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Supporting Information

Carbon Dots as a Promising Green Photocatalyst for Free Radical and ATRP-Based Radical Photopolymerization with Blue LEDs

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Materials: CDs were synthesized according to our previous reports[16c]. Tri(propylene glycol) diacrylate (TPGDA), methyl methacrylate (MMA) and styrene (St) were purchased from Sigma-Aldrich and passed through a plug of basic alumina before use to remove the inhibitor. Copper(II)bromide ($CuBr_2$) and Tris(2-pyridylmethyl) amine (TPMA, 98%) were purchased from Sigma-Aldrich and used as received. Dimethyl sulfoxide (DMSO, anhydrous, 99.8%) was purchased from Sigma Aldrich, and stored over activated molecular sieves (4Å). Ethyl □-bromophenylacetate (EBPA, 97%, Sigma Aldrich) and methanol (99.9%; Merck) were used as received. All onium salts were received from FEW Chemicals GmbH as commercially available materials (**1a**: **S2617**, **1b**: **S2430**, **2a**: **S2615**).

UV-Vis measurements of CDs: 3.23 mg of **CD**s was transferred to a glass vial and 2 mL of DMSO was added. After 45 minutes of mixing, 1 mL from this solution was transferred to measuring flask and completed to 10 mL.

General procedure for photo-induced ATRP of MMA: A vial equipped with a magnetic stir bar and fitted with a Teflon screw cap septum was charged with **CD**s (3 mg) and 1 mL of DMSO. To this mixture MMA (1 mL), 5.20 µL of a 180 mM $CuBr_2$ stock solution in DMSO and 15.6 mL of a 270 mM TPMA stock solution in DMSO and ethyl α-bromophenylacetate (5.5 µL) was added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask with a magnetic stirrer and degassed by four Freeze-Pump-Thaw cycles. The reaction mixture was irradiated at 405 nm in a distance of 5 cm. Solution was stirred during exposure. At the end of the irradiation, the resulting polymer was precipitated in methanol and then dried under reduced pressure. Conversion was determined gravimetrically.

Block copolymerization experiment (PMMA-*b*-PSt): A vial equipped with a magnetic stir bar and fitted with a Teflon screw cap septum was charged with PMMA macroinitiator (0.676 g, 0.045 mmol), 7.5 µL of a 180 mM CuBr2 stock solution in DMSO (1.35 µmol) and 45 µL of a 270 mM TPMA stock solution in DMF (6.09 µmol). Styrene (1.38 g, 13.5 mmol) and DMSO (1.38 g) were added to this mixture, and the resulting solution was homogenized by vigorous stirring. The solution was transferred to a Schlenk Flask comprising a magnetic stirrer and degassed by four Freeze- Pump-Thaw cycles. The reaction mixture was placed in a photoreactor and irradiated at 790 nm. The resulted polymers were precipitated in methanol at the end of the irradiation, and then dried under reduced pressure. Conversion was determined gravimetrically. Exposure occurred under conditions as mentioned *vide supra*.

Light on-off experiments: A vial equipped with a magnetic stir bar and fitted with a Teflon screw cap septum was charged with **CD**s-2 (3 mg) and 1 mL of DMSO. To this mixture MMA (1 mL), 5.20 µL of a 180 mM $CuBr_2$ stock solution in DMSO and 15.6 mL of a 270 mM TPMA stock solution in DMSO and ethyl α-bromophenylacetate (5.5 µL) was added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask with a magnetic stirrer and degassed by four Freeze-Pump-Thaw cycles. The reaction tube was exposed to repeated cycles at 405 nm for 30 minutes and kept in dark for 30 minutes. In these subsequent intervals, 1 mL volumes of reaction mixture were syringed out from the polymerization media and precipitated in methanol. Next, the polymers were analyzed gravimetrically to determine the conversions. The molecular weight was analyzed by GPC. Exposure occurred under conditions as mentioned *vide*

supra.

Kinetic studies of the polymerization: A vial equipped with a magnetic stir bar and fitted with a Teflon screw cap septum was charged with **CD**s-2 (3 mg) and 1 mL of DMSO. To this mixture MMA (1 mL), 5.20 µL of a 180 mM $CuBr_2$ stock solution in DMSO and 15.6 mL of a 270 mM TPMA stock solution in DMSO and ethyl α-bromophenylacetate (5.5 µL) was added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask with a magnetic stirrer and degassed by four Freeze-Pump-Thaw cycles. The reaction tube was exposed at 405 nm and every 30 minutes 1 mL volumes of reaction mixture were syringed out from the polymerization media and precipitated in methanol. Next, the polymers were analyzed gravimetrically to determine the conversions. The molecular weight was analyzed by GPC. Exposure occurred under conditions as mentioned *vide supra*.

