

Supporting Information for
Inflating Strategy to Form Ultrathin Hollow MnO₂ Nanoballoons

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EXPERIMENTAL

Materials

Graphite flakes (99.9995 %) with a lateral dimension of 2–14 μm were purchased from Alfa Aesar (USA). MB was purchased from Aladdin (Shanghai, China). KMnO₄, H₂O₂ (30 %), concentrated H₂SO₄ (98 %) and TBA were purchased from Sinopharm Chemical Reagent Co., Ltd. BQ was purchased from Adamas Reagent Co., Ltd. They were all analytical grade reagents and used without further purification. Pure water with a resistivity of 18.2 MΩ·cm at 25 °C was used in all experiments.

Synthesis of GO nanosheets

GO nanosheets were fabricated by the method described previously¹ with some modifications. Briefly, 15.0 mL of concentrated H₂SO₄ was added into the milled

graphite powder (0.5 g), reacting at 0 °C for 12 h in ice water bath under continuous stirring. Keeping the temperature below 20 °C, 1.3 g of KMnO₄ was slowly added into the above mixture, and stirred at 40 °C for 40 min. Then, another 1.2 g of KMnO₄ was added into the mixture followed by stirring at 80 °C for 60 min. After that, 50.0 mL of pure water was slowly added followed by adding 50.0 mL of H₂O₂ (30 %). The resulting bright yellow suspension was washed until the pH of supernatant was neutral. Finally, ultrasonication (KQ-600KDE, 40 kHz, 300 W, 4 h) was applied to further exfoliate GO nanosheets.

Catalysis performance of UMHNBs

The catalysis performance of UMHNBs was evaluated by degrading MB. The adsorption/desorption and catalytic process were done in the dark to avoid the possible influence of light. Firstly, the mixture of MB (1.0 mL, 400.0 mg/L) and UMHNBs (25.0 mL, 2.0 mg/L) was continuously stirred for 30 min at 50 °C in water bath to achieve an adsorption/desorption equilibrium. Then, 5.0 mL of H₂O₂ (30 %) was added to start the catalysis reaction. After given times, 1.0 mL of mixtures was taken out and quickly diluted to 5.0 mL. The visible spectra of the diluted mixtures are used to measure concentration of MB. MB (1.0 mL, 400.0 mg/L) with 30 mL of H₂O (without UMHNBs or H₂O₂) was used as blank solution, and its concentration was used as C₀. The absorbance of different concentrations of MB solutions at 664 nm was measured to plot a working curve. The concentrations of MB solutions (C_i) during the degradation process were determined on the basis of the working curve. According to Lambert-Beer's law, the degradation efficiency (r) was calculated by:

$$r = (C_0 - C_t)/C_0 = (A_0 - A_t)/A_0,$$

where A_0 and A_t represent the absorbance of MB solutions at the time 0 and t , respectively.

Characterization

Absorption spectra of GO dispersions, UMHNBs suspensions and MB solutions in quartz cells were measured with a double-beam ultraviolet-visible (UV-vis) spectrophotometer (UV-2550, Shimadzu Co., Japan). Fourier transform infrared (FTIR) spectra of GO and UMHNBs were recorded with a Vertex-70 FTIR spectrometer (Bruker, Germany), where they were mixed with KBr and pressed into a thin platelet. Raman spectra were obtained using a LabRAM HR 800 system (Horiba JY, France) excited with a 473 nm laser. Field emission scanning electron microscopy (SEM) measurements and elemental mappings were carried out on a SU8010 (Hitachi, Japan) instrument at an accelerating voltage of 5 kV. The samples for SEM were prepared by dropping 5 μ L of UMHNBs suspensions (2.0 mg/L) on silicon wafers, and immediately frozen by liquid nitrogen, followed by freeze-drying to maintain original hollow morphology. Transmission electron microscopy (TEM) images of UMHNBs were obtained with a JEM-1011 (Jeol, Japan) under an accelerating voltage of 100 kV. High resolution TEM (HRTEM) images and SAED were obtained on a JEOL-2100F TEM (Jeol, Japan) with an acceleration voltage of 200 kV. Both the instantly frozen dried and air dried UMHNBs were also observed by atomic force microscopy (AFM) (Nanoscope IIIA, Digital Instruments, USA) in tapping mode. The TEM samples (on copper grid) and AFM samples (on silicon wafers) were prepared similar to that of SEM. X-ray

