Manganese: Element 25

Sanni Ilmaranta
Naomi Lyle

Chemistry of the Elements

27 September, 2023

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]

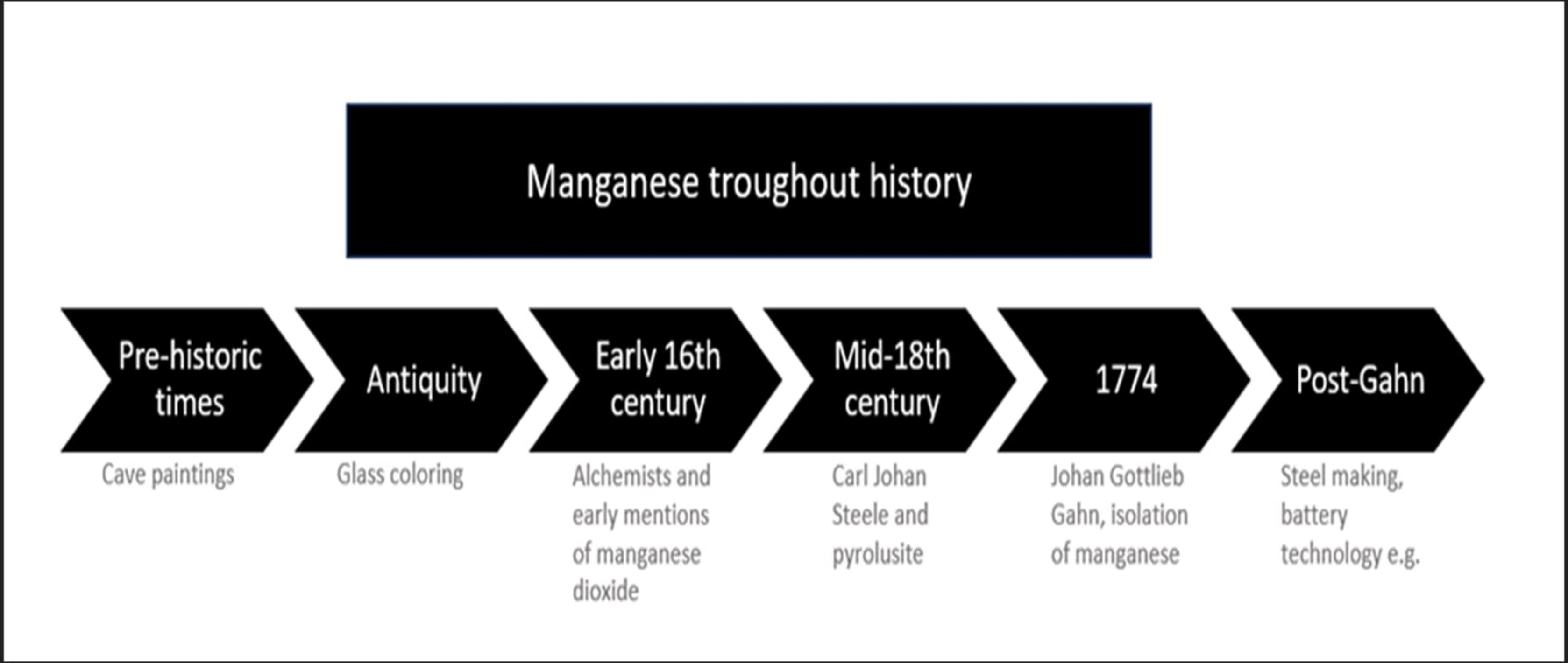
Johan Gottlieb Gahn[3]

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]

Pyrolusite[4]

Origins and history of manganese



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]

Manganese[5]

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]

Romanechite[6]

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]