Instrumentation

Gel permeation chromatography (GPC): GPC was used to determine number average molecular weight (M_n) and dispersity *Đ* (*Đ*=M_w/M_n) values. GPC measurements were conducted with a GPC Viscotek 270 max using TGuard Col 10 x 4.6 mm and two T6000M General Mixed 3000 x 7.8 mm columns, a column temperature of 30°C, an RI detector, and tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min. The column system was calibrated with 7 linear poly(methyl methacrylate) standards received from Shodex (1850 $g \cdot mol^{-1}$; 6380 $g \times mol^{-1}$; 20100 $g \times mol^{-1}$; 73200 $g \times mol^{-1}$; 218000 $g \times mol^{-1}$; 608000 $g \times mol^{-1}$; and 1050000 $g \times mol^{-1}$). GPC data were analyzed using Omni SEC 4.6.2:GPC. Polymers were reprecipitated three times before transferring them to GPC.

NMR spectroscopy: Fourier 300 from Bruker was used for all ^{1}H-NMR-measurements. 5-20 mg sample were dissolved in 0.7 mL solvent. This was pursued for all polymers before taking GPC data to ensure the absence of low molecular weight products.

UV-Visible spectroscopy: All characterizations were performed using a Varian Cary 5000 UV/Vis/NIR spectrometer. Measurements of activation rate coefficients were performed on Agilent 8453 UV-Vis Spectrometer.

Photo-DSC: Measurements were performed as previously described using an UV-LED emitting with an intensity of 100 mW/cm^2 at 405 nm and 0.5 mW/cm^2 at 470 nm for radical polymerization[17a]. Radiometric data were determined with a USB 4000 spectrometer from Ocean Optics. Tri(propylene glycole) diacrylate served as monomer.

Synthesis of **CD**s made from carboxylic acid and phytic acid

Carboxymethyl Cellulose Sodium Salt (10.8 g) and ethylenediamine (5 ml) were dissolved in ultrapure water (5 L) and mixed uniformly. The solution was transferred to a reaction kettle, stirred at 180 °C for 8 h and then allowed to cool to room temperature naturally. Solid CDs were obtained from the solution by freeze-drying.

Phytic acid（1g）and ethylenediamine (2 mL) were dissolved in ultrapure water (8 mL) and mixed uniformly. The solution was transferred to an open round-bottom flask, stirred at 180℃ for 2h. After cooling, the mixture solidified into a dark brown solid that can be dissolved with the addition of DI water (40 mL). An aqueous solution of the crude product was firstly centrifuged (8000 rpm/min for 11 min) and filtered through 0.22 µm membrane filter to remove large or agglomerated particles. Solid CDs were obtained from the solution by

freeze-drying.

TEM figures of the **CD**s made from carboxylic acid and phytic acid

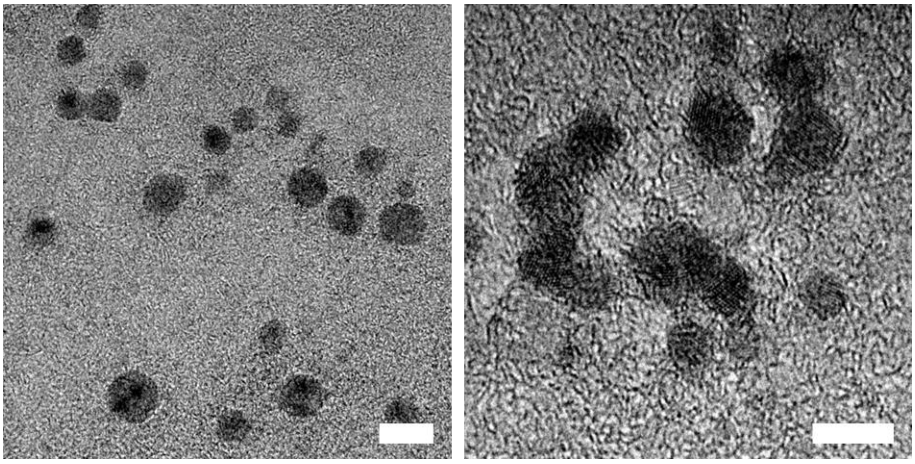

Figure S1. TEM images of CDs from carboxylic sodium cellulose and phytic acid, scale bar = 10 nm.