photoelectron spectroscopy (XPS) was carried out on a Phi 5300 ESCA (Perkin Elmer, USA) with the Mg ($K\alpha$) irradiation (X-ray energy, 1253.6 eV). The analysis spot area was $1.0 \times 3.5 \text{ mm}^2$. Powder X-ray diffraction (XRD) measurement of UMHNBs was performed using a D8 Advance X-ray diffractometer (Bruker, Germany) operating at 40 mA and 40 kV with the Cu ($K\alpha$) radiation ($\lambda = 1.54184 \text{ \AA}$). Nitrogen (N_2) adsorption-desorption isotherms were recorded with an ASAP 2020 HD88 instrument (Micromeritics, USA). The pore size distribution of UMHNBs was obtained by calculating the adsorption branch with the Barrett-Joyner-Halenda (BJH) method.

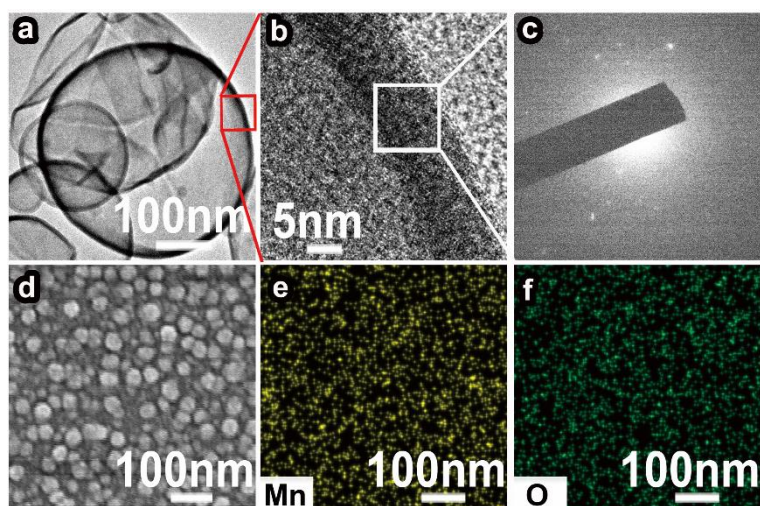


Figure S1. TEM and b) HRTEM images of UMHNB(s), c) SAED pattern for the framed area in b), d-f) SEM image of UMHNBs and corresponding elemental mappings.

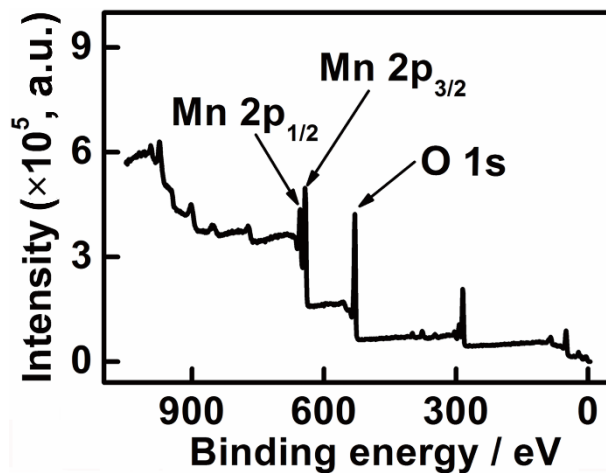


Figure S2. The XPS spectrum of UMHNBs.

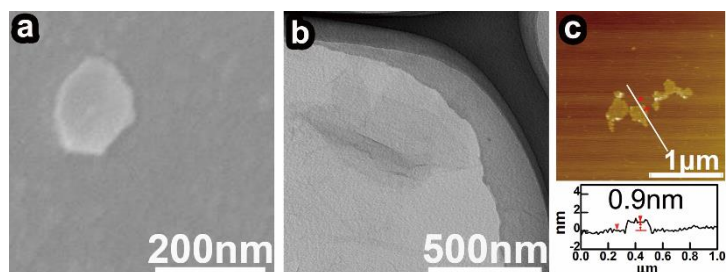


Figure S3. Morphology and thickness of GO. a) SEM image, b) TEM image and c) AFM height image and section analysis of GO nanosheets.

