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Electronic Supplementary Information

A Facile and Green Self-Assembly Preparation of Gold Nanoparticles/ZnO Nanocomposite for Photocatalytic And Photoelectrochemical Applications

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Synthesis of DTDTPA linker

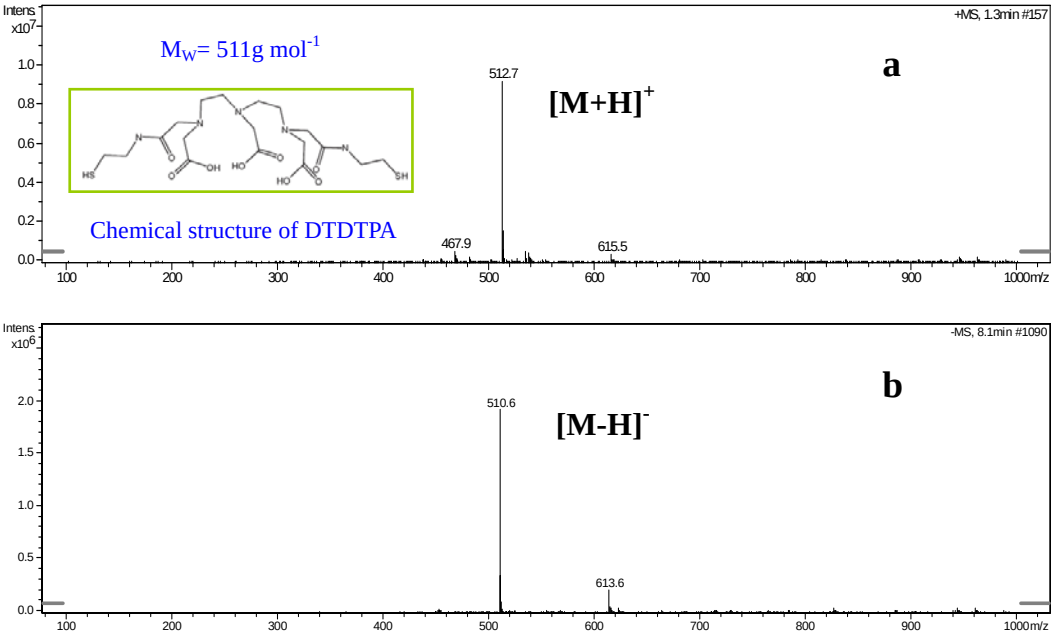

Figure. S1 Electrospray ionization mass spectrometry (EIS-MS) analysis of synthesized DTDTPA (a) *m/z* 512.7 $[M+H]^+$; (b) *m/z* 510.6 $[M-H]^-$; the inset of (a) shows the chemical structure of DTDTPA and molecular weight (theoretical M_W: 511 g mol^{-1}).

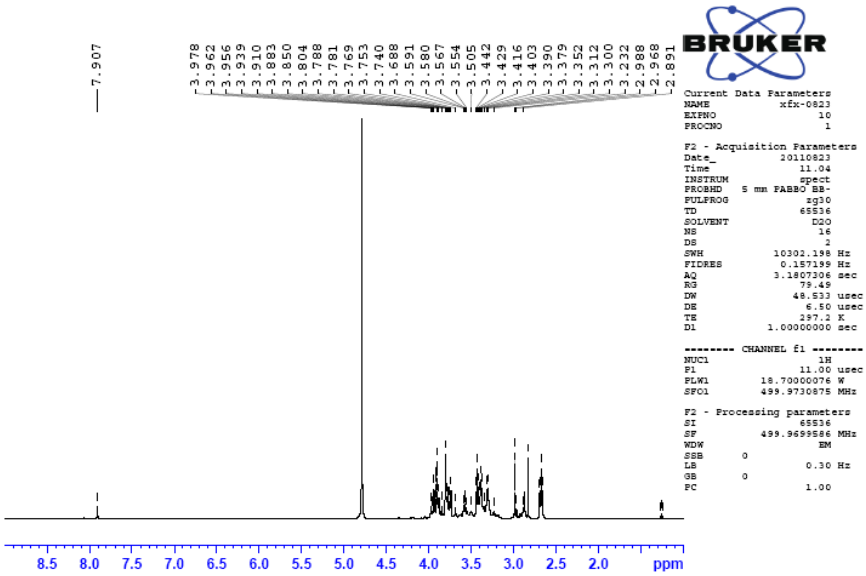

Figure. S2 (a) ^{1}HNMR spectrum of DTDTPA.