Cytotoxic studies

Cell Viability Measurement: The effects of the newly prepared LCDs on cell viability were examined in vitro using 3-(4,5dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assays in L929 fibroblasts. The L929 fibroblasts were seeded onto a 96-well plate, with 6000-7000 cells in 200 μL of culture medium per well. The plate was then incubated at 37 °C for 24 h in the presence of 5% CO_2 to allow the cells to attach to the wells, and the cells were exposed to CDs at different concentrations (0, 12.5, 25, 50, 100, 200, and 400 μg) and incubated for another 24 h at 37 °C in the presence of 5% CO_2. MTT solution (20 μL, 5 mg/mL) was then added to each well, and after incubation at 37 °C for 4 h, the absorbance of each well was measured using a microplate reader, with 490 nm as the detection wavelength. The average readings and standard deviations were based on four samples, and all tests were performed in triplicate. Cell viability was calculated using the following equation: cell viability (%) = A_{test}/ $A_{control}$, where Atest is the average cell viability in the presence of CDs and $A_{control}$ is the average cell viability in the absence of CDs (control experiment).

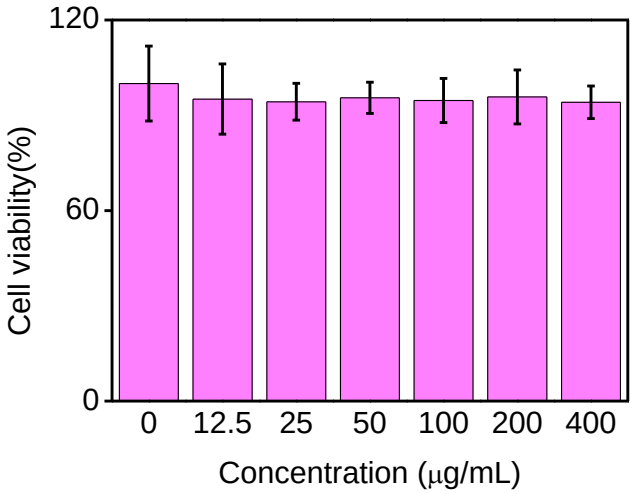

Figure S2. In vitro L929 fibroblast cell viability after incubation with LCDs with different concentrations for 24 h.

Cyclic voltammetry

Measurement conditions: Electrochemical experiments were performed with an CHI760E potentiostat (Chenhua Company, Shanghai, China) in a conventional three-electrode cell. The electrode assembly consists of a platinum wire as the counter electrode, an Ag-AgCl-KCl (SCE) electrode as the reference electrode, and a glass carbon (GC) electrode as the working electrode. The measurement buffer contains 1 M KCl and 5 mM $[Fe(CN)_6]^{4-/3-}$ as redox indicator. Cyclic voltammetry (CV) was recorded in the range from −1 to 1 V with a scan rate of 0.01 V s^{-1}.

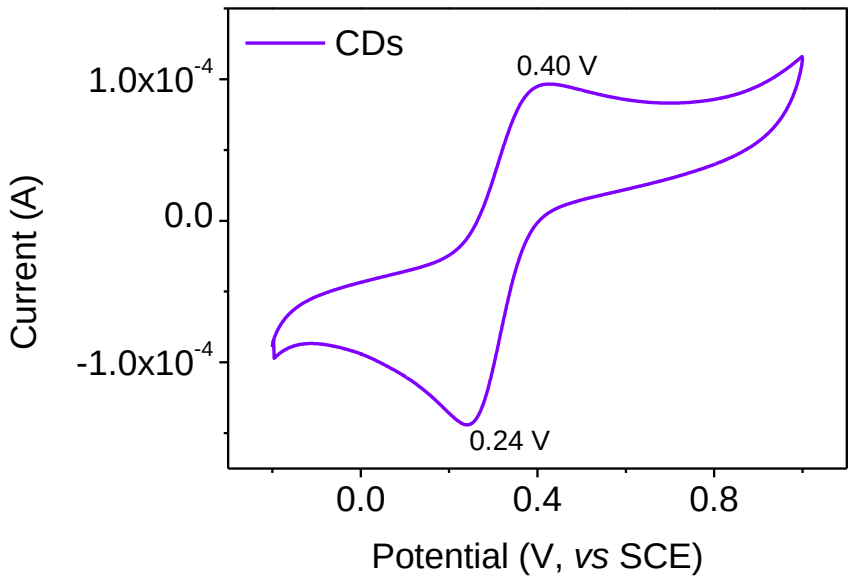

Figure S3. Cyclic voltametry curves of CDs.

