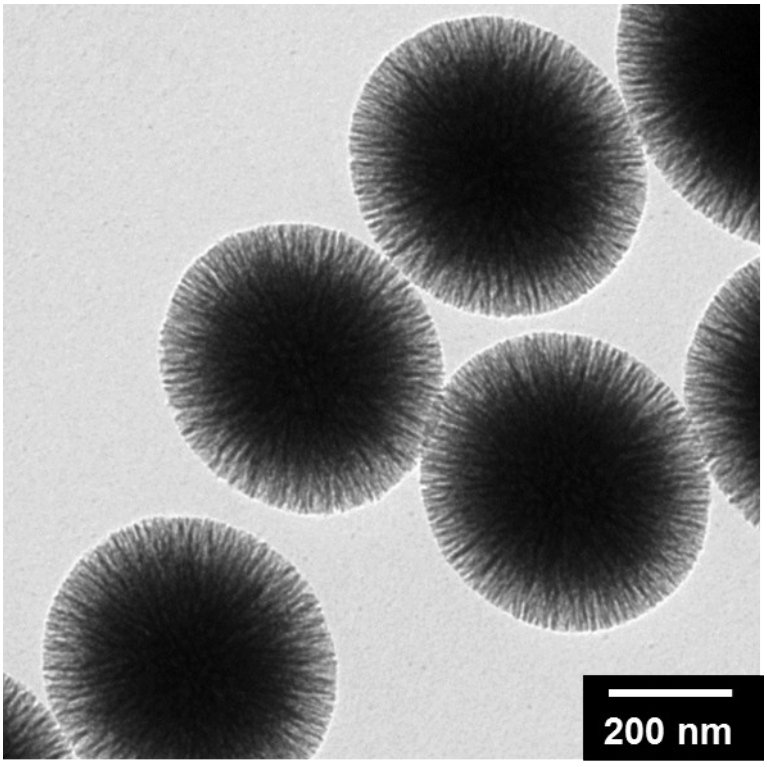

Fig. S2 TEM image of fabricated WSNs after 20 h of heating time.