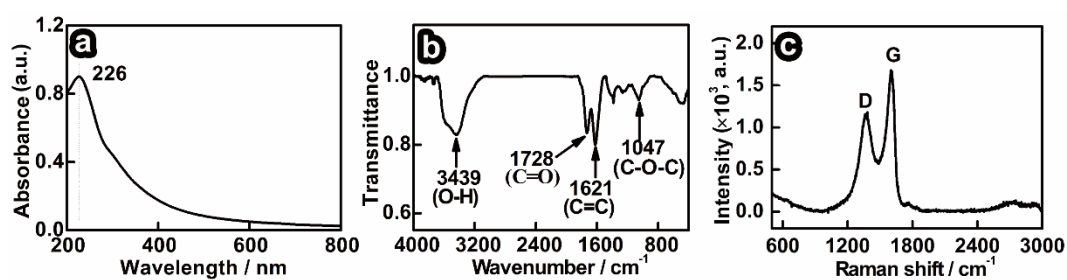


Figure S4. The spectroscopic characteristics of GO. a) UV-vis absorption, b) FTIR and c) Raman spectra of GO nanosheets.

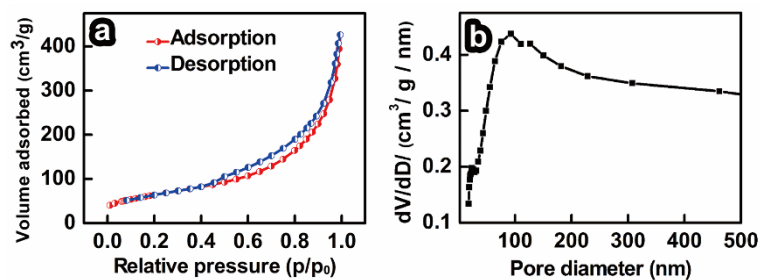


Figure S5. a) N₂ adsorption/desorption isotherms and b) the corresponding pore size distribution of UMHNBs calculated using the BJH method.

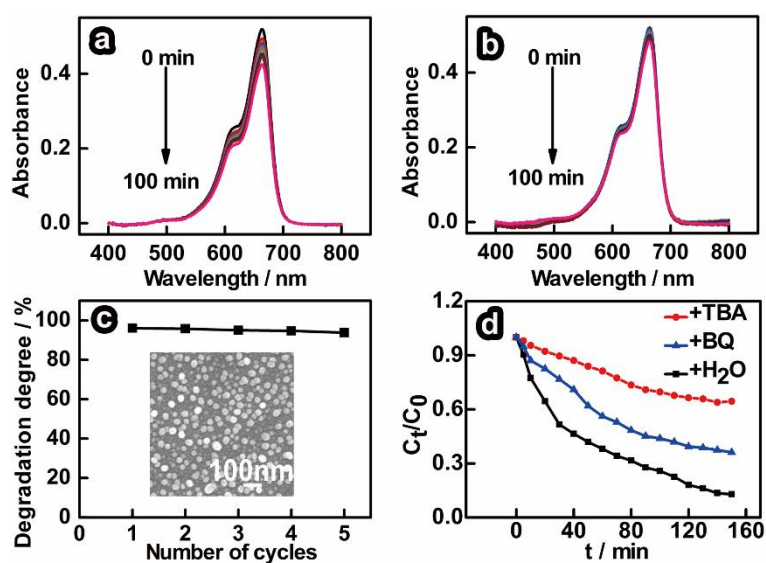


Figure S6. The contrast experiments and cycling stability of the degradation of MB with the original concentration of 400 mg/L. The visible absorbance spectra of a) MB + H₂O₂ + H₂O and b) MB + UMHNBs + H₂O; c) degradation of MB with the recycled UMHNBs, the inset is the SEM image of UMHNBs after the 5th catalytic cycle, d) degradation of MB over time in the presence of TBA, BQ and H₂O.

REFERENCES

1. Xin, J.; Zhang, R.; Hou, W. Aggregation Inhibition for Graphene Oxide Nanosheets in Polyelectrolyte Solutions and Assembly of Nanocapsules with Graphene Oxide Nanosheets as Template.

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