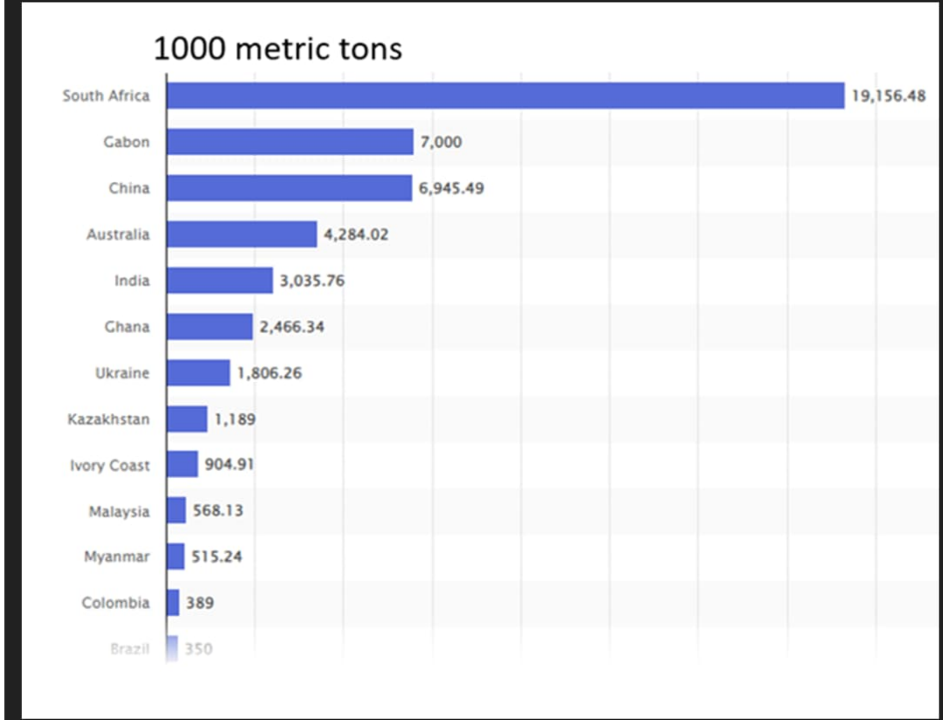
- It is not found naturally in its pure form, but manganese ores are widely distributed.
- Large areas of **nodules** (mineral concretions) are also found in the ocean floor, called manganese or polymetallic nodules. Amount of manganese is estimated to be even larger in these nodules than in land.[2]

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]

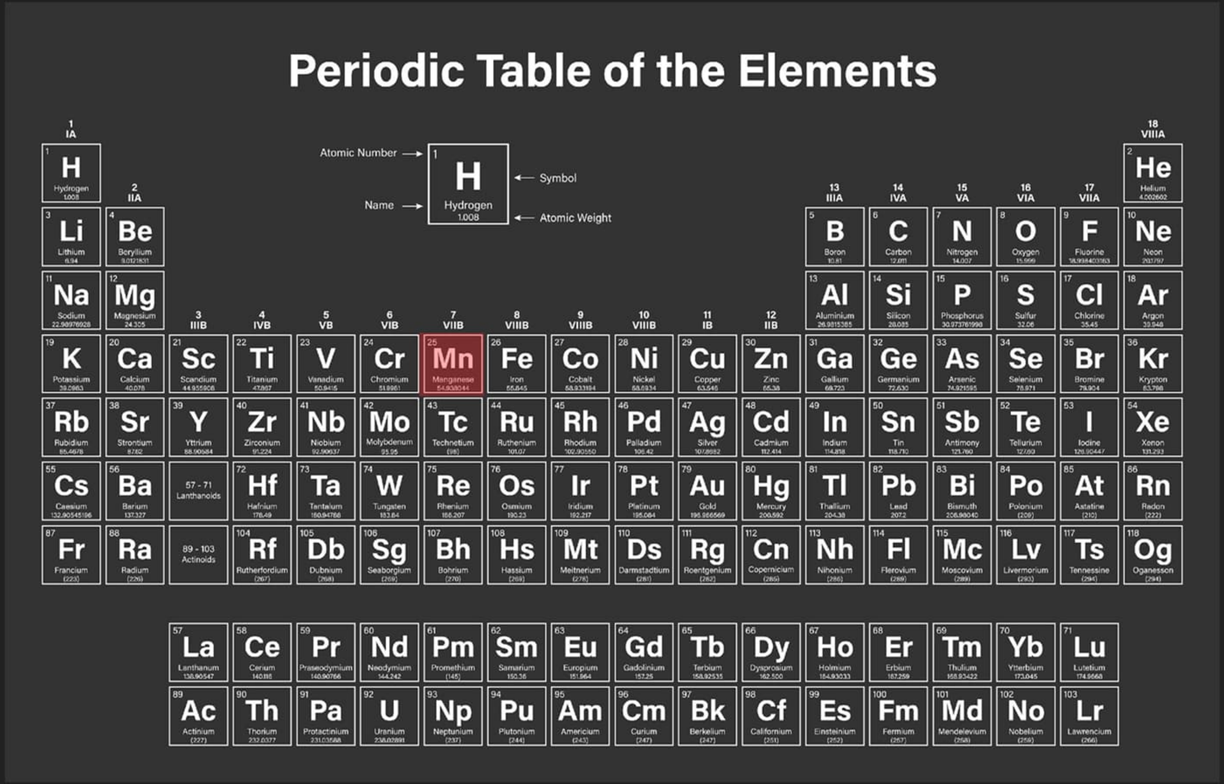
- More about manganese's unique properties are discussed in the next slides parallel to chemical properties and specific applications.

