Electronic Supplementary Material (ESI) for Green Chemistry.

Supplemental Information Legends

Figure S1. FTIR spectra for (A) DLPE- and HDPE-derived CDs and (B) LDPP- and HDPP-derived CDs.

Figure S2. Emission-dependent excitation and excitation-dependent emission of (A) CDP and (B) CDM.

Figure S3. Raman spectra for mask-derived CDs (CDM) and bag-derived CDs (CDP).

Figure S4. Emission-dependent excitation and excitation-dependent emission of (A) CDPC and (B) CDMC.

Figure S5. (A, B) Photostability test of (A) CDM and (B) CDP under continuous UV irradiation. (C, D) Thermal stability of (C) CDM and (D) CDP at different temperatures.

Figure S6. Photoluminescence intensity of CDP and CDM at different weights of plastic and mask loads using small (100 ml) and large (200 ml) autoclave reactors.

Figure S7. MTT assay results on the viability of HeLa cells after exposure to different concentrations (0.1, 0.25, 0.5, 1, and 2 mg/ml) of CDP after (A) 4 and (B) 24 hours of incubation.

Figure S8. Cyclical deformation response of the QD-doped PDMS. (A) Cyclical force-displacement response for the PDMS only control samples. (B) Cyclical force-displacement response for the PDMS + QD (10:1) samples. (C) Cyclical force-displacement response for the PDMS + QD (5:1) samples. (D) Cyclical force-displacement response for the PDMS + QD (3.3:1) samples.

Table S1. Publications and patent prior art on carbon dots synthesis

METHODS

Synthesis of CDs. The CDs were synthesized following an oxidative degradation pathway. In a typical experiment, 0.5 g of the polyethylene-based trash bag was added to 20 ml of nitric acid solution (0.15 g/ml). The mixture was heated to 180°C using an autoclave reactor for 12 hours. The autoclave reactor had a volume of 100ml, an external shell of 80mm in diameter, 160mm in height, an external shell of 304 stainless steel, inner liner material polytetrafluoroethylene (diameter 49mm), a temperature rating of 230°C, a pressure rating of 3 MPa. Pictures of the reactor and inner vessel are below (https://www.desertcart.ae/products/149177981-autoclave-reactor-100-ml-hydrothermal-synthesis-autoclave-reactor-230-%E2%84%83-3-mpa-with-ptfe-liner-49-mm-diameter)

The aqueous portion of the product (CDP) was transferred into a beaker and the solid residue in the autoclave reactor was washed 3 times with distilled water. Methanol was then added to dissolve all the remaining black residue in the autoclave reactor. The aqueous portion of the product (that contains nitric acid) was first purified using centrifugation at 8000 rpm for 30 minutes, so the CDs precipitates in the bottom of the centrifuge tube and the nitric acid solution is collected as the supernatant to be used for further batches. Both portions of the product were further purified using a dialysis membrane against methanol (MWCO of 1 KDa, Spectra/Por® 6 Standard RC Pre-wetted Dialysis Tubing, diameter 29 mm). The collected nitric acid solution was reduced in concentration from 1.44M (starting concentration) to 0.41M. In the absence of plastics, hydrothermal processing of nitric acid solution in an identical process does not affect concentration. The concentration can be adjusted back to 1.44M prior to re-use in subsequent batches. The resulting sewage from the synthesis and purification of CDs can be processed with sodium hydroxide to neutralize any excess nitric acid to yield salt and water as the main products. The produced salt, as well as any other solid impurities contained in the aqueous portion, can be removed by gravity filtration, and the water reused for the following batches of plastic upcycling. The previous procedures were repeated for polypropylene-based face masks as the carbon source to produce CDM (Scheme 1). For synthesis testing in the presence of organic contaminants, we mixed 0.4 g of plastics with 0.1 g of organic waste [mixture of eggs (60%), tomato sauce (20%), and peanut butter (20%)].

Materials. Nitric acid (puriss. p.a., 65.0-67.0%) was purchased from Sigma-Aldrich. Clear trash bags [Aluf Plastics, HDPE (High-Density Polyethylene)] and disposable 3-Ply face masks (SP-LAMP, Polypropylene) were used as the carbon source. Low-density polyethylene (LDPE) and low-density polypropylene (LDPP). All chemicals and materials were used as received.

Scalability. The CDs of each batch were made using our reported method here. In a typical reaction, an amount of plastic waste of 0.5, 1, and 1.5 g each is immersed in 20 ml of nitric acid solution (0.15 g/ml) in an autoclave reactor. The mixture was heated at 180°C for 12 hours and the produced carbon dots were purified using a combination of centrifugation and dialysis.

Characterization. XPS analyses were carried out using a Kratos Axis Nova spectrometer utilizing a monochromatic Al K(alpha) source (15 mA, 14 kV). The TEM images were recorded using Libra 200 MC operated at 150 kV. It is worth mentioning that the bright field images of the carbon-based sample cannot be easily distinguishable due to the low contrast between CDs and carbon-coated copper grids. The obtained average diameter was determined by analyzing more than 180 dots from different regions of the grid. The FTIR spectra were measured using a Nicolet 6700 FTIR spectrometer equipped with a smart iTR diamond horizontal attenuated total reflectance (ATR).

The UV–Vis absorption spectra were recorded using a Shimadzu UV-1800 double beam spectrophotometer with a 1 cm path length quartz cuvette. Steady-state emission and excitation spectra were recorded on a Photon Technology International (PTI) spectrofluorometer equipped with a xenon short-arc lamp. All measurements were carried out using Felix X32 PTI software for data collection and analysis at 298 K under ambient oxygen. The confocal microscope measurements were carried out using Leica Microsystems (SP8) in xyλ mode. The detection bandwidth was 10 nm, and the step size was 3 nm. The excitation lasers were 405, 470, 488, and 514 nm.

