

Manganese: Element 25

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Chemistry of the Elements

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Origins and history of manganese

- **Manganese** is an element with the symbol **Mn** in the periodic table
- It was first isolated in pure form and recognized as an element by Swedish chemist **Johan Gottlieb Gahn** in the year **1774**.
- Even though Gahn is credited with the discovery of manganese, many other chemists had already been working and conducting experiments with it beforehand^{1,2}



Johan Gottlieb Gahn³

Origins and history of manganese

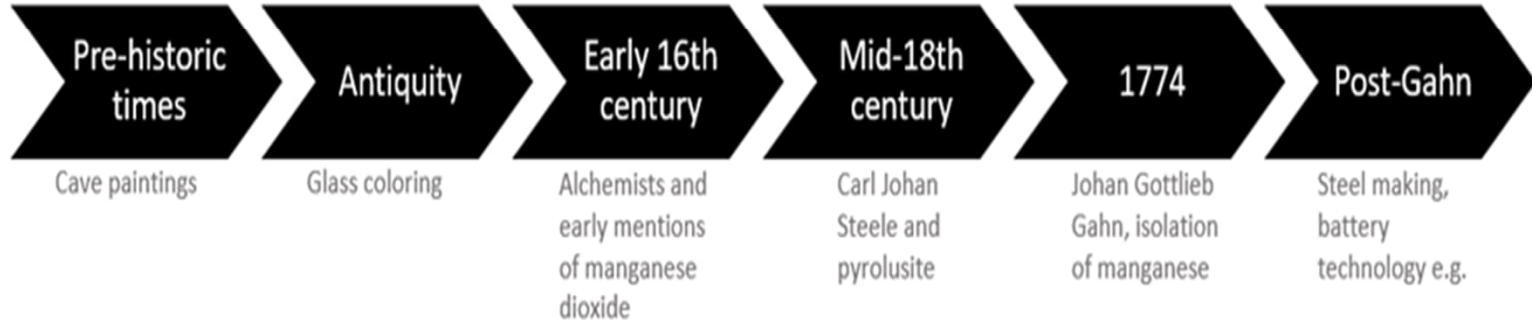
- It was actually a fellow Swedish mineralogist **Carl Wilhelm Steele** who was the first to recognize manganese as an element before Gahn in the same year **1774**.
- Steele was conducting experiments with the mineral **pyrolusite** (manganese dioxide)
- Later it was Gahn who managed to isolate manganese from pyrolusite by heating it in the presence of charcoal.
- Before the Swedes, manganese had already been studied in **1740** by **Johann Heinrich Pott**, who managed to confirm that manganese did not contain iron as had been assumed.^{1,2}



Pyrolusite⁴

Origins and history of manganese

Manganese throughout history



Origins and history of manganese

- The name "manganese" comes from the Latin word "magnes," which means "magnet"
- This is a little misleading since manganese itself is not magnetic.
- The term might have been applied because the mineral pyrolusite resembles magnate, a magnetic mineral.^{1,2}



Manganese⁵

Abundance and occurrence

- Manganese is a common element in the earth's crust
- → about **0,1 % of the crust by weight**
- → from the transition metals **only Iron** is more abundant than manganese.^{1,2}

- It is commonly found in the form of ores such as pyrolusite MnO_2 and romanechite.^{1,2}