Elemental manganese

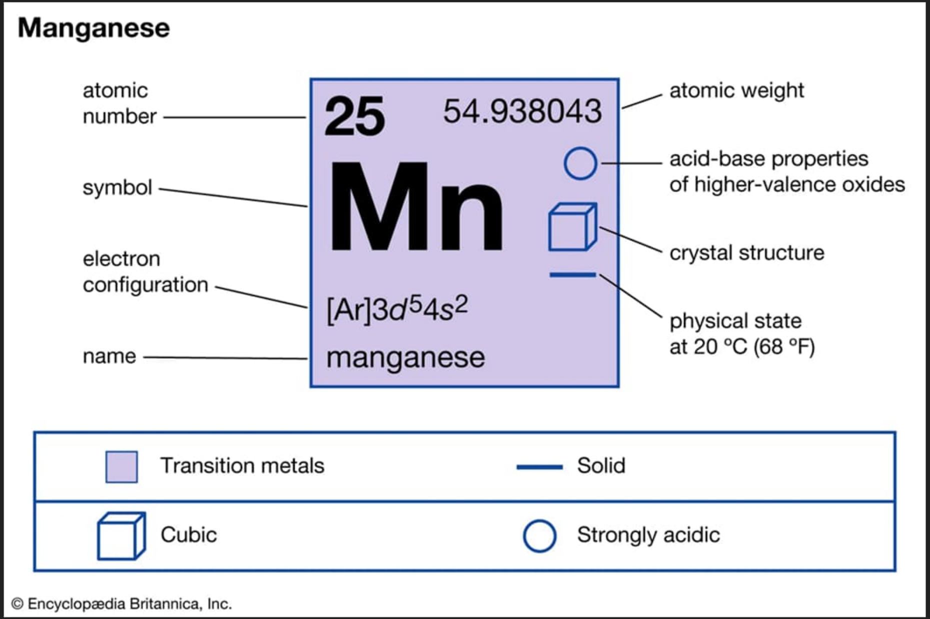
Chemistry of Mn

Chemistry: Location

- Period IV
- Group VII
- D-Block Metal



Chemistry: Physical Properties



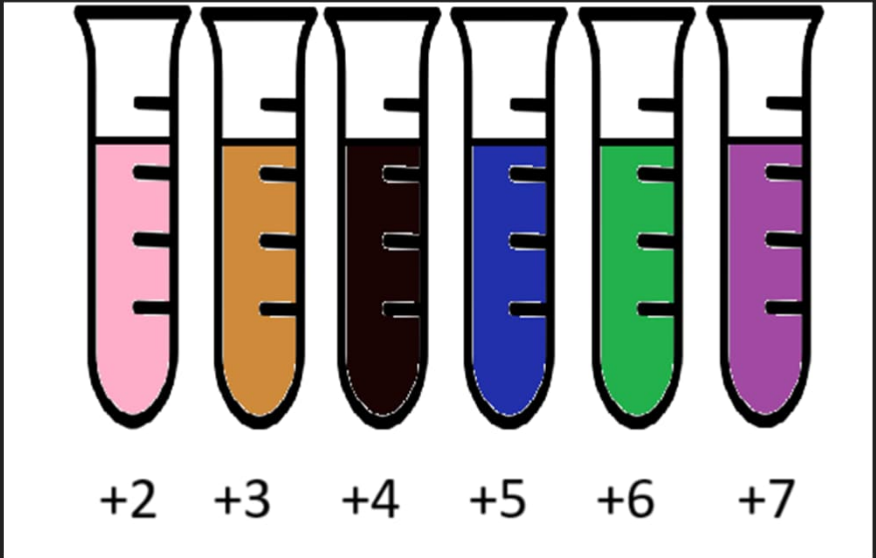
Properties of Mn[10]

