Supporting Information

Electrocatalytic Activity of Polyaniline in Magnesium-Sulfur Batteries

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Experimental Methods

Preparation of polyaniline-coated carbon cloth: Commercially available carbon cloth was first chemically treated in a mixture of sulfuric acid and nitric acid (1:3 molar ratio). The acid-treated carbon cloth was then stirred in 20 mL diluted aqueous solution of sulfuric acid. Later, 2 ml of aniline was added to the acidic solution and stirred continuously. The resulting solution was cooled down to 5 ^{o}C. An aqueous solution of ammonium persulfate (APS) was then added to the solution dropwise and the resulting solution was stirred on an ice bath to initiate the polymerization process. The stirring was continued for overnight to complete the polymerization reaction. The resulting polyaniline-coated carbon cloth was dried overnight at 60 ^{o}C in a vacuum oven.

Synthesis of magnesium-polysulfide catholyte: 0.1 M magnesium-polysulfide (MgS_x) catholyte was synthesized by dissolving stoichiometric amount of elemental sulfur (Sigma-Aldrich) and magnesium sulfide (MgS, Sigma-Aldrich) in an electrolyte comprised of 1.55 g magnesium bis(hexamethyldisilazide) (Sigma-Aldrich), 1.2 g aluminium chloride ($AlCl_3$, Sigma-Aldrich, 99%) and 0.4 g magnesium chloride ($MgCl_2$, Sigma-Aldrich, 98%) in 5 ml tetraethylene glycol dimethyl ether (TEGDME, Sigma-Aldrich). A dark-brown colored solution was obtained after vigorous stirring the above solution at 60 ^{o}C for 24 h.

Materials characterization: Microstructure and morphology of the samples were investigated using field-emission gun scanning electron microscope (FEG-SEM; JEOL-7600F) and field-emission gun transmission electron microscope (FEG-TEM, JEOL-2100F). Raman spectra were collected on HR800-UV confocal micro-Raman spectrometer. UV-Visible spectroscopy data was recorded on JASCO V-530 spectrometer. X-ray photoelectron spectra were recorded on X-ray photoelectron spectrometer (AXIS Supra, Kratos Analytical, and monochromatic Al Kα 600 W X-ray source).

Cell assembly and electrochemical characterization: Swagelok-type cells were fabricated using Mg disc as an anode and MgS_x catholyte infiltrated polyaniline-coated carbon cloth (abbreviated as CC@PANI@MgS_x) as a cathode. Borosilicate glass microfiber filters (GF/D Whatman®) was placed as a separator between anode and cathode. To compare the electrochemical performance, MgS_x catholyte infiltrated pristine carbon cloth (abbreviated as CC@MgS_x) has been used as a control cathode. The average areal mass loading of sulfur in both the cathodes was estimated to be 1 mg cm^{-2}. Cyclic voltammetry experiments were carried out using Biologic VMP-3 instrument. Galvanostatic charge/discharge tests were performed on an Arbin instrument (BT2000 model). All electrochemical experiments were at the temperature of 20 (±2) ^{o}C. Specific capacities were calculated based on areal loading of sulfur.

Electron spin resonance spectroscopy experiments: Electron spin resonance (ESR) spectra of the individual sample of polyaniline powder, MgS_x catholyte and their mixture were recorded on an ESR spectrometer (JEOL, JES-FA200) with X-band operating at a microwave frequency of 9.447 GHz. The samples were loaded into a quartz tube, inside an argon-filled glove box. In acquire each ESR spectrum, the magnetic field was swept repeatedly for 20 sweeps. All the ESR spectra were recorded at room-temperature.

Sample preparation for post-cycling XPS characterization: To investigate the nature of end-discharge products, XPS spectra were recorded on both CC@MgS_x and CC@PANI@MgS_x electrodes after they were completely discharged to 0.5 V (vs Mg^{2+}/Mg). To avoid the contact with air, the samples were transferred to XPS instrument from argon-filled glove box using an air-sealed container. Each of the as-collected XPS spectra was deconvoluted and fitted using the XPS software.

