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Supporting Information for

Carbon nanodots-catalyzed free radical polymerization of water-soluble vinyl monomers

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Fig. S13 The digital photographs of acrylamide polymerized at 50 °C (a) without and (b) with T-CNDs for 20, 40 and 60 min, respectively.

1. Experimental Details

Materials

Green tea was purchased from the local tea market. Catechin content in green tea is c. a. 16.65 wt% determined by the thermo-gravimetric curve (as shown in Fig. S1). Ethanol, methanol, sodium hydroxide (NaOH), hydrochloric acid (HCl), quinine sulfate, sodium *4*-styrenesulfonate (NaSS), Potassium persulfate (KPS), ammonium persulphate (APS), N,N'-Methylenebisacrylamide (Bis), 2,2'-azodiisobutyronitrile (AIBN), toluene, deuterium oxide (D_2O), dimethyl pyridine N-oxide (DMPO), N,N- diethylaniline (DEA) and 2,4-dinitrotoluene were purchased from the Sinopharm Chemical Reagent Co., Ltd. All above chemicals were used as received without further purification. Acrylamide (AM) was recrystallized and methyl methacrylate (MMA) was distilled under reduced pressure before use. Deionized water was used in the experiments.

Preparation of T-CNDs

1 g green tea powder was pyrolyzed at 450 °C for 1.5 h under air atmosphere. After programmed cooling to ambient temperature, the black, carbonized solid was ground into fine powder, then the powder was soaked in 20 mL distilled water for 20 min to extract the T-CNDs. Next, the solution was filtrated with a 0.22 μm filter membrane and the filtrate was collected and dried by using a rotary evaporator at 60 °C. The obtained brown powder was re-dispersed in 10 mL ethanol under ultrasound and filtered with a 0.22 μm filter membrane again, and then the filtrate was collected and dried by using a rotary evaporator at 45 °C. Finally, a yellow solid product of T-CNDs was obtained after using distilled water and ethanol to extract T-CNDs repeatedly for several times. The product yield of T-CNDs is ca.1.2 %.

Catalytic Polymerization of NaSS by Using T-CNDs

1 g of NaSS was dissolved in 10 mL deionized water and the solution was purged with nitrogen for 30 min at room temperature. Next, 1 mL aqueous solution containing T-CNDs (0.01 g) and KPS (0.013 g) was poured into the NaSS solution, and then the solution was heated to 70 °C. The polymerization was continued for 6 h and the final product of poly (sodium *4*-styrenesulfonate) (PSSNa) was obtained by dropping the reaction mixture into methanol, and unreacted initiator, monomer, and ligand were removed. After centrifugation and drying the floc, the dried product was

then dissolved in water and purified again (this precipitation clean-up was repeated up to three times). The purified aqueous polymer solution was then freeze-dried, the obtained dried product was named as Sample ***B*****,** and ^{1}H NMR spectra were recorded in D_2O to determine the structure. For comparison, a similar KPS-initiated polymerization without T-CNDs was performed, and the obtained polymeric product was named as Sample ***A***. Sample ***B*** was purified in the same way as above-mentioned, and molecular weights of the two polymerized products were measured by means of gel permeation chromatography (GPC). Kinetic data were obtained by removing aliquots at regular intervals of 20 min. Approximately 1 mL of the reaction solution was transferred under nitrogen by double-tipped needle into an ice box (-4 ^{o}C) to terminate the reaction. And the reaction solution was then freeze dried. ^{1}H NMR spectra were recorded in D_2O to determine the conversion at the time of sampling. As a control, we have used T-CNDs alone to initiate polymerization of NaSS upon heating at 70 ^{o}C, but no polymer was produced even though the reaction time was prolonged to 24 h.

As a control, sample ***C*** (PSSNa with T-CNDs) and sample ***D*** (PSSNa without T-CNDs) were also synthesized in a similar polymerization procedure except at a different temperature of 50 °C.