- Melting Point: 1246°C
- Boiling Point: 2061°C
- Isotope(s): Mn^{55} ~100%
- Metal Form: Solid, silvery, brittle[1,9]

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 Symbol[2]

- Reactivity: Hydrogen when >200C 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]

$MnCO_3$ powder[13]

Compounds: $MnCO_3$ (Rhodochrosite)

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

My Mom's Collection

Compounds: Metallic Alloys

1% Steel Alloy

13% Steel Alloy (Manganese Steel or Hadfield Steel)

- Properties: Decreased brittleness, improve strength, resistance to wear, ferromagnetic.

- Applications: Aluminum, Antimony, Copper, **Steel production** (1% and 13% vol/wt varieties)[1, 9,15]

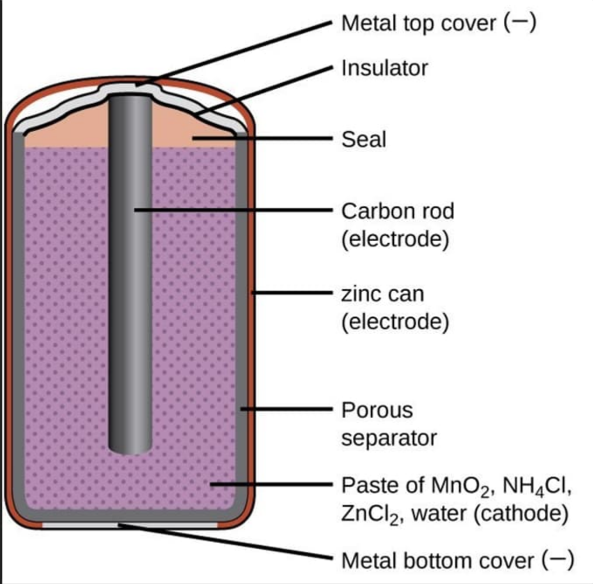
Compounds: MnO_2

MnO_2 Powder[16]

- 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 batteries[2]

Basic structure of a dry-cell battery[17]

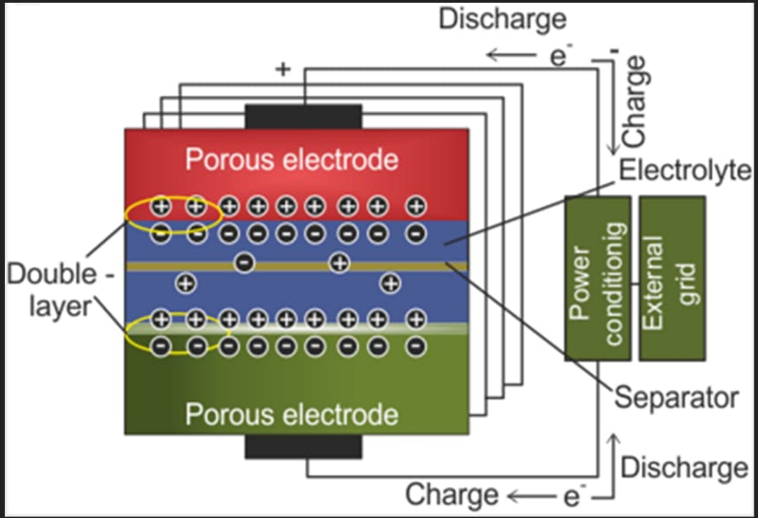


Specific Functionalities and Applications

Supercapacitators

- 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 supercapacitator. [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/MnO_2**.[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