Lifetime measurements using fluorescence spectroscopy: A time-resolved confocal fluorescence microscopy (MicroTime 200, PicoQuant, Germany) equipped with an inverted microscope (Olympus IX71) with a water-immersion objective (UPlansApo NA 1.2, 60×, WD = 0.28 mm) was used for fluorescence lifetime measurements and imaging (FLIM), utilizing the time-tagged time-resolved (TTTR) methodology. Individual polyaniline, MgS_x polysulfide and their composite were excited at an excitation wavelength (λ_{ex}) of 405 nm using a pulsed diode laser source (PDL 828 S Sepia II, PicoQuant) with a full width at half maximum of 176 ps and 40 MHz repetition rate. Fluorescence spectra were collected from the samples using the AME objective and has been filtered through a 425 nm long-pass filter (425LP AHF/Chroma, Germany). Each characteristic fluorescence signal is then focused onto a 50 μm pinhole and directed into a single-photon avalanche photodiode (SPAD). To acquire fluorescence images from the region of interest, raster-scanning with an x–y piezo-driven device was used. Samples were scanned at a resolution of 256 × 256 pixels with a dwell time of 0.7 ms per pixel. Samples for fluorescence characterization were prepared inside glovebox by drop casting polyaniline and catholyte solutions onto the glass coverslips.