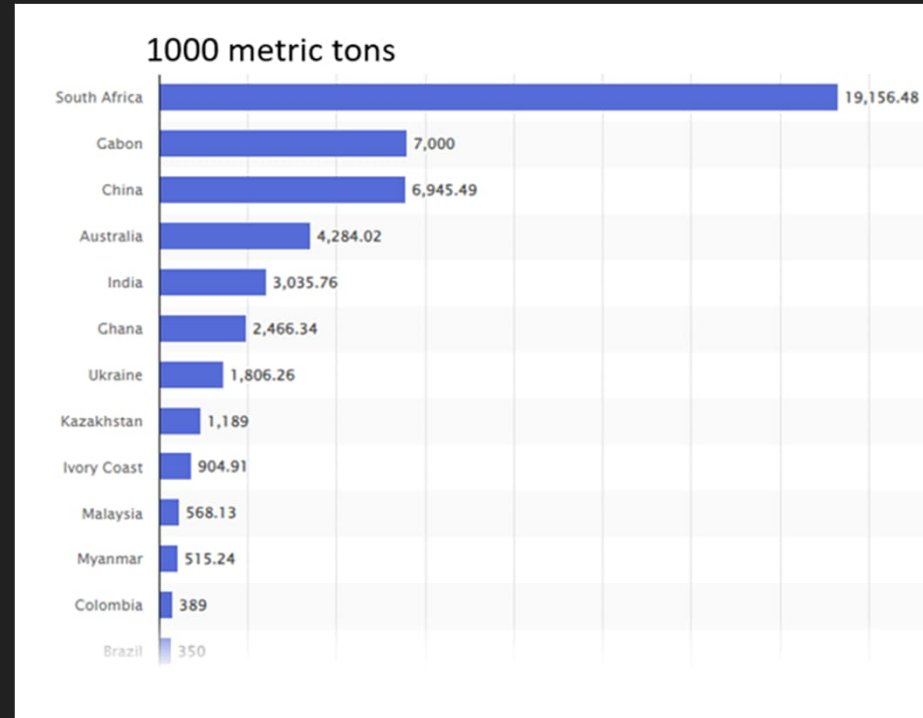
Romanechite⁶

Abundance and occurrence

- Manganese is considered an essential trace element.
 - It's required for the proper functioning of enzymes responsible for processes like bone formation, blood clotting, and nutrient metabolism. However, it's only needed in very small amounts.²
-
- It is not found naturally in its pure form, but manganese ores are widely distributed.
 - Large areas of **nodules** (mineral concretions) are also found in the ocean floor, called manganese or polymetallic nodules. Amount of manganese is estimated to be even larger in these nodules than in land.²

World production

- Manganese is primarily produced in South Africa, Gabon, China, and Australia (2021)
- Large amounts of **manganese ores** are present in these countries.
- Manganese is mostly produced in the form of different alloys for iron and steel manufacture.^{2,7}



Largest manganese producers in 2021.⁷

Special features

- Manganese exhibits a wide range of oxidation states (from -3 to +7), making it versatile in various chemical processes.⁸
- More about manganese's unique properties are discussed in the next slides parallel to chemical properties and specific applications.