Catalytic Polymerization of AM and MMA by Using T-CNDs

1.4 g of AM, 0.0376g of Bis and 2 mg of T-CNDs were dissolved in 5 mL deionized water and we got solution *M1*; 0.014g APS was dissolved in 10 mL deionized water and the solution we got was named *M2*. Next, we mixed solution *M1*, deionized water and solution *M2* with the volume ratio of 1:1:2, and then the mixture was put into water bath of 50 ^{o}C. The polymerization of MMA was conducted in steps as follows: 1 mL of MMA and 1 mg of T-CNDs was dissolved in 4 mL of toluene, the mixture was purged with nitrogen for 30 min at room temperature. Next, 0.0155 g of AIBN was added into the mixture, and the reaction system was transferred in oil bath of 60 ^{o}C, the polymerization was continued for 5 h and the final product of poly (methyl methacrylate) (PMMA) was obtained by dropping the reaction mixture into methanol, and unreacted initiator, monomer, and ligand were removed. As controls, both polymerization of AM and MMA were conducted without T-CNDs.

Characterizations

The morphology of the products was observed on a transmission electron microscope (TEM, JEM-2100). Fourier Transform Infrared (FT-IR) and ultraviolet-visible (UV-vis) spectra of samples were recorded on a NEXUS-870 spectrometer and a UV759 spectrophotometer, respectively. Samples dissolved in deuteroxide (D_2O) were examined by using nuclear magnetic resonance spectroscopy (^1H NMR, 400 MHz, Bruker AV 400). Zeta potential was measured using a particle size analyzer (Delsa 440SX, Beckman Coulter Ltd). Photoluminescence (PL) measurements were performed on a fluorescence spectrophotometer (F-7000, Hitachi) with excitation wavelength of 330 and 485 nm. To have Stern−Volmer plots for the quenching of luminescence quantum yields (485 nm excitation) of T-CNDs, the fluorescence intensity τ_o of the T-CNDs solution was measured before quenchers were added, then the fluorescence intensity τ was measured with different quencher concentrations at a fixed T-CNDs concentration. The fluorescence lifetimes of the T-CNDs were measured by HORIBA FluoroMax-4. Thermogravimetric analysis (TGA) and the related derivative thermogravimetry (DTG) were recorded on a SDT Q600, and carried out from 25 °C to 1000 °C under air atmosphere for green tea while from 25 °C to 800 °C under N_2 atmosphere for the T-CNDs, the heating rate was 10 °C/min. The cyclic voltammetric (CV) measurements were performed on a Zahner PP123 electrochemical workstation in a typical three-electrode system with the working electrode of T-CNDs-coated glassy carbon (GC). Platinum wire served as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. Samples of T-CNDs, (T-CNDs + KPS) were dispersed in 25 °C, N_2-saturated deionized water containing 0.5 M Na_2SO_4 and their CV curves were obtained at a scan rate of 100 mV/s.

Electron paramagnetic resonance (EPR) measurment was conducted on a JEOL JES-FA200 spectrometer. For unpaired electrons of T-CNDs test, the aqueous solutions of T-CNDs, (T-CNDs+KPS) and (T-CNDs+KPS+NaSS) were transferred into EPR tubes after heat treating at 70^{o}C for 20 min, respectively. For free radicals test, the aqueous solutions of KPS and (KPS+T-CNDs) were heated to 50 ^{o}C for 5 min, and then added DMPO to capture free radicals to test. And all EPR data were collected at room temperature with a full spectrum light irradiation which is produced by a Xe-lamp (500 W) in Instruments' Center for Physical Science, University of Science & Technology of China (USTC). The number and weight-average molecular weight (M_n and M_w) as well as the polydispersity (PDI = M_w/M_n) of PSSNa and PMMA were determined by gel permeation chromatography (GPC) on a Waters 2414, in which 50 mM NaCl solution for PSSNa [S1] and tetrahydrofuran for PMMA were used as the mobile phase at a flow rate of 1.0 mL/min respectively.

Quantum Yield (QY) Measurements

Quinine sulfate[S2] dissolved in 0.1 M H_2SO_4 (QY=0.54) was selected as a control standard. The QYs of T-CNDs dissolved in deionized water at different concentrations were estimated according to the equation: $\Phi = \Phi_r \times \frac{I}{A} \times \frac{A_r}{I_r} \times \frac{n^2}{n_r^2}$

Where the *Φ* is the QY, *I* is the integrated PL emission intensity (excited at 330 nm for T-CNDs and quinine sulfate), *n* is the refractive index (1.334 for distilled water), and *A* is the absorbance value (less than 0.1) of UV-Vis absorbance at 330 nm (distilled water). The subscript "r'' refers to the standard.