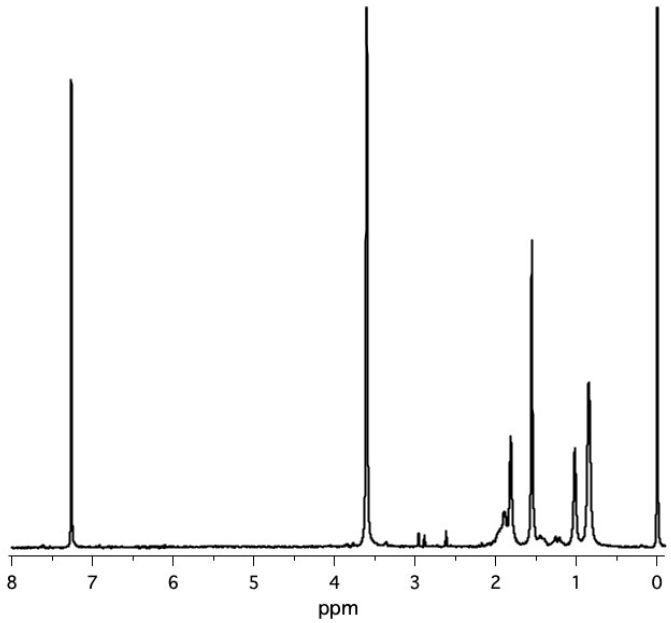

Figure S4: ^{1}H-NMR spectrum of the PMMA taken in CDCl3.

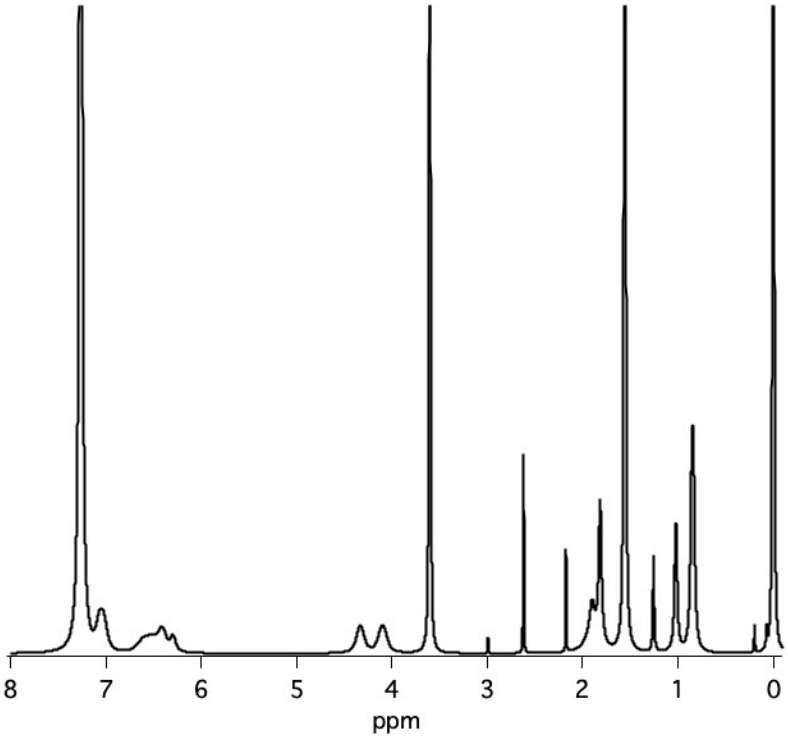

Figure S5: ^{1}H-NMR spectrum of the block copolymer (PMMA-*b*-PSt) taken in $CDCl_3$.

Figure S6: xxx

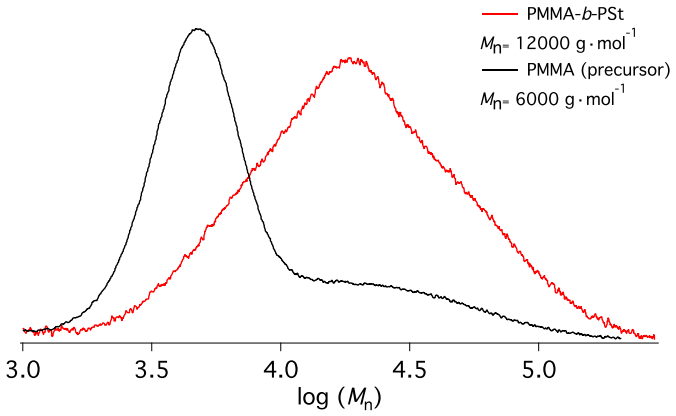

Figure S7: Comprasion of GPC traces of precursor PMMA with PMMA-*b*-PSt.