Elemental manganese

Chemistry of Mn

Chemistry: Location

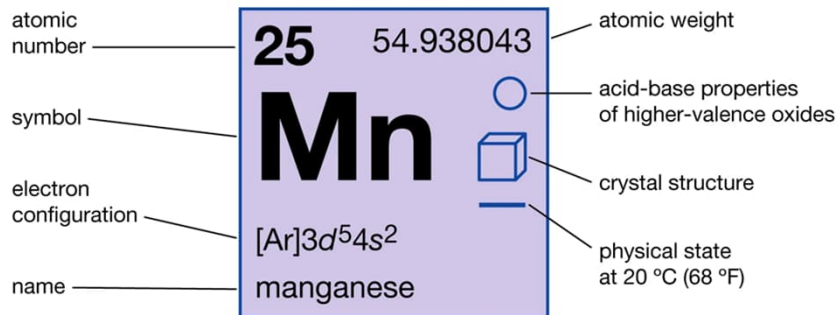
- Period IV
- Group VII
- D-Block Metal

Periodic Table of the Elements

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 1 IA | | | | | | | | | | | | | | | | | | 2 IIA | | | | | | | | | | | | | | | | | | | | | | | | | | | | 18 VIIIA | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1 H Hydrogen 1.008 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 2 He Helium 4.002602 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3 Li Lithium 6.94 | | | | | | | | | | | | | | | | | | 4 Be Beryllium 9.012182 | | | | | | | | | | | | | | | | | | | | | | | | | | | | 5 B Boron 10.81 | | 6 C Carbon 12.011 | | 7 N Nitrogen 14.007 | | 8 O Oxygen 15.999 | | 9 F Fluorine 18.99840323 | | 10 Ne Neon 20.1797 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 11 Na Sodium 22.98976928 | | | | | | | | | | | | | | | | | | 12 Mg Magnesium 24.305 | | | | | | | | | | | | | | | | | | | | | | | | | | | | 13 Al Aluminum 26.9815385 | | 14 Si Silicon 28.0855 | | 15 P Phosphorus 30.973761998 | | 16 S Sulfur 32.06 | | 17 Cl Chlorine 35.45 | | 18 Ar Argon 39.948 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 19 K Potassium 39.0983 | | | | | | | | | | | | | | | | | | 20 Ca Calcium 40.078 | | | | | | | | | | | | | | | | | | 21 Sc Scandium 44.95591 | | | | | | | | | | 22 Ti Titanium 47.88 | | | | | | | | | | 23 V Vanadium 50.9415 | | | | | | | | | | 24 Cr Chromium 51.9961 | | | | | | | | | | 25 Mn Manganese 54.938044 | | | | | | | | | | 26 Fe Iron 55.845 | | | | | | | | | | 27 Co Cobalt 58.933194 | | | | | | | | | | 28 Ni Nickel 58.6934 | | | | | | | | | | 29 Cu Copper 63.546 | | | | | | | | | | 30 Zn Zinc 65.38 | | | | | | | | | | 31 Ga Gallium 69.723 | | | | | | | | | | 32 Ge Germanium 72.630 | | | | | | | | | | 33 As Arsenic 74.921595 | | | | | | | | | | 34 Se Selenium 78.971 | | | | | | | | | | 35 Br Bromine 79.904 | | | | | | | | | | 36 Kr Krypton 83.798 | | | | | | | | | |
| 37 Rb Rubidium 85.4678 | | | | | | | | | | | | | | | | | | 38 Sr Strontium 87.62 | | | | | | | | | | | | | | | | | | 39 Y Yttrium 88.90584 | | | | | | | | | | 40 Zr Zirconium 91.224 | | | | | | | | | | 41 Nb Niobium 92.90637 | | | | | | | | | | 42 Mo Molybdenum 95.94 | | | | | | | | | | 43 Tc Technetium (98) | | | | | | | | | | 44 Ru Ruthenium 101.07 | | | | | | | | | | 45 Rh Rhodium 102.90550 | | | | | | | | | | 46 Pd Palladium 106.42 | | | | | | | | | | 47 Ag Silver 107.8682 | | | | | | | | | | 48 Cd Cadmium 112.414 | | | | | | | | | | 49 In Indium 114.818 | | | | | | | | | | 50 Sn Tin 118.710 | | | | | | | | | | 51 Sb Antimony 121.760 | | | | | | | | | | 52 Te Tellurium 127.60 | | | | | | | | | | 53 I Iodine 126.90544 | | | | | | | | | | 54 Xe Xenon 131.293 | | | | | | | | | |