^{1}HNMR (500MHz, D_2O, 298K): δ_H 3.80 (s, 4H, -N-CH_2-CO-N-), 3.69 (s, 4H, -N-CH_2-COOH), 3.59 (s, 2H, -N-CH_2-COOH), 3.38-3.20 (m, 12H, -N-CH_2-CH_2-SH, -N-CH_2-CH_2-N), 2.59 ppm (t, 4H, N-CH_2-CH_2-SH).

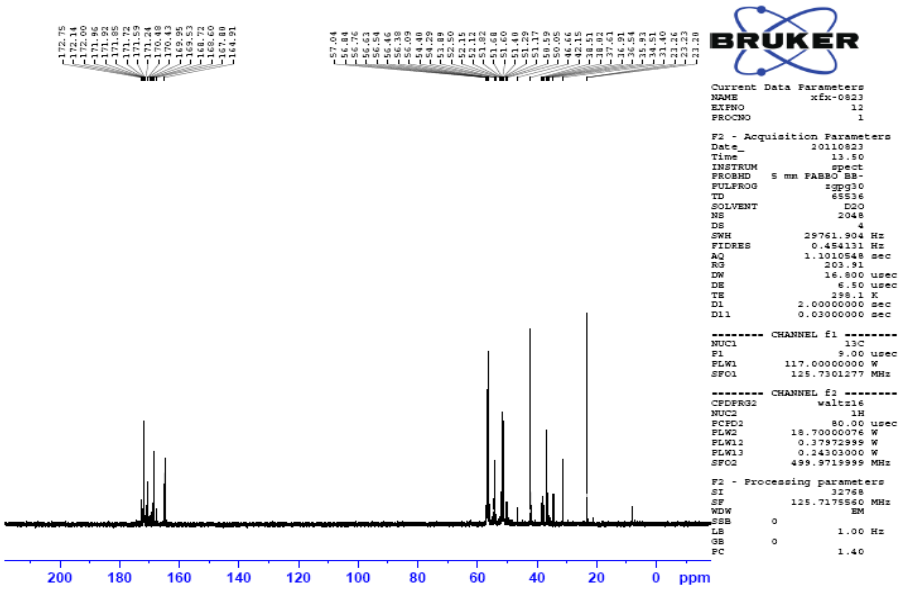

Figure. S2 (b) ^{13}CNMR spectrum of DTDTPA.

^{13}CNMR (75MHz, D_2O, 298K); δ_C 172.75 and 172.14 (-N-CH_2-COOH), 168.72 (-N-CH_2-CO-N), 57.04 and 56.84 (-N-CH_2-COOH), 54.40 (-N-CH_2-CO-N), 52.15 and 51.60 (-N-CH_2-CH_2-N-), 42.15 (-N-CH_2-CH_2-SH), 23.26 ppm (-N-CH_2-CH_2-SH).