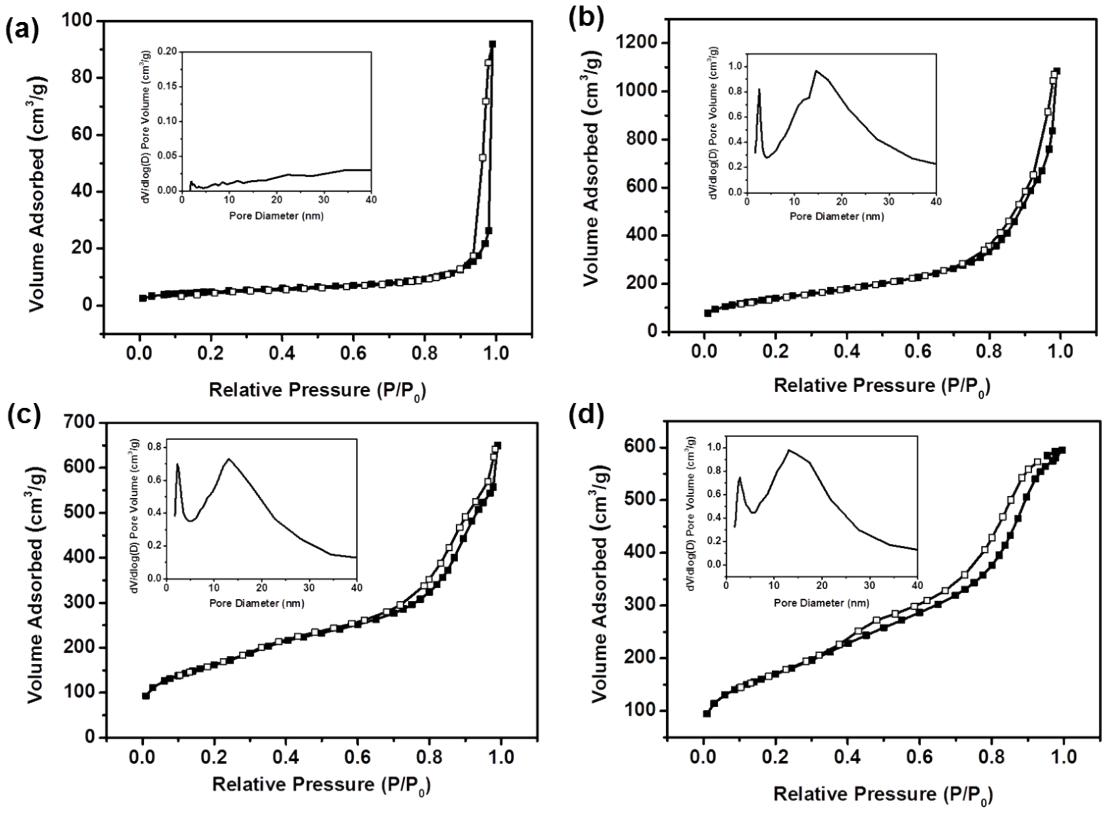

Fig. S3 N_2 adsorption-desorption isotherms and pore volume distribution plots (inset) of (a) 220 nm silica spheres and WSNs with (b) 220 nm, (c) 320 nm, (d) 430 nm diameters.

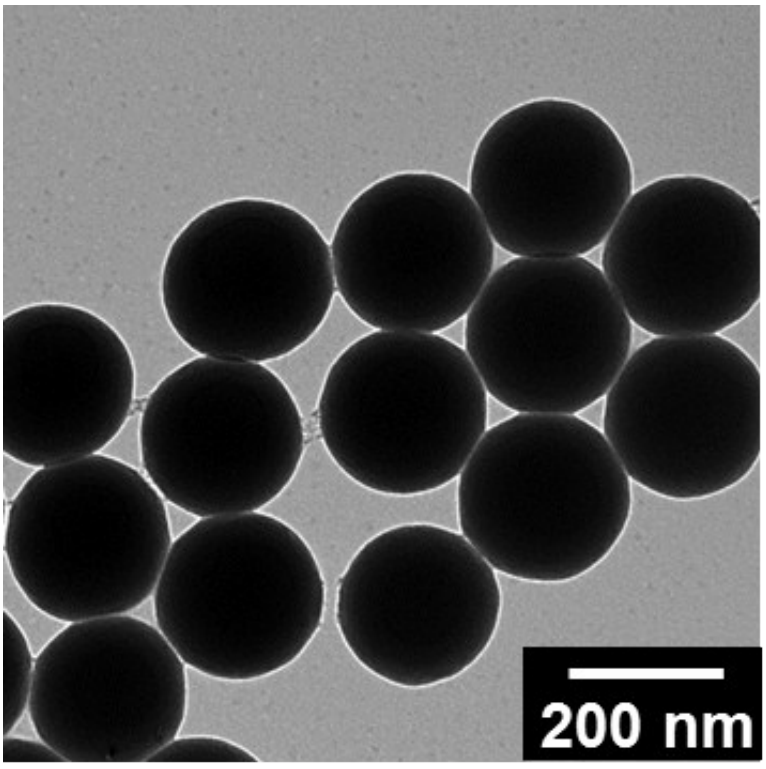

Fig. S4 TEM image of 220 nm silica spheres.

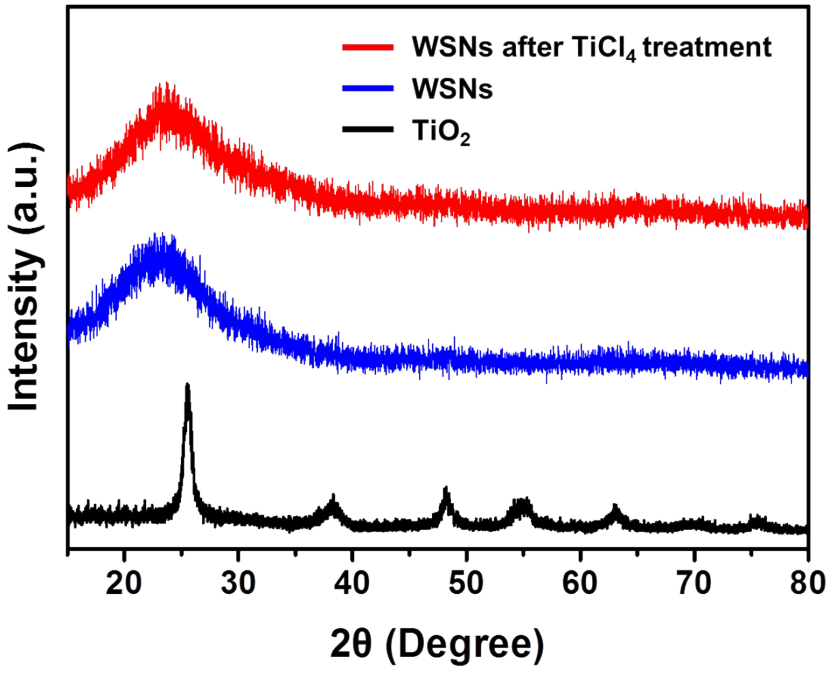

Fig. S5 XRD spectroscopy data of WSNs before and after $TiCl_4$ treatment, and TiO_2.