| 55 Cs Cesium 132.90545196 | | | | | | | | | | | | | | | | | | 56 Ba Barium 137.327 | | | | | | | | | | | | | | | | | | 57 - 71 Lanthanoids | | | | | | | | | | 72 Hf Hafnium 178.49 | | | | | | | | | | 73 Ta Tantalum 180.94786 | | | | | | | | | | 74 W Tungsten 183.84 | | | | | | | | | | 75 Re Rhenium 186.207 | | | | | | | | | | 76 Os Osmium 190.23 | | | | | | | | | | 77 Ir Iridium 192.222 | | | | | | | | | | 78 Pt Platinum 195.084 | | | | | | | | | | 79 Au Gold 196.966569 | | | | | | | | | | 80 Hg Mercury 200.592 | | | | | | | | | | 81 Tl Thallium 204.38 | | | | | | | | | | 82 Pb Lead 207.2 | | | | | | | | | | 83 Bi Bismuth 208.98040 | | | | | | | | | | 84 Po Polonium (209) | | | | | | | | | | 85 At Astatine (210) | | | | | | | | | | 86 Rn Radon (222) | | | | | | | | | |
| 87 Fr Francium (223) | | | | | | | | | | | | | | | | | | 88 Ra Radium (226) | | | | | | | | | | | | | | | | | | 89 - 103 Actinoids | | | | | | | | | | 104 Rf Rutherfordium (261) | | | | | | | | | | 105 Db Dubnium (268) | | | | | | | | | | 106 Sg Seaborgium (269) | | | | | | | | | | 107 Bh Bohrium (278) | | | | | | | | | | 108 Hs Hassium (285) | | | | | | | | | | 109 Mt Meitnerium (288) | | | | | | | | | | 110 Ds Darmstadtium (291) | | | | | | | | | | 111 Rg Roentgenium (293) | | | | | | | | | | 112 Cn Copernicium (286) | | | | | | | | | | 113 Nh Nihonium (288) | | | | | | | | | | 114 Fl Flerovium (289) | | | | | | | | | | 115 Mc Moscovium (290) | | | | | | | | | | 116 Lv Livermorium (293) | | | | | | | | | | 117 Ts Tennessine (294) | | | | | | | | | | 118 Og Oganesson (294) | | | | | | | | | |
| 57 La Lanthanum 138.90547 | | | | | | | | | | | | | | | | | | 58 Ce Cerium 140.12 | | | | | | | | | | | | | | | | | | 59 Pr Praseodymium 140.90766 | | | | | | | | | | 60 Nd Neodymium 144.242 | | | | | | | | | | 61 Pm Promethium (145) | | | | | | | | | | 62 Sm Samarium 150.36 | | | | | | | | | | 63 Eu Europium 151.964 | | | | | | | | | | 64 Gd Gadolinium 157.25 | | | | | | | | | | 65 Tb Terbium 158.92515 | | | | | | | | | | 66 Dy Dysprosium 162.50 | | | | | | | | | | 67 Ho Holmium 164.93033 | | | | | | | | | | 68 Er Erbium 167.259 | | | | | | | | | | 69 Tm Thulium 168.93422 | | | | | | | | | | 70 Yb Ytterbium 173.054 | | | | | | | | | | 71 Lu Lutetium 174.964 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 89 Ac Actinium (227) | | | | | | | | | | | | | | | | | | 90 Th Thorium 232.0377 | | | | | | | | | | | | | | | | | | 91 Pa Protactinium 231.03688 | | | | | | | | | | 92 U Uranium 238.02891 | | | | | | | | | | 93 Np Neptunium (237) | | | | | | | | | | 94 Pu Plutonium (244) | | | | | | | | | | 95 Am Americium (243) | | | | | | | | | | 96 Cm Curium (247) | | | | | | | | | | 97 Bk Berkelium (247) | | | | | | | | | | 98 Cf Californium (251) | | | | | | | | | | 99 Es Einsteinium (252) | | | | | | | | | | 100 Fm Fermium (257) | | | | | | | | | | 101 Md Mendelevium (261) | | | | | | | | | | 102 No Nobelium (265) | | | | | | | | | | 103 Lr Lawrencium (260) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