Table S1. QYs of the T-CNDs Dispersed in Deionized Water

Samples	Abs. (A)	Integrated emission intensity (I)	Refractive index of solvent (n)	QY (Φ)
Quinine sulfate	0.0775	63110	1.334	0.54
T-CNDs with different concentration	0.0866	81760	1.334	0.63
	0.0826	79719	1.334	0.64
	0.0769	70737	1.334	0.61
	0.0641	64077	1.334	0.66
	0.0625	59972	1.334	0.64
Average QY of T-CNDs		0.64		

2. Elemental analysis

Table S2. Elemental Analysis Result of T-CNDs

Elemental content (wt. %)			
Sample	C	N	H
T-CNDs	35.75	0.746	8.46

3. Supplemental Figures of Green Tea, T-CNDs, and (T-CNDs +NaSS)

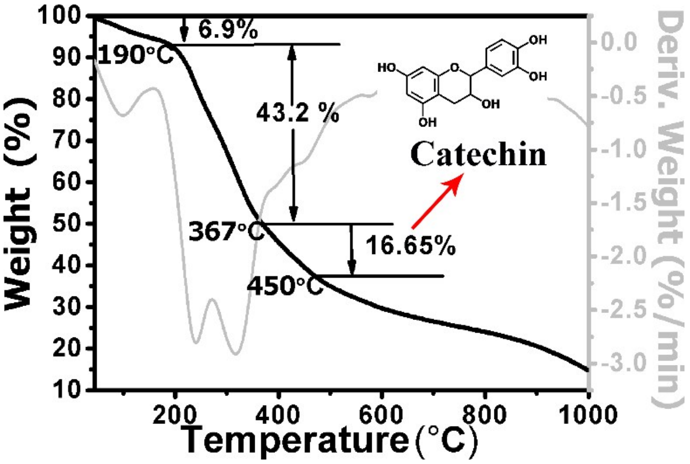

Fig. S1 TG and TGA curves of green tea in air atmosphere.

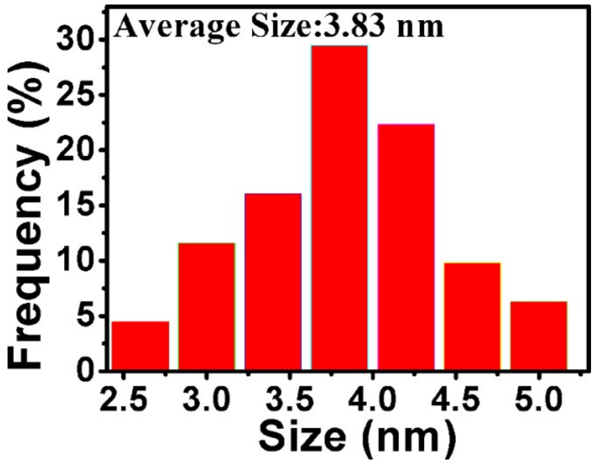

Fig. S2 T-CNDs size distribution histogram.

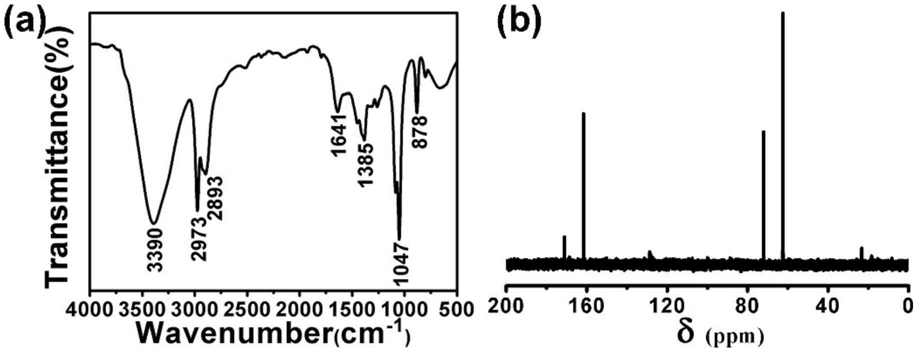

Fig. S3 FT-IR (a) and ^{13}C NMR (b) spectra of T-CNDs.