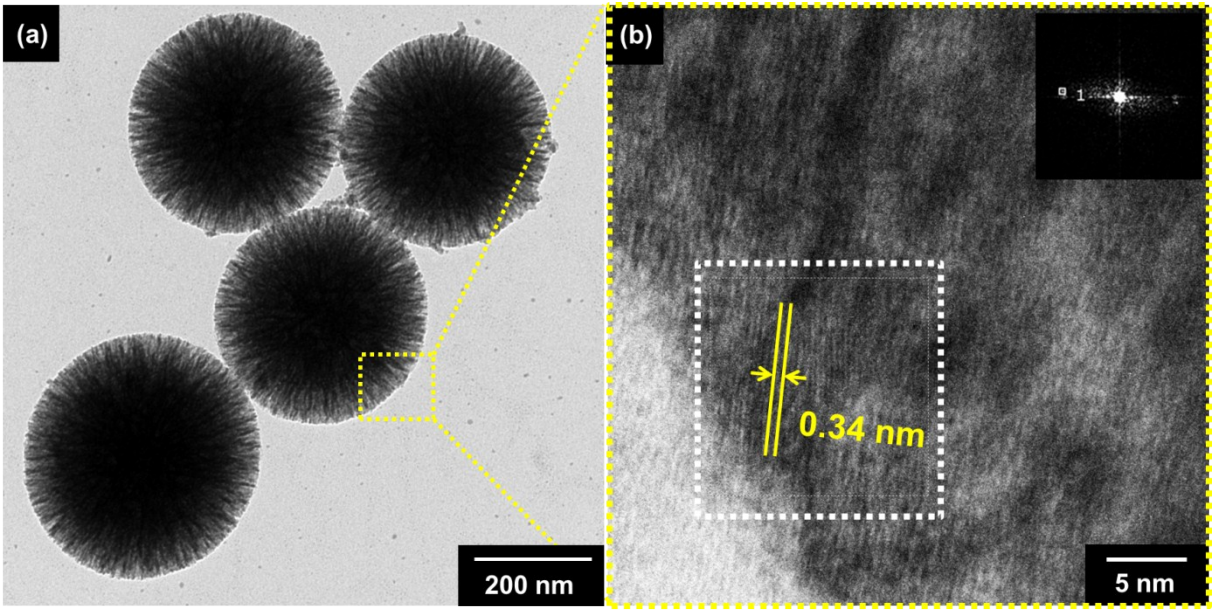

Fig. S6 (a) TEM and (b) High resolution TEM (HR-TEM) images of the WSNs coated with thin TiO_2 layer after $TiCl_4$ post-treatment (inset : the corresponding fast Fourier transform (FFT) pattern).

Table S1. Summary of BET analysis of the $TiCl_4$ treated-silica spheres and TiCl4 treated-WSNs with various sizes

Sample	BET area [$m^2 g^{-1}$]	Inter-wrinkle distance [nm][a)]
$TiCl_4$ treated-220 spheres	15.94	–
$TiCl_4$ treated-220 WSNs	546.45	10–20
$TiCl_4$ treated-320 WSNs	557.83	10–20
$TiCl_4$ treated-430 WSNs	579.82	10–20

[a)] Corresponding to wide peak in BJH pore distribution plots; There are two peaks in BJH plot, consisting sharp peak (2 nm) and wide band (ca. 15 nm)