Chemistry: Physical Properties

Manganese



| | |
|---|---|
|  Transition metals |  Solid |
|  Cubic |  Strongly acidic |

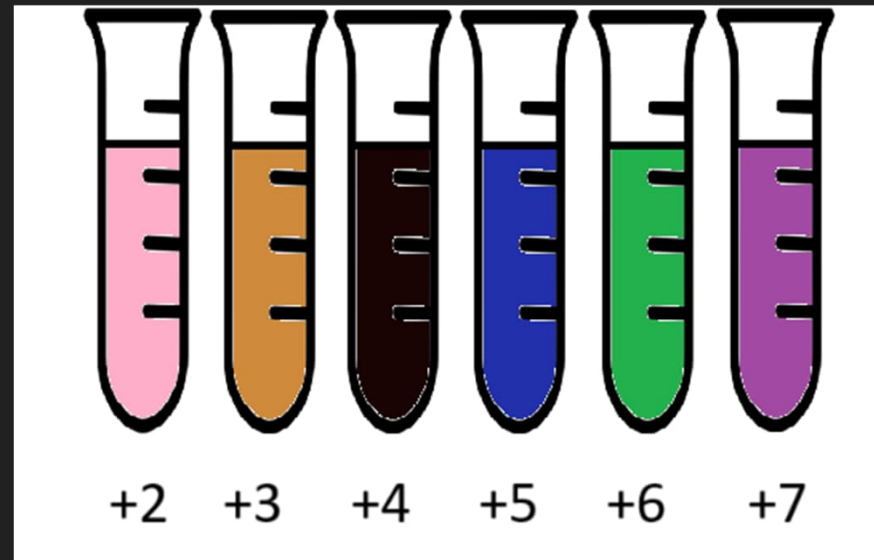
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- Melting Point: 1246°C
- Boiling Point: 2061°C
- Isotope(s): Mn⁵⁵ ~100%
- Metal Form: Solid, silvery, brittle^{1,9}