Note: The FT-IR spectrum (Fig. S3a) revealed the presence of C–OH (1385 cm^{-1}), C=O (1641 cm^{-1}), C−O (1047 cm^{-1}), and Ar–H (2973 cm^{-1}) groups on the T-CNDs. The broad band around 3390 cm^{-1}

suggests the existence of abundant hydroxyl groups probably derived from the decomposition of catechin in green tea.[S3] Moreover, a signal at 8.26 ppm in ^{1}H NMR spectrum of T-CNDs in D_2O (Fig. 1d) confirms the existence of Ar–OH, and the enlarged signals within 3.34~3.64 ppm can be assigned to –O–CH– groups of protons.[S4] In the range of 1~2 ppm, peaks assigned for the protons connected with the saturated carbons of the CD moiety are also visible.[S5] ^{13}C NMR spectrum of T-CNDs in D_2O is shown in Fig. S3b, the signals appearing in the region of 40.08~72.30 ppm correspond to carbon atoms that are connected to electronegative atoms such as oxygen. The intense signal near 126 ppm reveals the presence of sp^2-hybridized carbon or aromatic carbon atoms connected to hydrogen atoms and the signals appearing in the region of 162~170 ppm evidence the presence of carbonyl carbon atoms.[S4a]

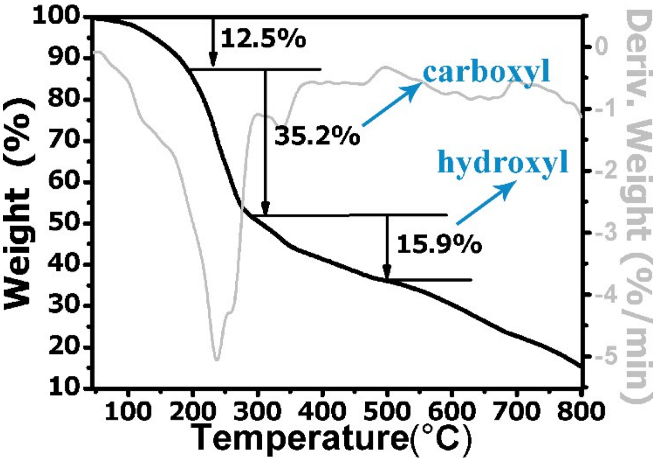

Fig. S4 TGA and DTG curves of T-CNDs in N_2 atmosphere.

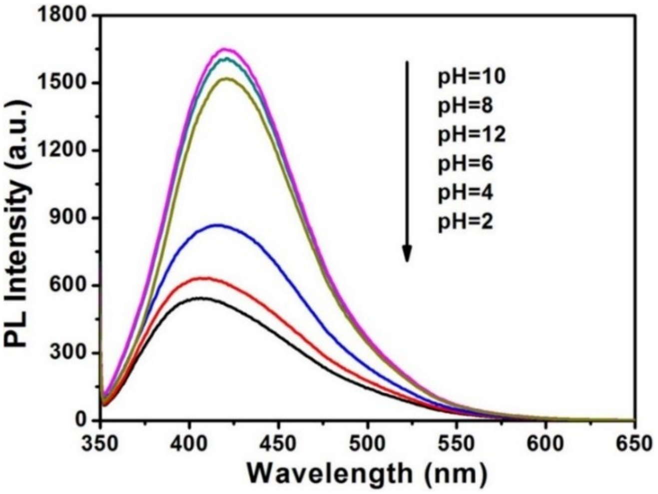

Fig. S5 The pH-dependent behavior of the T-CNDs in deionized water.

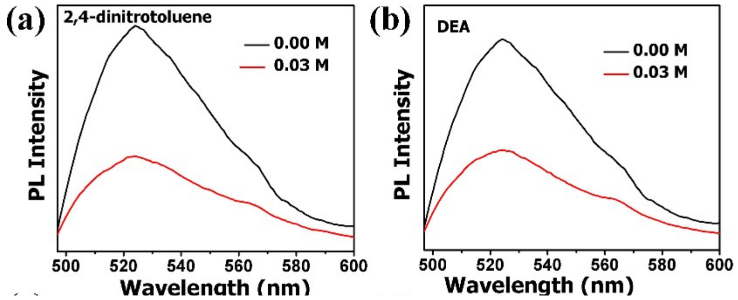

Fig. S6 Photoluminescence (PL) quenching of the T-CNDs by adding (a) 2,4-dinitrotoluene and (b) DEA ($\lambda_{ex} = 485$ nm), respectively.