Synthesis of GNP@DTDTPA nanoparticle

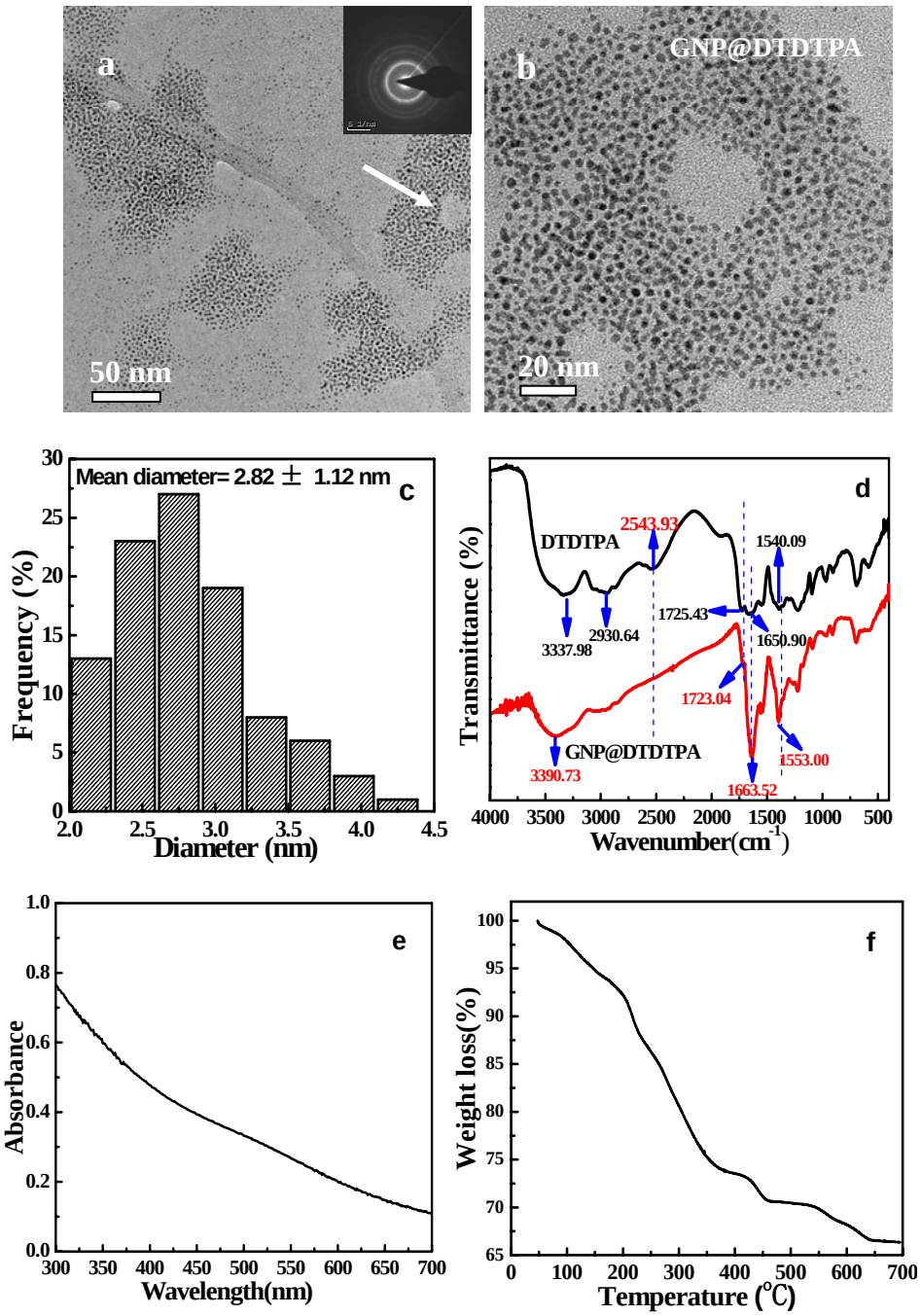

Figure S3 (a-b) TEM images of GNP@DTDTPA, the inset of (a) illustrates the SAED pattern of GNP@DTDTPA. (c) Mean diameter histogram of GNP@DTDTPA. (d) FTIR spectrum comparison of DTDTPA and GNP@DTDTPA. IR: 2930.64 cm^{-1}(ν CH-alkyl), 2543.93 cm^{-1} (ν -SH), 1725.43 cm^{-1} (ν C=O, COOH), 1650.90 cm^{-1} (ν C=O, RCONR'R''), 1540.09 cm^{-1} (ν C=O, RCONHR') for DTDTPA, (e) UV-vis absorption spectrum and (f) TG result of GNP@DTDTPA.

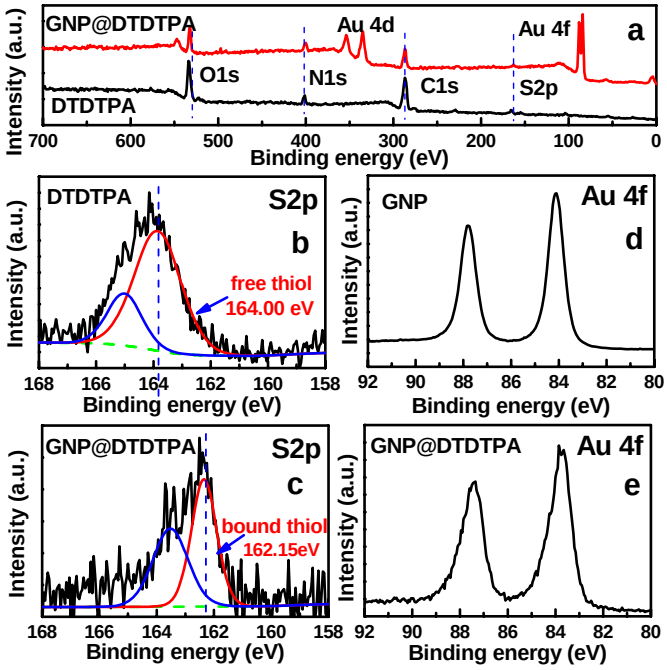

Figure S4 (a) Survey XPS spectra of DTDTPA and GNP@DTDTPA with the corresponding high-resolution spectra of (b, c) S 2p and (e, f) Au 4f.

