1	Supporting information
2	Efficient Graphene-Wrapped Bi <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> Core-Shell
3	Structures with Enhanced Quantum Efficiency Profit from
4	Ultrafast Electron Transfer Process
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29	Experimental Section

#### 30 Section S1: Synthesis of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> hierarchical microspheres.

During a typical fabrication, bismuth citrate (1.6 g) and urea (0.72 g) are mixed with 75 mL of H<sub>2</sub>O in a 100 mL autoclave Teflon stainless steel vessel and stirred for 30 min. Then, the precursor suspension is hydrothermally treated at 180 °C for 12 h. The obtained solid is filtered, washed with water and ethanol three times, and dried at 60 °C for 24 h under vacuum to obtain rose-like Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> hierarchical microspheres.<sup>1</sup>

#### 36 Section S2: Synthesis of graphene-wrapped Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> microspheres (WBGR).

Graphene oxide (GO) is synthesized from graphite powder according to the modified 37 Hummers method.<sup>2</sup> To wrap GO on the Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> surface, Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (0.4 g) is first 38 dispersed in 200 mL of ethanol with sonication for 30min. Subsequently, 1 mL of 3-39 aminopropyl-trimethoxysilane (APTMS) is added, heated and refluxed for 4 h.<sup>3</sup> 40 APTMS-modified Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> are thoroughly rinsed with ethanol to wash away any 41 remaining APTMS. Subsequently, the APTMS-modified Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (0.4 g) is re-42 dispersed in 100 mL of ethanol and a negatively charged GO suspension (0.2 mg/mL) 43 is added to the positively charged amine-functionalized Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> dispersion in a 44 weight ratio of GO to Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (0.02: 1) with vigorous stirring. After stirring for 30 45 min, the suspension is autoclaved in a Teflon stainless steel vessel at 180 °C for 2 h to 46 reduce GO. After the hydrothermal reduction reaction, the samples are dried at 60 °C 47 for 24 h under vacuum to obtain WBGR. In additional, the graphene-Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (BGR) 48 physical mixture is obtained via by mechanically stirring GO with Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (no 49 amine-functionalized formed) for 1h, with a GO to Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> weight ratio of 0.02: 1; 50

the suspension is autoclaved in a Teflon stainless steel vessel at 180 °C for 2 h to
reduce GO. After the hydrothermal reduction reaction, the samples are dried at 60 °C
for 24 h under vacuum to obtain graphene-Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (BGR).

# 54 Section S3: Photocatalytic degradation of carbamazepine (CBZ) and Radicals 55 control experiment.

First, 0.1g of photocatalyst (Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, BGR, and WBGR) is added into 100 mL of 56 CBZ solution (20 mg/L). A 300W Xe lamp (PerfectLight PLS-SXE300C, USA) is 57 used as light source and equipped with a cutoff filter to provide light ( $\lambda \ge 365$  nm). 58 Before irradiation, the suspension is magnetically stirred in darkness for 30 min to 59 achieve the adsorption-desorption equilibrium for CBZ on the photocatalyst (a 60 preliminary study indicates that 30 min is sufficient to achieve adsorption 61 equilibrium). With the light on, 3 mL of the suspension is collected every 30 min. The 62 solution is centrifuged at 5000 rpm for 5 min and filtered through a 0.45 µm nylon 63 membrane before the CBZ analysis. 64

The radical control experiments are performed by adding different radical scavengers during the photocatalytic CBZ degradation:<sup>4</sup> ammonium oxalates (BQ) for the  $\cdot O_2^$ radicals, Ammonium oxalate (AO) for the holes, AgNO<sub>3</sub> for the electrons and Tertbutyl alcohol (TBA) for the  $\cdot$ OH radicals.

# 69 Section S4: Analysis of Carbamazepine (CBZ).

The HPLC analyses are performed on an Agilent 1200 (Agilent Technologies, USA) 70 HPLC system equipped with a G1329A auto sampler, a G1311A quaternary pump, a 71 G1322A degasser, a G1314B VWD-detector and a G1316A column oven. The UV 72 detection wavelength is 230 nm and the column temperature is set at 30°C. A Gemini-73 NX C18 column (250 mm x 4.6 mm, 5 mm) is used for separation. The mobile phase 74 consists of 60% mixed solution of methanol-acetonitrile (1:1, 0.1% acetic acid) and 75 40% Millipore water (0.1% phosphoric acid). The flow rate is 1.0 mL/min, and the 76 injection volume is 2 mL. The samples are filtered through a 0.45 µm syringe filter 77 (Millipore) before injection and the CBZ is quantified using an external standard 78 method. The linear range is between 0.1 and 1.0 mg/L with a correlation coefficient 79  $(R^2)$  of 0.9992. For CBZ, the limit of detection (LOD) is 0.01 mg/L and the limit of 80 quantitation (LOQ) is 0.1 mg/L 81

# 82 Section S5: EPR spectroscopy and $\cdot O_2^-$ radical Analysis.

The EPR measurements are performed by a Bruker EMX spectrometer operating at 83 the X-band frequency. The samples are contained in quartz glass tube connected to an 84 appropriate high vacuum pumping system at 10<sup>-5</sup> mbar. This setup enables thermal 85 sample activation and light irradiation in situ. A 300 W Xe lamp (Oriel) is used as the 86 light excitation source and the output radiation is focused on the samples in the quartz 87 glass tube using an optical fiber. The light power is measured with bolometer and held 88 at 1.8 mW  $\cdot$  cm<sup>-2</sup> for the energy range 3.39 eV < E < 6.2 eV throughout all experiments. 89 During the UV irradiation, the samples are held at 90 K to eliminate any UV-induced 90