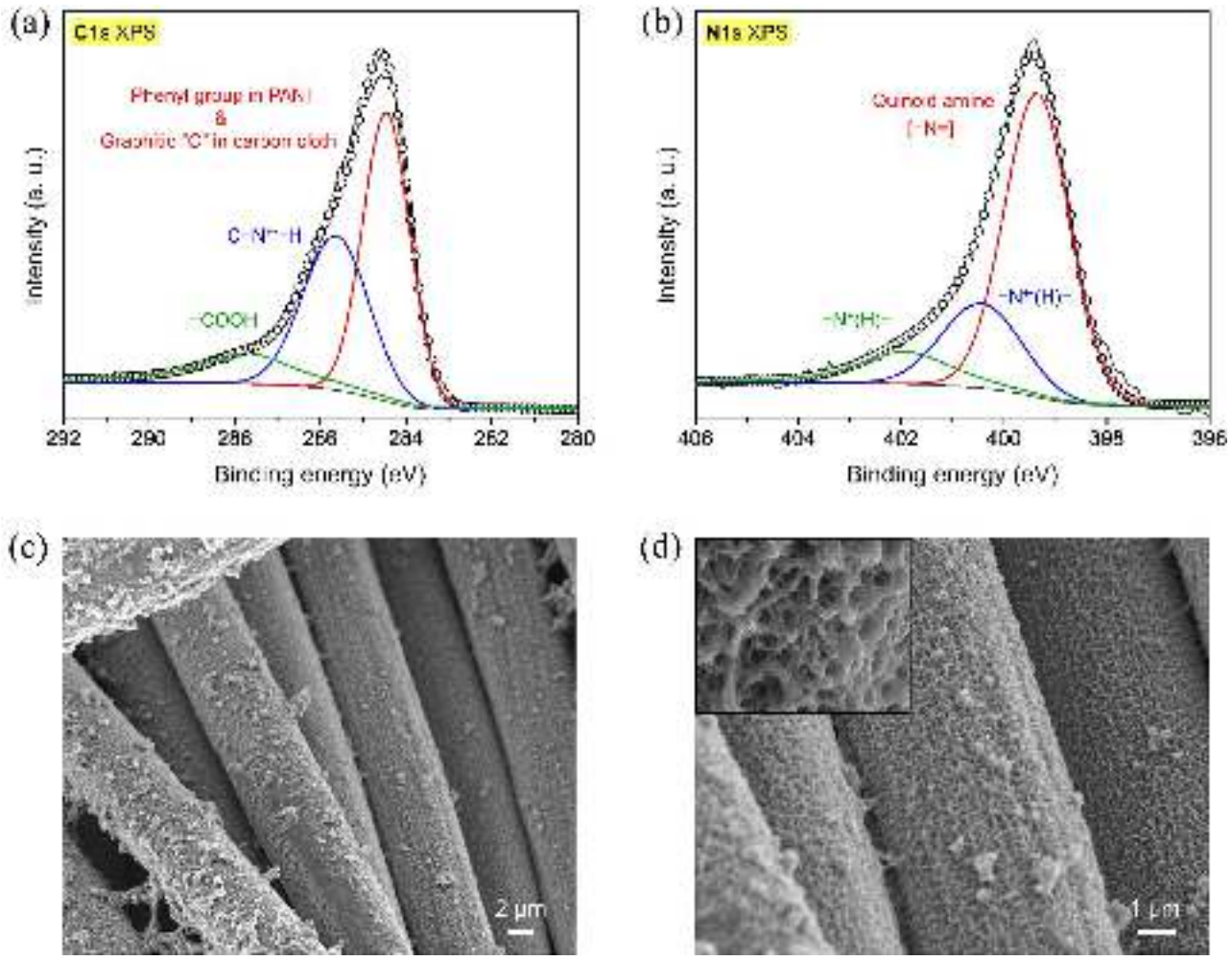

Figure S1: (a, b) Deconvoluted XPS of C(1s) and N(1s) XPS spectra of CC@PANI and (c, d) low- and high-resolution SEM images of CC@PANI current collector.

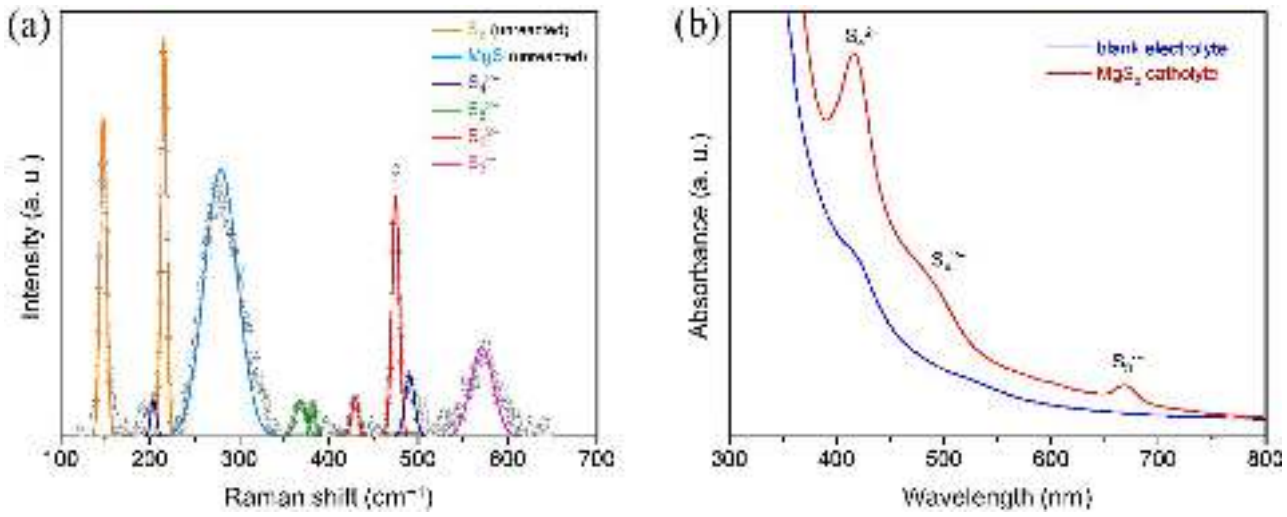

Figure S2: (a) Deconvoluted Raman spectrum of MgS_x catholyte, (b) UV-Visible spectra of blank electrolyte and MgS_x catholyte.