Properties of Mn¹⁰

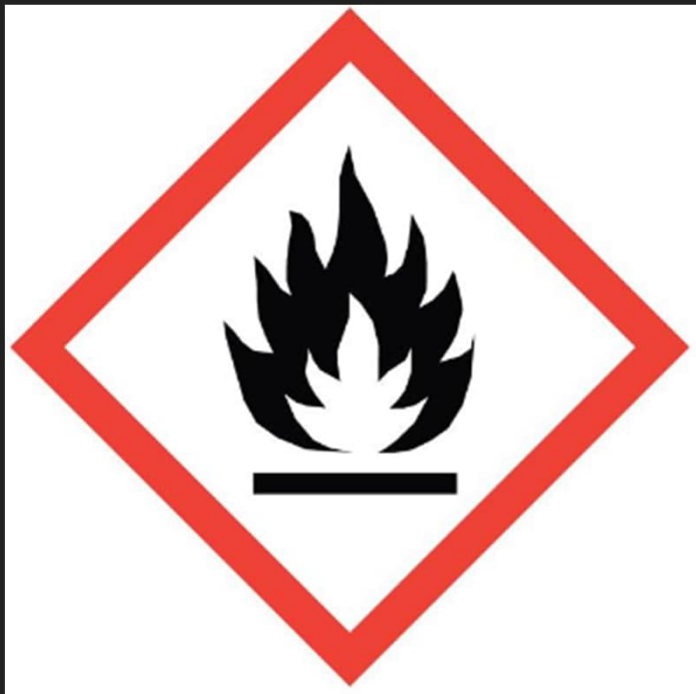
Chemistry: Size and Oxidation

- Atomic Radius (pm): 161
- Ionic Radii (pm)(charge): 67/+2, 83/+2
58/+3, 65/+3, 39/+4, 53/+4
- Oxidation States: 0, ± 1 , ± 2 , ± 3 , +4, +5, +6, $+7$ ^{1,8}



Oxidation States of Mn and their associated colors

Chemistry: Reactions



Flame Warning Symbol²

- Reactivity: Hydrogen when $>200^{\circ}\text{C}$ and with Nitrogen
- Solubility: Soluble in acid/base, not water or organic solvents
- Flammability: When exposed to flame (explosive in powder form)²

Compounds of Mn

Compounds: MnCO_3

- Properties: Soluble in acidic solutions, melting point of 350°C , white/pink/brown in powder form, red/pink in crystal form.
- Applications: source of Mn for metal alloys, additive in plant fertilizer, jewelry
11,12



MnCO_3 powder¹³

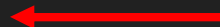
Compounds: MnCO_3 (Rhodochrosite)



Alma, CO. Currently
located at Denver
Museum of Nature
and Science ¹⁴



My Mom's Collection



Compounds: Metallic Alloys



13% Steel Alloy (Manganese Steel or Hadfield Steel)



1% Steel Alloy



- Properties: Decreased brittleness, improve strength, resistance to wear, ferromagnetic.
- Applications: Aluminum, Antimony, Copper, **Steel production** (1% and 13% vol/wt varieties)^{1, 9, 15}

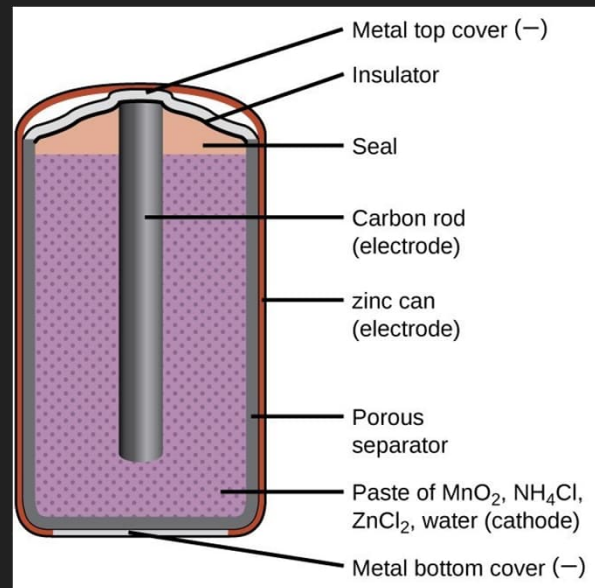
Compounds: MnO_2



MnO_2 Powder¹⁶

- Properties: Black powder, insoluble in water, hydrogen binder
- Applications: Source of Mn for metal alloys, drying agent for black paints, decolors glass, multiple medical therapies, dry cell batteries²