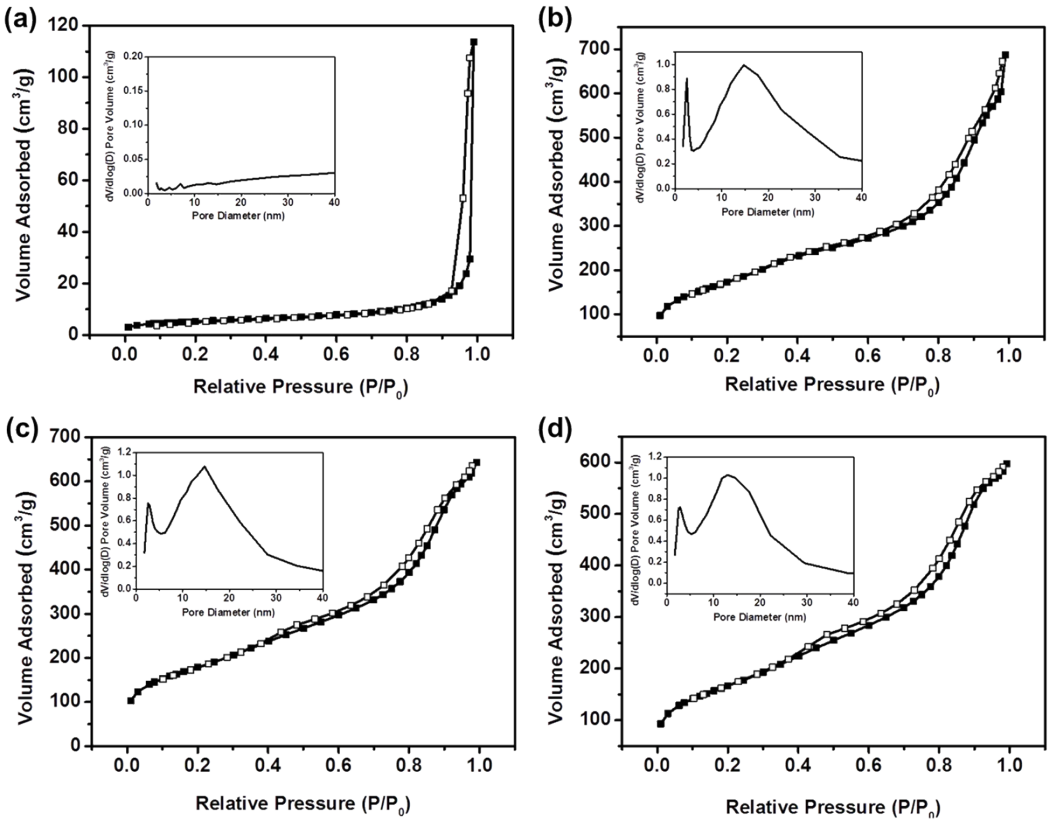

Fig. S7 N_2 adsorption-desorption isotherms and pore volume distribution plots (inset) of (a) $TiCl_4$ treated-220 nm silica spheres and TiCl4 treated-WSNs with (b) 220 nm, (c) 320 nm, (d) 430 nm diameters.

Table S2. Summary of the dye adsorption amount on scattering layer of WSNs and silica spheres-based DSSCs

Sample	Dye adsorption amount [$\times 10^{-7}$ mol·cm^{-2}]
Ref[c)]	1.000
220 spheres	0.891
220 WSNs	0.966
320 WSNs	0.972
430 WSNs	0.988