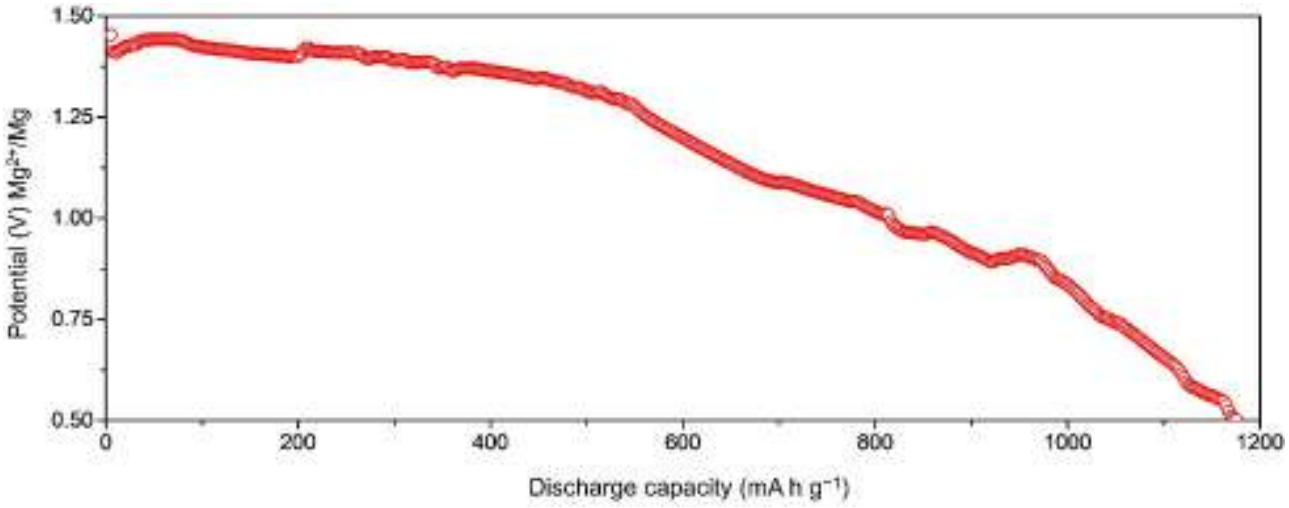

Figure S3: Enlarged discharge profile of CC@PANI@MgS_x cathode at the scan rate of 20 mA g^{-1}.

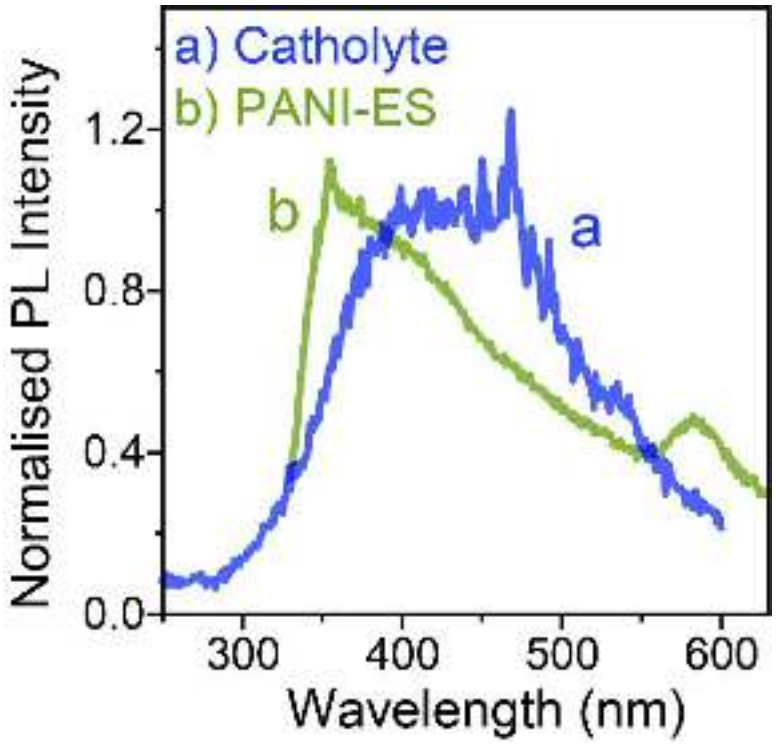

Figure S4: Photoluminescence spectra of polyaniline and MgS_x.

Table S1. Fitting parameters of photoluminescence transients obtained from FLIM measurements.