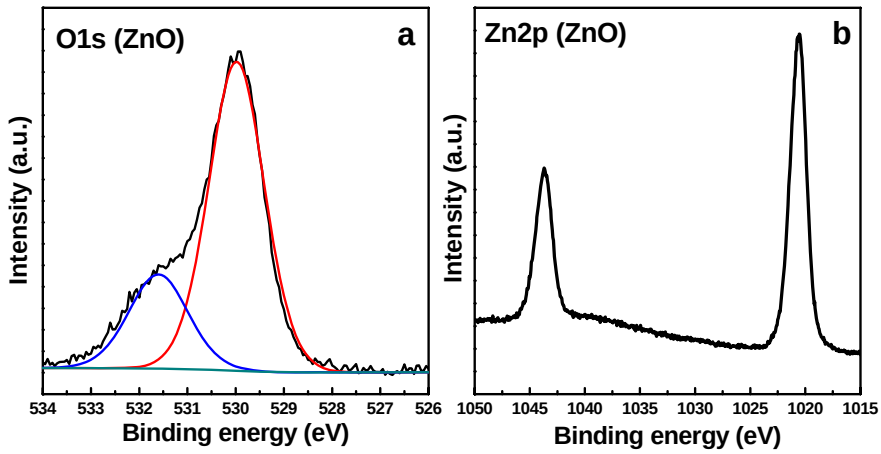

Figure S5 High-resolution XPS spectra of (a) O 1s and (b) Zn 2p of ZnO, respectively.

Table S1 Collection of carbon-relating chemical bond species versus BE in GNP@DTDTPA and GNP@DTDTPA/ZnO. (unit: eV)

Element	GNP@DTDTPA	**Chemical bond**	GNP@ DTDTPA /ZnO	**Chemical bond**
C 1s A	284.60	C-C/C-H	284.60	C-C/C-H
C 1s B	285.62	C-N[1]	285.66	C-N
C 1s C	286.30	C-OH	288.60	OH-C=O
C 1s D	287.27	NH-C=O	------	-------

Table S2 Collection of oxygen-relating chemical bond species versus BE in GNP@DTDTPA and GNP@DTDTPA/ZnO, and ZnO. (unit: eV)

Element	**GNP@DTDTPA**	**Chemical bond**	**GNP@ DTDTPA /ZnO**	**Chemical bond**	**ZnO**	**Chemical bond**
O 1s A	531.68	Carbonyl(C=O)	529.73	Lattice Oxygen [1,2]	529.98	Lattice Oxygen
O 1s B	533.43	Hydroxyl(C-OH)	531.16	Zn-OH/Carbonyl(C=O)	531.60	Zn-OH
O 1s C	-----	-----	532.19	C-O moieties [3]	-----	-----

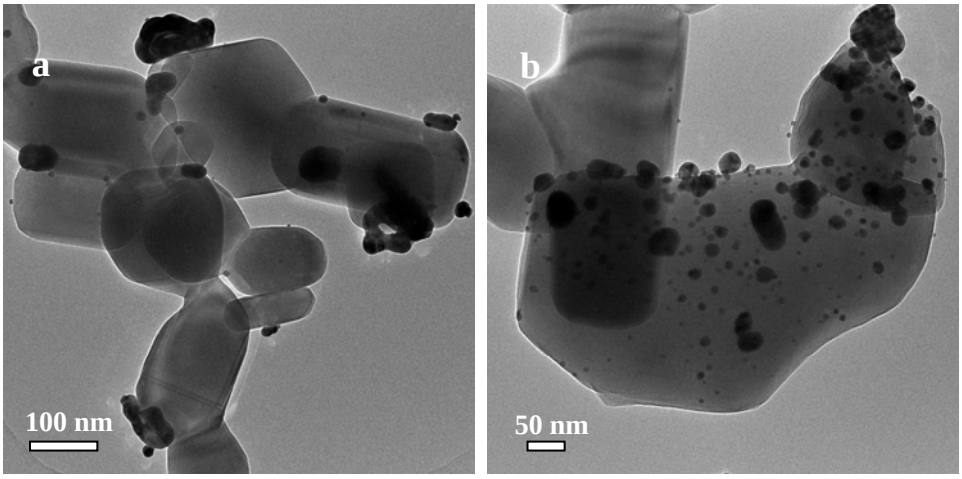

Figure S6 (a-b) TEM images of bare GNP functionalized ZnO (B-GNP/ZnO) nanocomposite