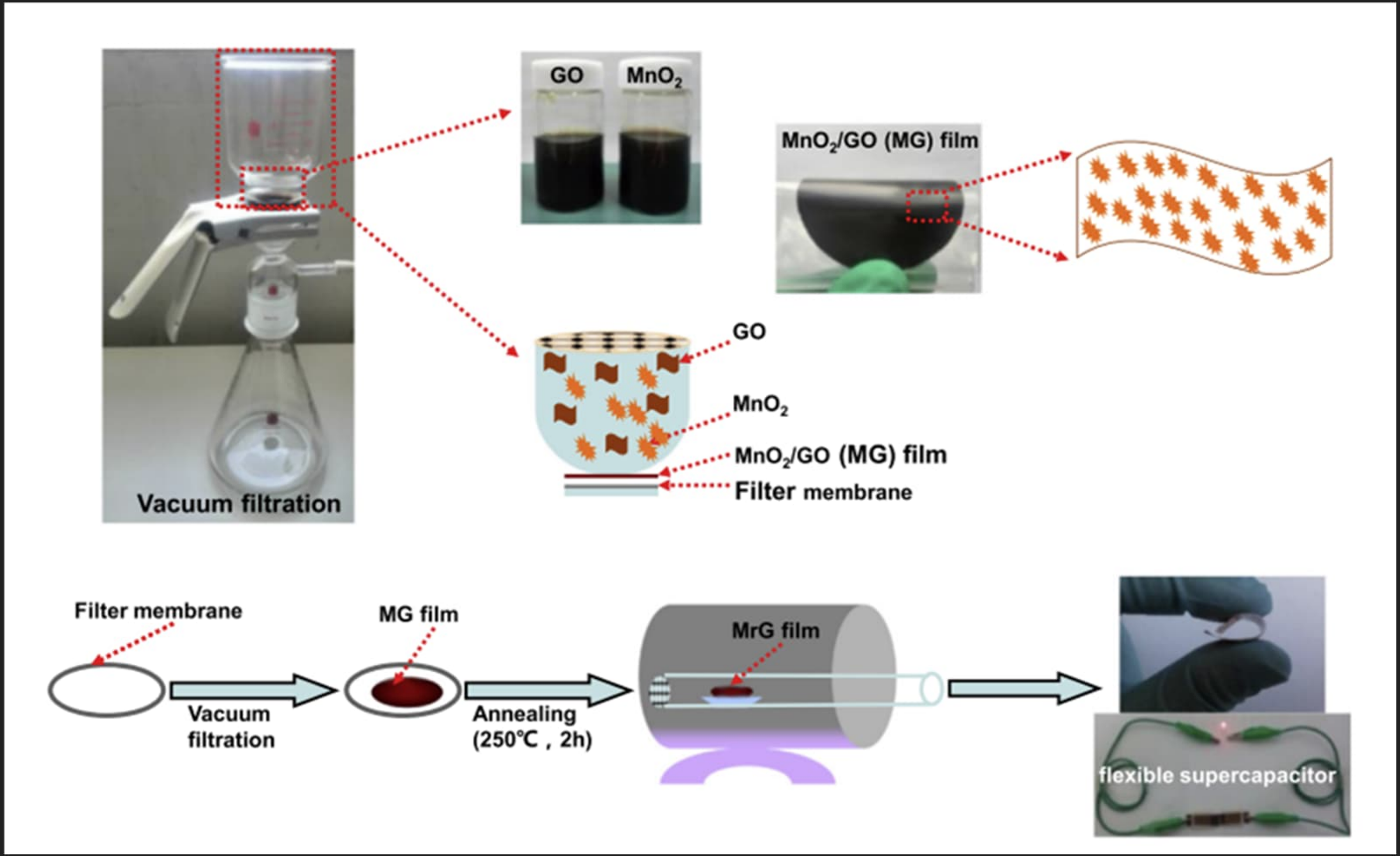
- Ultrathin, flexible MnO_2 nanosheets used for modeling
- MnO2-GO (graphene oxide nanocomposite hybrid films

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 MnO_2/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 stability[19]