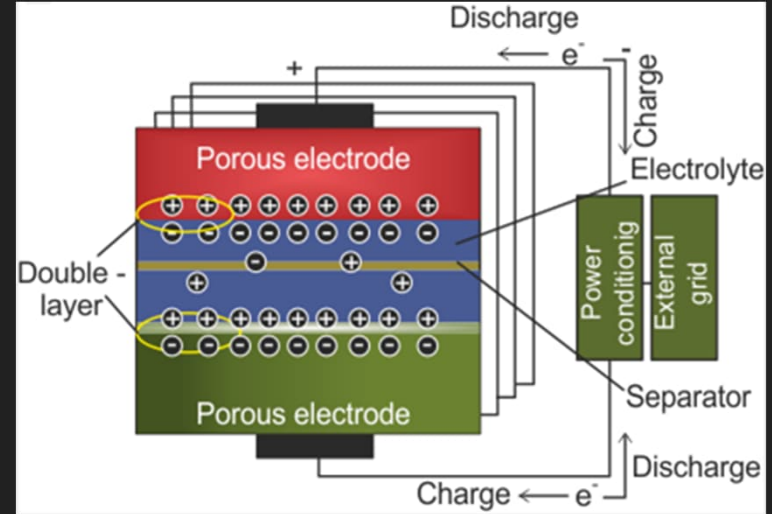
Basic structure of a dry-cell battery¹⁷



Specific Functionalities and Applications

Supercapacitors

- In recent years the scientific community has been interested in **supercapacitors** - energy storage devices that store energy through the electrostatic separation of charges.
- Supercapacitors use electrolytes and porous materials to create an extremely large surface area for charge storage. This allows them to store significantly more energy than regular capacitors. ¹⁸



Overview of a supercapacitor. ¹⁸

Suitable materials for supercapacitors, especially for electrodes, have been examined widely and promising experiments have been done with graphene-based materials such as **graphene/MnO₂**.¹⁸

Why carbon-manganese materials are suitable for electrodes?

Low electrical resistance

significant thermal stability

large specific surface area

Porosity

School of
Petrochemical
Engineering,
Changzhou
University

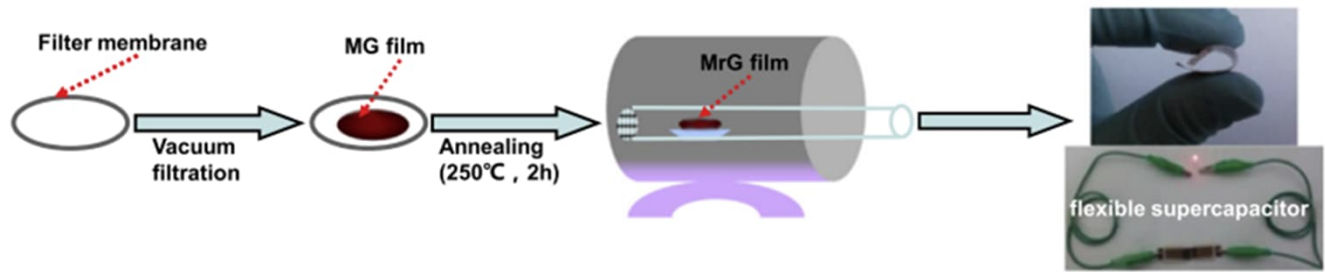
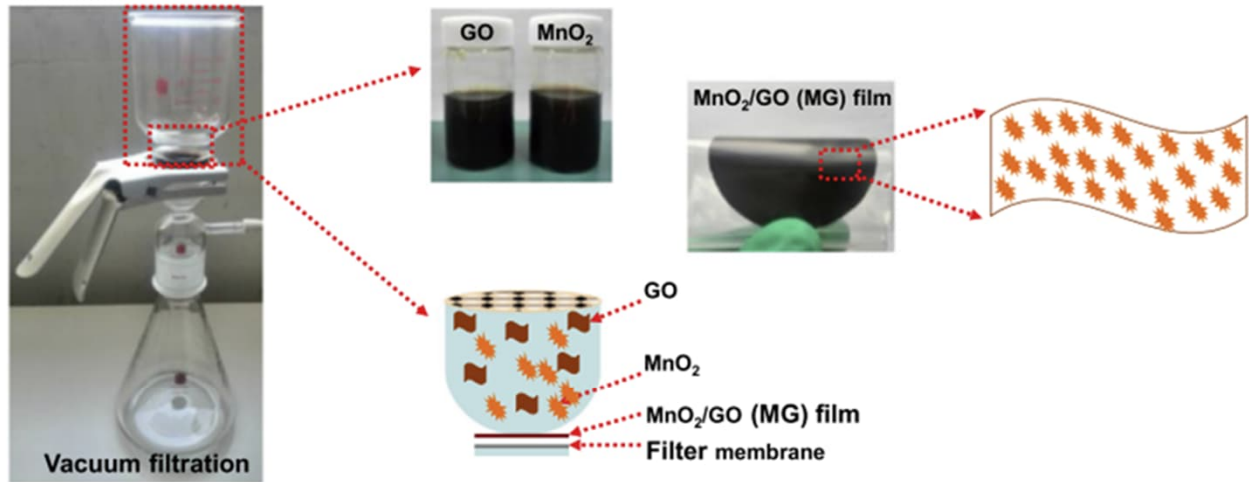
- Ultrathin, flexible MnO₂ nanosheets used for modeling
- MnO₂-GO (graphene oxide nanocomposite hybrid films)