4. Supplemental data of Catalytic Free Radical Polymerization Using T-CNDs

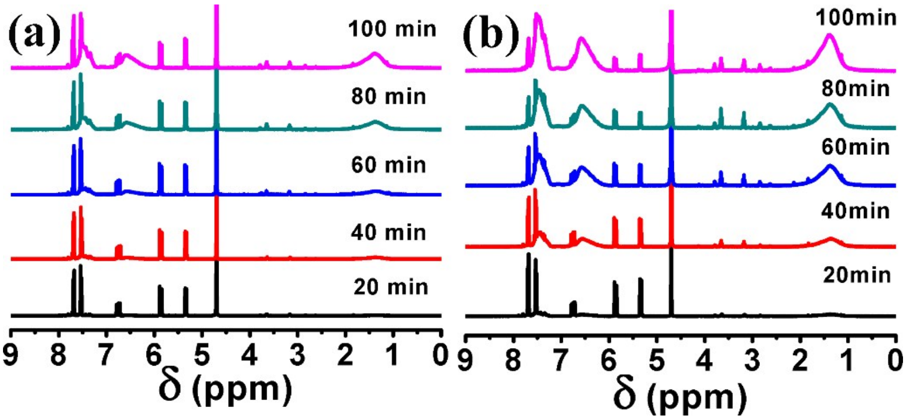

Fig. S7 ^{1}H NMR spectra of intermediate products during polymerization of NaSS reacted at 70 °C (a) without and (b) with T-CNDs.

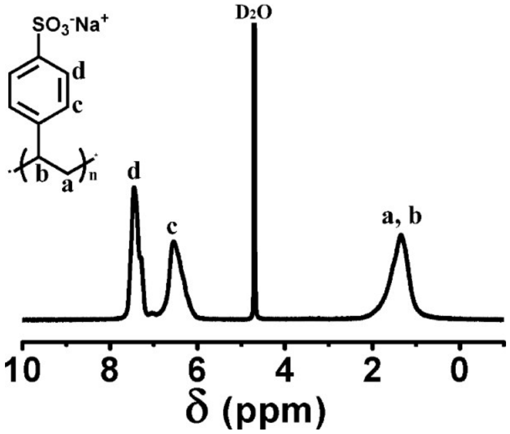

Fig S8 ^{1}H NMR spectrum in D_2O of T-CNDs-catalyzed PSSNa that has polymerized for 6 h.

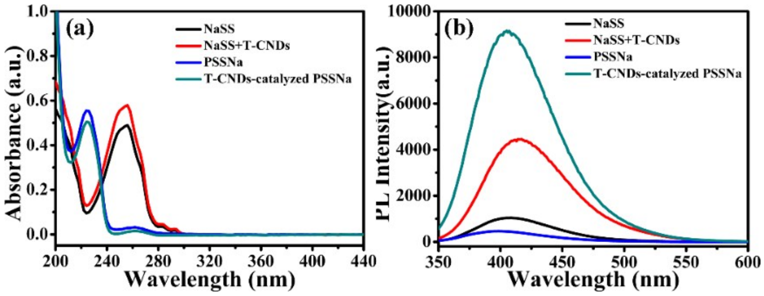

Fig. S9 (a) UV-Vis absorbance and (b) PL emission spectra (λ_{ex} = 330 nm) of NaSS, (NaSS + T-CNDs), PSSNa polymerized without T-CNDs, and T-CNDs-catalyzed PSSNa in deionized water.