	τ_1	a_1	τ_2	a_2	τ_3	a_3
PANI	0.59	0.50	2.04	0.37	5.2	0.12
Catholyte	-	-	1.3	0.97	3.08	0.03
PANI + Catholyte	0.78	0.64	1.33	0.22	6.1	0.15

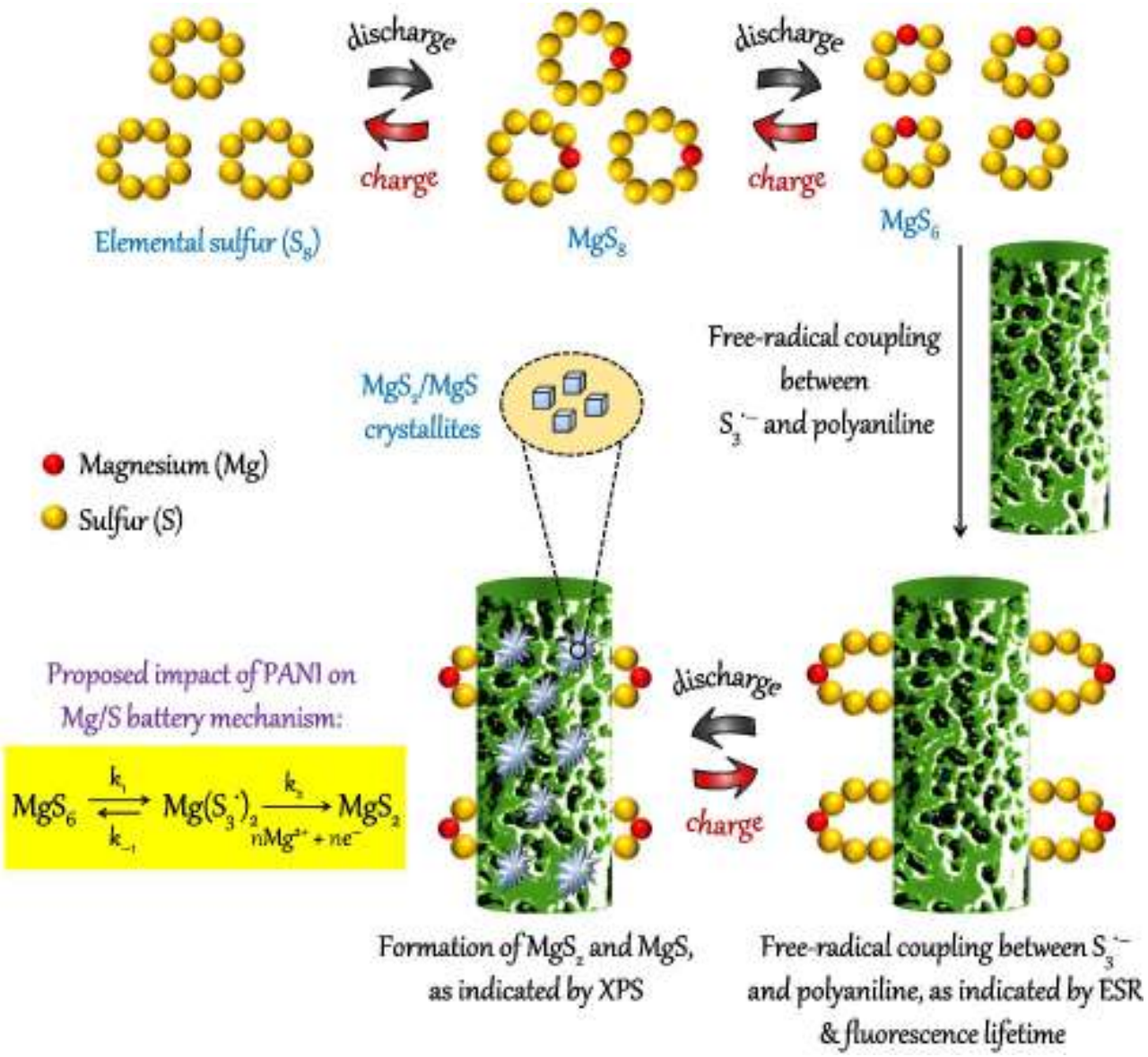

Figure S5: Proposed reaction mechanism illustrating the catalytic effect of polyaniline in the Mg/S batteries.