





Figure S1. Calibration curve for the determination of manganese dioxide in the samples. The absorbance maximum at 525 nm is plotted against the concentration of MnO₄⁻ in aqueous solution.

 MnO_{4^-} has a characteristic absorbance maximum at 525 nm, which can be used to qualitatively determine the mass loading of MnO_2 using UV–vis spectrophotometry [32]. The process was as follows: first the sample with electrodeposited MnO_2 is immersed into 10 mL of concentrated nitric acid to dissolve the oxide; then, the manganese ions are oxidized to MnO_{4^-} using a definite amount of K₂S₂O₈ and AgNO₃; the concentration of MnO_{4^-} ions is determined by UV–vis spectrophotometry (using Figure S1 as the calibration curve); finally, the loading mass of MnO_2 is calculated based on the concentration of MnO_{4^-} and the volume of the solution.



Figure S2. Energy dispersive x-ray spectrum of a MnO₂/GNWs composite sample after galvanostatic electrodeposition of MnO₂.



Figure S3. XPS spectra of galvanostatically electrodeposited MnO2 without thermal treatment [33].

XPS was used to evaluate the elemental composition and oxidation state of manganese. Figure S3a shows Mn 2p spectra of galvanostatically electrodeposited MnO₂ without thermal treatment. The Mn 2p spectrum exhibits three peaks; Mn 2p_{3/2} was positioned at (641.85 ± 0.1) eV, Mn 2p_{1/2} at (653.5 ± 0.1) eV [1], and a shoulder appears at around 644.5 eV. The binding energy difference between the Mn 2p_{3/2} and Mn 2p_{1/2} peaks is about 11.7 eV which is very much like the reported values in other studies [2]. These results indicate that manganese is in the Mn⁴⁺ oxidation state [3].

Deconvolution of the O1s spectra in 4 peaks (see Figure S3b) reveals the chemical environment of oxygen. The peak located at (529.30 ± 0.1) eV can be ascribed to (Mn-O-Mn). Peaks around (530.9 ± 0.1) eV, (532.7 ± 0.2) eV, and (535.10 ± 0.2) eV could be attributed to (Mn-O-H), (H-O-H), and chemisorbed oxygen, respectively [4,5]. The position and percentage area of the deconvoluted O1s peaks were 529.44 eV/33.79%, 530.88 eV/24.36%, 532.39 eV/13.89%, 535.26 eV/27.96%, which correspond to Mn-O-Mn, Mn-O-OH, H-O-H and chemisorbed oxygen, respectively.

References

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