Supercapacitor

- The film was used as the electrode of a flexible supercapacitor
- The film was proven to be very stable under repeated charging/discharging
- **delivery over 95% of the initial capacitance after 6000 cycles.**

Significance

- The study was conducted in 2016, and since then several kinds of MnO₂/carbon composites as supercapacitor electrodes have been designed and fabricated. ¹⁹



Free-standing film refers to a thin layer of material that is self-supporting and doesn't require an additional substrate for mechanical stability¹⁹

One-Dimensional Manganese Oxide Nanostructures for the Removal of Air Pollutants

Manganese oxide (MnO_x) nanostructures have been of significant interest for their potential applications in environmental remediation, particularly in the removal of air pollutants.

Nanorods

Nanowires

Nanotubes

Nanofibers

Why?

- One-dimensional morphology can provide high surface area and improved chemical stability.
- Efficient electron transport pathways, making them ideal candidates for pollutant removal.²⁰

One-Dimensional Manganese Oxide Nanostructures for the Removal of Air Pollutants

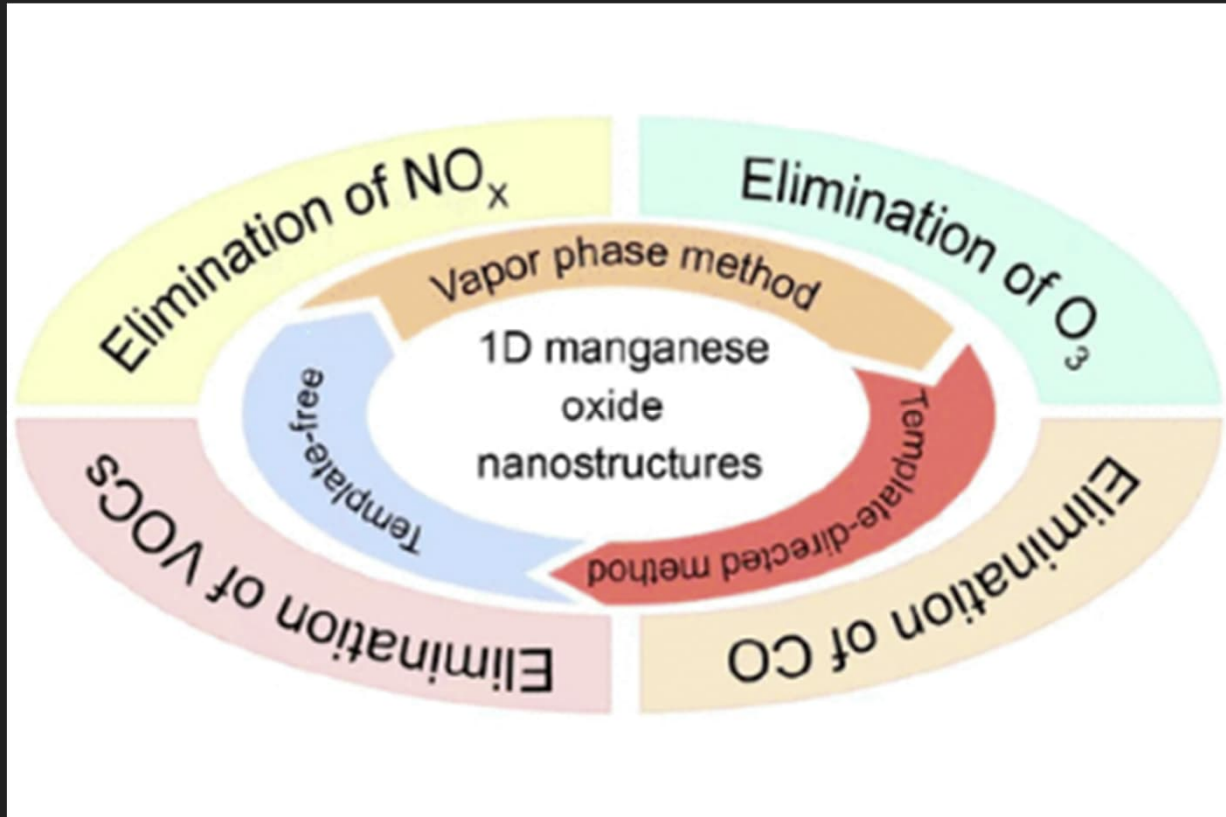
Article

- This subject was discussed 2023 in an article "**Minireview and Perspective of One-Dimensional Manganese Oxide Nanostructures for the Removal of Air Pollutants**"

Two main pathways for preparation

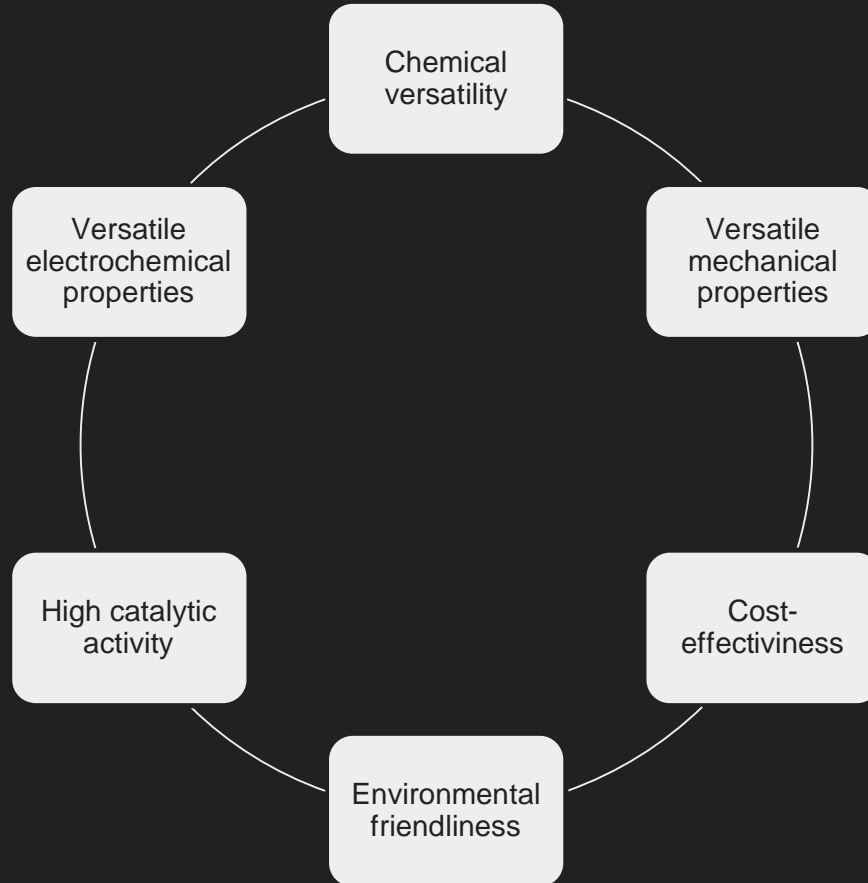
- **Vapor phase** → technique for preparing one-dimensional manganese oxide (MnOx) nanostructures directly from gas-phase reactants
- **Solution phase** → technique for preparing nanoparticles by separating solutes from solvents in homogeneous solutions. The formed solute particles serve as precursors that are then turned into nanoparticles through pyrolysis.²⁰

Applications for MnO_x in air pollution control



MnO_x nanostructures can be used to remove NO_x, O₃, CO and VOCs ²⁰

Why is manganese ideal for these applications?



Thank you!

Comments or Questions?
Please Ask!

Citations

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Thank you!

Comments or Questions?
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