[a)]Active area of the assembled DSSC samples is 0.16 cm^2

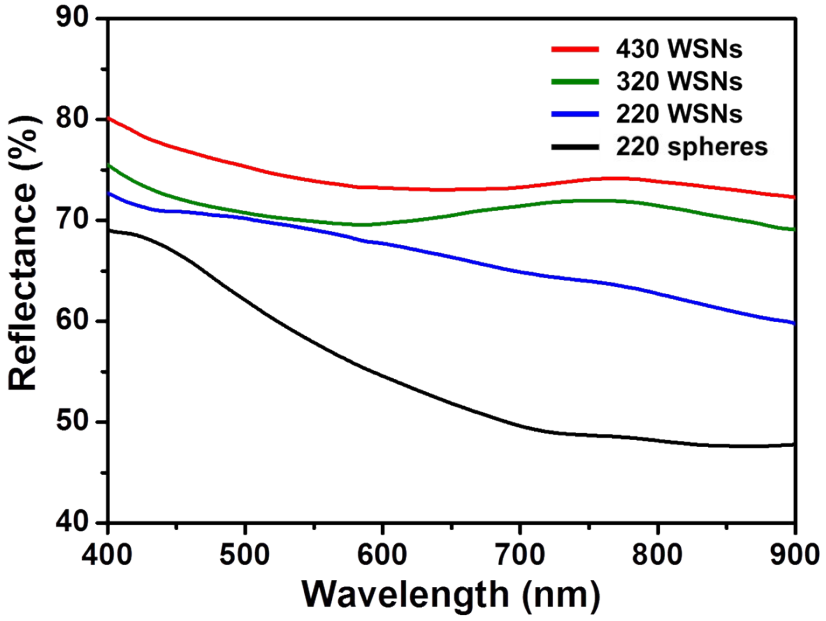

Fig. S8 Diffused reflectance spectra for $TiCl_4$ treated-200 nm silica spheres and $TiCl_4$ treated-WSNs with various sizes (220, 320, 430 nm).

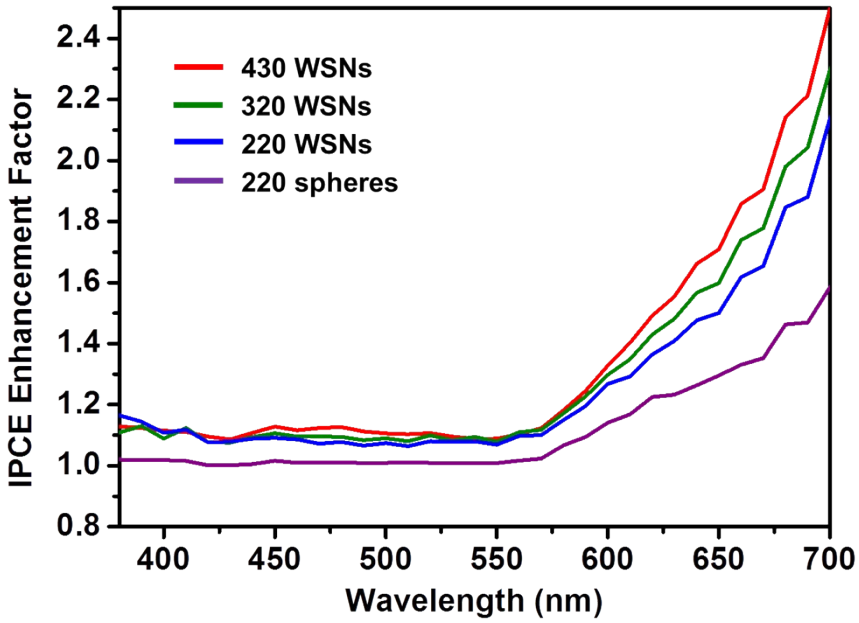

Fig. S9 IPCE enhancement factor based on reference cells (=$IPCE_{sample}/IPCE_{ref}$).

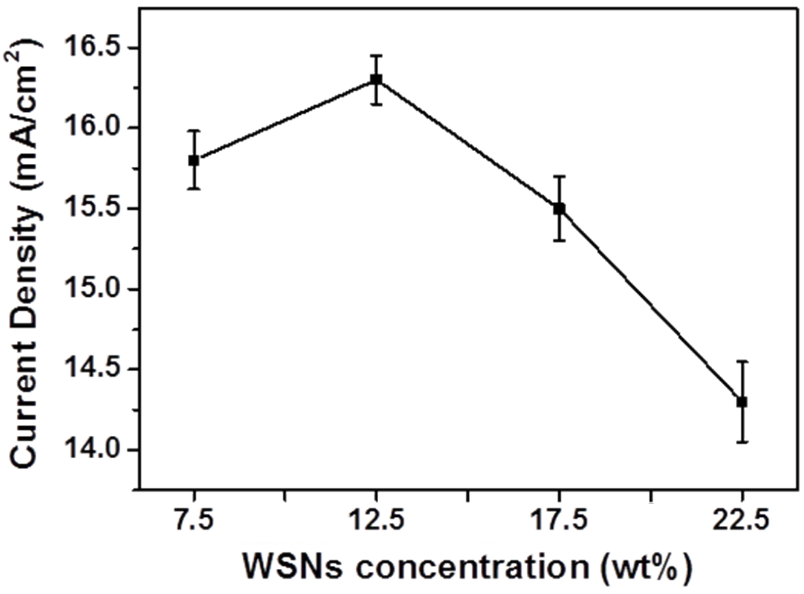

Fig. S10 Current density (J_{SC}) of the anode film as a function of WSNs concentration in the scattering layer.