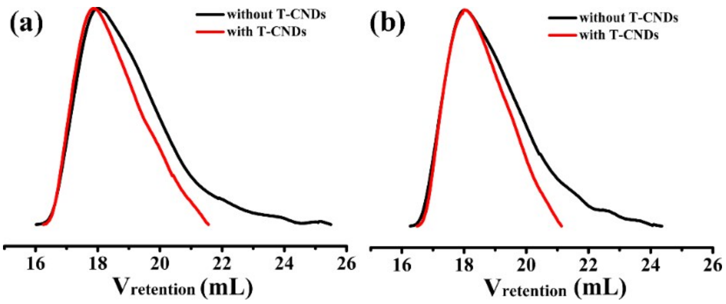

Fig. S10 GPC curves of PSSNa polymerized with or without T-CNDs at (a) 70 °C and (b) 50 °C, respectively.

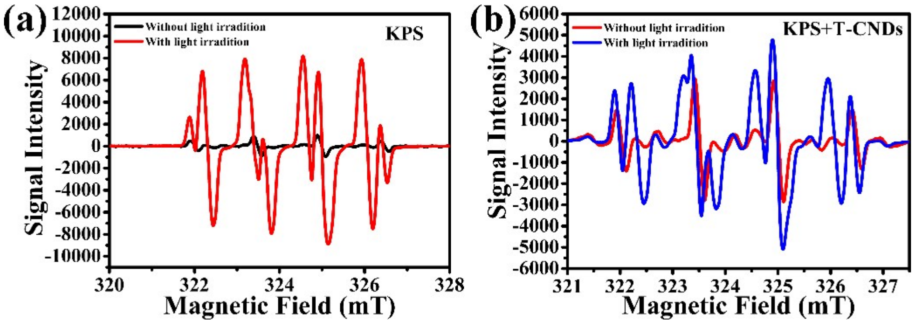

Fig. S11 EPR signals of the DMPO−·OH and other radicals trapped by DMPO produced by (a) KPS and (b) (KPS+T-CNDs) in aqueous solution after heated to 50 °C before and after light irradiation, respectively (A visible light produced by a 300 W Xe-lamp with a 420 nm cut-off optical filter was used to irradiate the solution).

Table S3. GPC Data of PSSNa Polymerized at 50 °C under the visible light irradiation

T-CNDs	$M_n \times 10^4$ (g/mol)	$M_w \times 10^4$ (g/mol)	PDI
0	11.6	23.1	1.98
10 mg	14.6	23.9	1.63

(Note: A visible light produced by a 300 W Xe-lamp with a 420 nm cut-off optical filter was used to irradiate the aqueous solution containing NaSS, KPS and T-CNDs.)

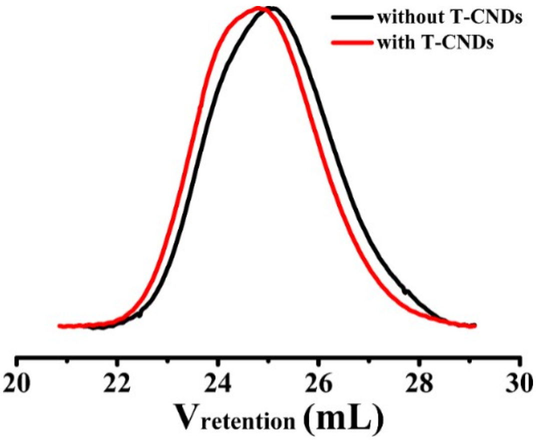

Fig. S12 GPC curves of PMMA polymerized at 60 °C with and without T-CNDs.

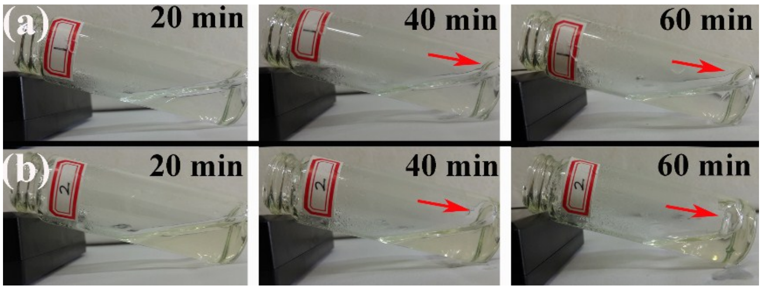

Fig. S13 The digital photographs of acrylamide polymerized at 50 °C (a) without and (b) with T-CNDs for 20, 40 and 60 min, respectively.

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