Fluorescence quantum yields (QY) were measured using the optically dilute method. A stock solution with an absorbance of around 0.5 was prepared, and then four different dilutions were prepared with dilution factors between 2 and 20 to give solutions with absorbances of 0.094, 0.066, 0.052, and 0.019, respectively. The emission spectra were then measured. Individual relative quantum yield values were calculated for each solution and the values reported represent the slope value. We used the equation:

$$\phi_s = \phi_r(\frac{A_r}{A_s})(\frac{l_s}{l_n})(\frac{n_s}{n_r})$$

to calculate the relative quantum yield of each sample[1], where ϕ_r is the absolute quantum yield of the reference, n is the refractive index of the solvent, A is the absorbance at the excitation wavelength, and l is the integrated area under the corrected emission curve. The subscripts s and r refer to the sample and reference, respectively. A solution of quinine sulfate in 0.5 M H_2SO_4 (Φ_r = 54.6%) was used as an external reference.[2]

MTT Protocol

The level of cytotoxicity of the CDP was determined against HeLa cells using MTT (3-(4,5-dimethyl-2-yl)-2,5-diphenyltetrazolium bromide) proliferation assay (Abcam ab211091). A concentration of 10^4 HeLa cells was seeded in 96 well plates containing 100 µl of Dulbecco's Modified Eagle Medium (Thermo Fisher, 11965092), supplemented with 10% (v/v) fetal bovine serum (Sigma F0804) and 100 U/mL penicillin and 0.1 mg/mL streptomycin solution (Sigma P0781-100ML) in each microwell. The cells were kept at 37ºC in a CO_2 incubator with an atmosphere of 5% CO_2 in 95% humidified air and were allowed for 48 hours to reach optimal population densities. Per triplicate, different concentrations (0.1, 0.25, 0.5, 1, 2 mg/ml) of CDP were added into the well of the microplates and incubated in a CO_2 incubator for 4 and 24 hours. After incubation time, the procedure was done following the instructions of the manufacturer. Then, the absorbance was analyzed using a Microplate Reader at 590 nm and the cell viability was calculated using the following equation:

$$\text{Percentage of Cell viability (\%)} = \frac{Treatment}{Control} \times 100$$

Development and characterization of anticounterfeiting fluorescent PDMS. The fabrication of fluorescent PDMS involved mixing PDMS polymer with a silicon-based curing agent (SYLGARD 184 silicone elastomer) in a ratio of 10:1 and followed by the addition of different volumes of carbon dots suspended in tetrahydrofuran (THF). The PDMS film was fabricated by mixing PDMS substrate with CDP. We performed optical and mechanical characterization tests on dog-bone-shaped PDMS samples with varying CPD concentrations (10:0 (I), 10:1(II), 5:1 (III), and 3.3:1 (IV) of PDMS: CDP). We performed mechanical properties testing following the ASTM D412 Type C standard. Using an Instron® universal testing machine, we uniaxially deformed the sample by 30 mm in a displacement-controlled way with a displacement rate of 5 mm/s and recorded the change in the force values using a 5 kN load cell.

Economic Analysis. The main contributors to the cost of our method are the nitric acid solution and the power needed for the hydrothermal process. Up-front capital equipment costs include the oven and reactor, estimated at $50,000. The average price of nitric acid was evaluated at $420/ton during the first quarter of 2022 as per Chemanalyst website (https://www.chemanalyst.com/), or $ 0.58/l. According to our reported data, processing 0.5 g of plastics requires 20 ml of 0.15 g/ml nitric acid solution (2 ml concentrated nitric acid added to 18 ml of DI water). Therefore, it is required to use 4 l of the concentrated nitric acid solution for 1 kg of processed plastic waste, which costs around $ 2.35/ kg. The cost of electricity consumption when using an oven of ~~a~~ power of 2KW for 12 hours is $ 2.88 (assuming the price of 1kw is 12 cents). Thus, the total cost to process 1 kg of plastics using this method is $ 5, which is equivalent to $5000 per ton of plastic. At ~~a~~ large-scale production, the cost of operating an oven of 3000 l capacity and power of 36KW for 12 hours will be $ 4.3 for each 3000 l (1 cycle). To process 1 ton of plastic waste, it is required to utilize 40,000 l of 0.15 g/ml nitric acid solution, which can be performed in 13 cycles bringing the total electricity consumption to $ 57. We can further reduce costs by increasing the weight of the processed plastic waste in the same volume of nitric acid to be 1.5 g of plastic instead of 0.5 g for each 20 ml of the nitric acid solution, which will reduce the cost of nitric acid significantly by more than 50%. Our method produces a minimum of 600 g CDs for each 1 kg processed plastic waste. The average commercial price of carbon dots is estimated to be around $ 300 per 100 mg of quantum dots. Therefore, 1 g of CDs brings a value of more than $ 3000/g. We summarize these costs relative to existing mechanical and recycling methods below.[3]

Property	**Mechanical Recycling**	**Chemical Recycling (Pyrolysis)**	**Chemical Recycling (gasification)**	**Chemical Upcycling (Our method)**
Investment cost for 1 ton/day	USD 2K- 10K	USD 857K	USD 385K	USD 70K
Annual cost to process one ton/day	USD 500- 1500	USD 500 - 1000	USD 18K	USD 3670

Product	Recycled plastics which are inefficient substitutes for virgin plastics.	- 0.68 m^3 of diesel and naphtha -0.22m^3 of industrial wax.	2.5 tons of plastic waste will give energy equivalent to 1 ton of natural gas.	CDs worth $ 1800 per Kg.

References

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