91 heating effects. The spectra are recorded under in vacuum (10<sup>-5</sup> mbar) at 90 k, before
92 and after 30 min of UV irradiation. The g values are determined based on a DPPH
93 standard. The EPR computer simulation is undertaken using the SIM 14S program.<sup>5, 6</sup>

Here, NBT is used to indirectly determine the amount of  $\cdot O_2^-$  radical excited from the as-prepared samples. In a typical test, the NBT solution (5 × 10<sup>-5</sup> mol/L) is placed in a quartz beaker before 20 mg photocatalyst is added. Before irradiation, the suspension is magnetically stirred in darkness for 30 min to reach the adsorption-desorption equilibrium. After 180 min of irradiation, the suspension is centrifuged at 5000 rpm for 5 min. The clear supernatant containing NBT is analyzed by UV-vis spectroscopy using the maximum absorption band (259 nm) (Shimadzu UV-3600).<sup>7, 8</sup>

# 101 Section S6: Electrochemical measurements.

The electrochemical measurements are performed on CHI 660D electrochemical 102 workstation (Shanghai Chenhua, China) in the standard three-electrode system with a 103 platinum foil as counter electrode and a Ag/AgCl in saturated KCl as reference 104 electrode. The working electrode is prepared by dip-coating. Briefly, 20 mg of 105 photocatalyst is suspended in 5 mL of ethanol to produce slurry. Then the as-prepared 106 slurry is dip-coated onto a 3 cm  $\times$  1.5 cm fluorine-tin oxide (FTO) glass. After the 107 films are dried under ambient conditions, they are thermal treated at 180 °C for 1h. All 108 the as-prepared electrodes show a similar thickness (0.9-1µm). The flatband potentials 109 (V<sub>fb</sub>) are determined from Mott-Schottky (MS) plots by electrochemical method.<sup>9</sup> The 110

111 MS measurements are performed at a fixed frequency of 100 Hz with 10 mV 112 amplitude, at various applied potentials.

#### 113 Results and Discussion Section.

# 114 Section S7 XRD Analysis.

115 The structure and compositions of the as-prepared samples are characterized using 116 powder X-ray diffraction (XRD). Fig S1 displays the XRD spectra for  $Bi_2O_2CO_3$ , 117 BGR, and WBGR. All of the diffraction peaks for  $Bi_2O_2CO_3$ , BGR, and WBGR are 118 similar and can be indexed to the tetragonal  $Bi_2O_2CO_3$  phase (JCPDS No. 41-1488).<sup>1</sup> 119 Additionally, no obvious diffraction peaks for GR are observed, suggesting that the 120 GR peaks are overlapped with tetragonal  $Bi_2O_2CO_3$  phase due to the lower amount 121 encapsulation.



122 Figure S1. The X-ray diffraction patterns (XRD) on Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, BGR and WBGR.

# 123 Section S8: Raman Analysis.

To clarify the composition of WBGR, Raman analysis is performed. Fig S2 displays 124 the Raman spectra for Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, GO-wrapped Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (WBGO) and WBGR. The 125 Raman peaks at 162, 305, 512, 610 cm<sup>-1</sup> originate from the tetragonal Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> 126 phase.<sup>10</sup> The two typical peaks at 1344 and 1586 cm<sup>-1</sup> are assigned to the D line (for 127 the disordered sp<sup>2</sup> carbon) and the G line (for the ordered graphitic structure), 128 respectively.<sup>11</sup> Notably, The hydrothermal reduction treatment increases the D/G ratio 129 from 0.6 in WBGO to 0.95 in WBGR, suggesting that GO has been well 130 deoxygenated and reduced to GR; therefore, a new smaller sp<sup>2</sup> domains form.<sup>3</sup> 131



**133** Figure S2. The Raman spectra on  $Bi_2O_2CO_3$ , WBGO and WBGR.

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#### 135 Section S9: The Brunauer-Emmett-Teller (BET) analysis.

Fig S3 reveals the nitrogen adsorption-desorption isotherms and the corresponding 136 pore size distribution for the as-prepared samples. The mesopores attributed to the 137 hierarchical structures are of size form 2-50 nm (Fig S3 inset). The BET surface areas 138 of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, BGR and WBGR are 36.3957, 46.1827, and 54. 2813 m<sup>2</sup>·g<sup>-1</sup>, 139 respectively. Apparently, the highest specific surface area of WBGR suggests that GR 140 encapsulation may effectively prevents the aggregation of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> microspheres. 141 Increasing the S<sub>BET</sub> can enhance the adsorption capacity toward pollutants and 142 therefore improve the photocatalytic activity. 143



145 Figure S3. Nitrogen adsorption-desorption isotherms on Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, BGR and
146 WBGR. The inset show the corresponded pore-size distribution curves.

# 148 Section S10: Optical Characterization.



150 Figure S4. The UV-vis DRS of  $Bi_2O_2CO_3$ , BGR and WBGR. The inset shows the

151 band-gap energy of the photocatalysts.

160 Section S11: The Mott-Schottky (MS) plots of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and WBGR electrodes.





# 170 Section S12: Stability.

Figure S6 displays the time profile of eight repeated photocatalytic CBZ degradation
experiments using WBGR under the same experimental conditions. The results
clearly show good reproducibility; a degradation rate of 88.1 % is retained even after
repeating the experiment eight times.





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