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

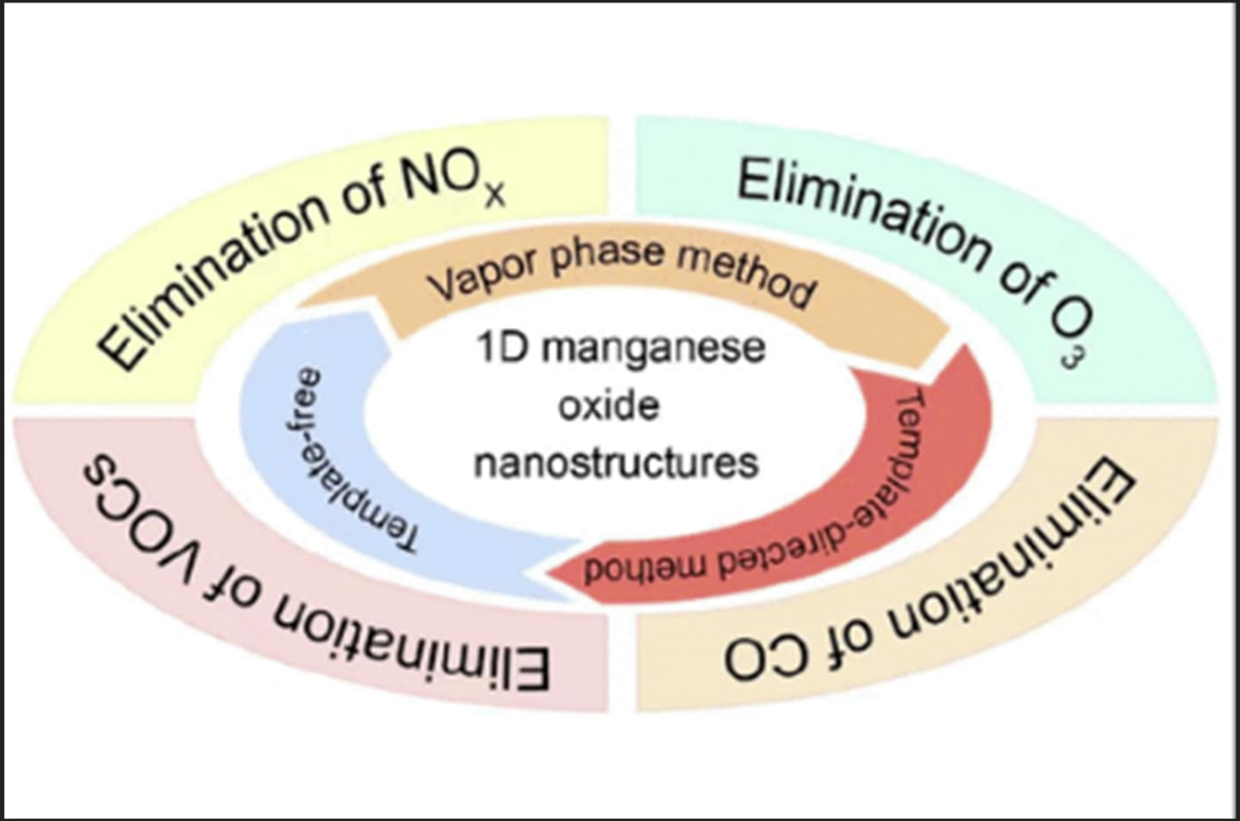
Article

- 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

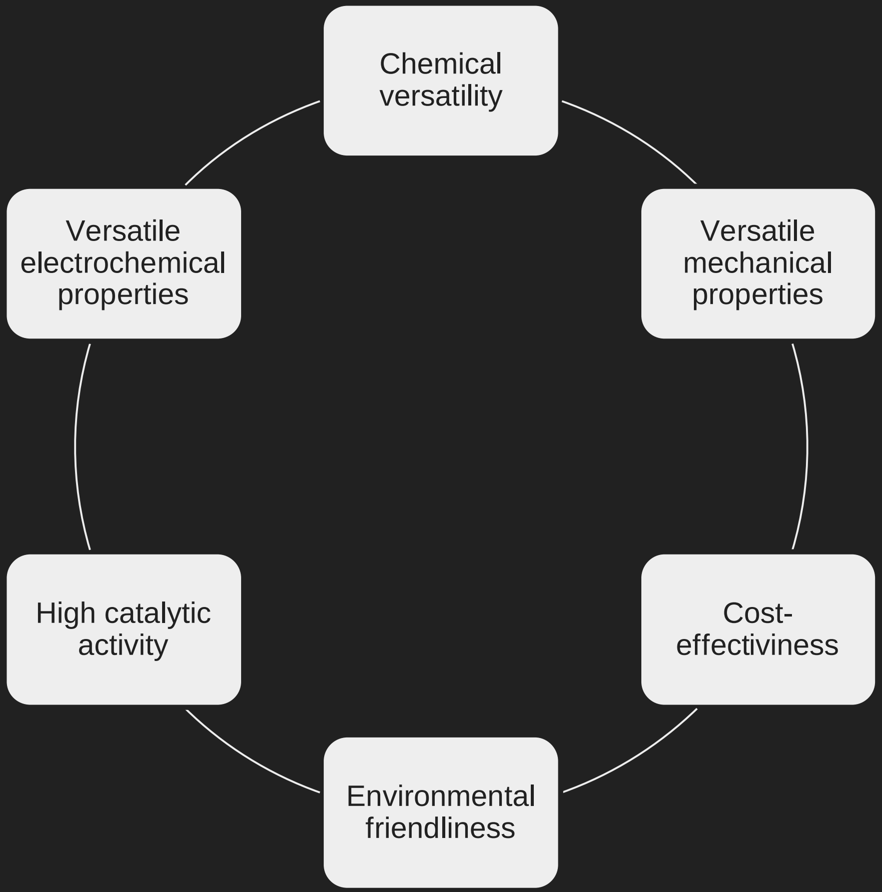
- **Vapor phase →** technique for preparing one-dimensional manganese oxide (MnOx) nanostructures directly from gas-phase reactants
- **Solution phase →** technique for preparing nanoparticles by separating solutes from solvents in homogeneous solutions. The formed solute particles serve as precursors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

Applications for MnO_x in air pollution control



MnO_x nanostructes can be used to remove NO_x, O_3, CO and VOCs [20]

Why is manganese ideal for these applications?



Thank you!

Comments or Questions?
Please Ask!

Citations

1) Manganese - Element information, properties and uses | Periodic Table [Internet]. [cited 2023 Sep 24]. Available from: https://www.rsc.org/periodic-table/element/25/manganese

2) National Center for Biotechnology Information. PubChem. 2023 [cited 2023 Sep 24]. Manganese | Mn (Element) - PubChem. Available from: https://pubchem.ncbi.nlm.nih.gov/element/Manganese#section=Estimated-Oceanic-Abundance

3) Johan Gottlieb Gahn. In: Wikipedia [Internet]. 2022 [cited 2023 Sep 25]. Available from: https://en.wikipedia.org/w/index.php?title=Johan_Gottlieb_Gahn&oldid=1106480055