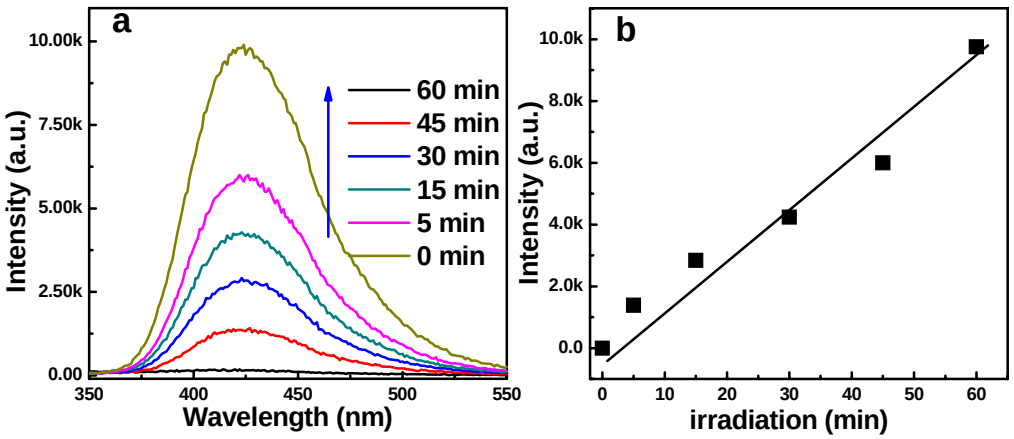

Figure S7 (a) PL spectra of •OH-trapping for GNP/ZnO nanocomposite under the irradiation of UV light (365 ± 15 nm), (b) The integrated fluorescence intensity versus irradiation time.

For liquid PL measurement, the formation of hydroxyl radicals (•OH) on the surface of photoilluminated samples/water interface was detected by the photoluminescence (PL) technique with terephthalic acid (TA) as a probing molecule. The detailed experimental procedure was similar to that of the photocatalytic activity test except MO was replaced by 5×10^{-3} M terephthalic acid in the solution of 0.01 M NaOH. After UV irradiation for regular interval, the PL intensity of 426 nm was recorded.

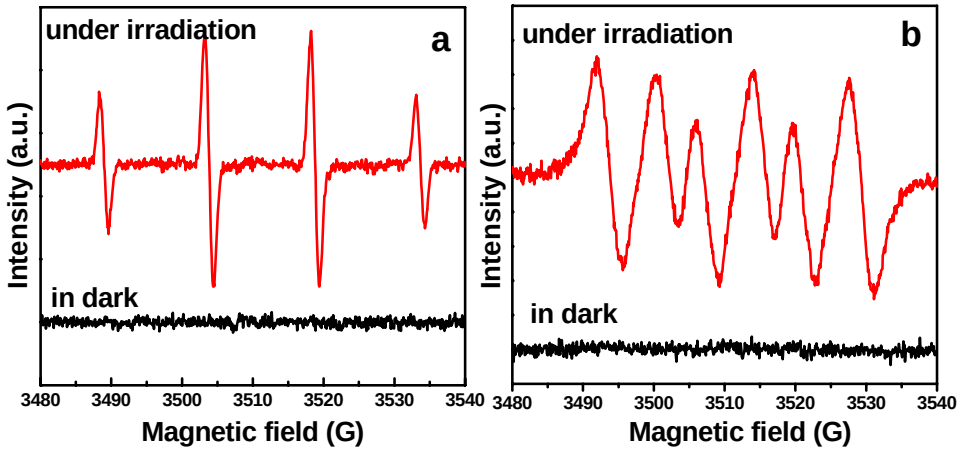

Figure S8 ESR spectra of radical adducts trapped by DMPO in GNP/ZnO dispersion. (a) DMPO-•OH formed in irradiated aqueous solution; (b) DMPO-O_2^-• formed in irradiated methanol dispersion.

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Reference

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