4) Pyrolusite: The manganese mineral pyrolusite information and pictures [Internet]. [cited 2023 Sep 24]. Available from: https://www.minerals.net/mineral/pyrolusite.aspx

5) Multiview. Belmont Metals. 2020 [cited 2023 Sep 24]. Manganese Availability and Applications: It's Growing Importance. Available from: https://www.belmontmetals.com/manganese-availability-and-applications-its-growing-importance/

6) Romanechite: The mineral romanechite information and pictures [Internet]. [cited 2023 Sep 24]. Available from: https://www.minerals.net/mineral/romanechite.aspx

7) Statista [Internet]. [cited 2023 Sep 24]. Global manganese production by country 2021. Available from: https://www.statista.com/statistics/1244066/global-manganese-production-volume-by-country/

8) Housecroft, Sharpe AG. Inorganic Chemistry(Principles of structure and reactivity) [Internet]. NOIDA, INDIA: Pearson; 2006 [cited 2023 Sep 24]. Available from: http://ebookcentral.proquest.com/lib/aalto-ebooks/detail.action?docID=5483690

9) Haynes WM, Lide DR, Bruno TJ. CRC Handbook of Chemistry and Physics [Internet]. 97th ed. 2017 [cited 2023 Sep 24]. Available from: https://web-s-ebscohost-com.libproxy.aalto.fi/ehost/ebookviewer/ebook/bmxlYmtfXzEzNjcwMzNfX0FO0?sid=725f8958-aa09-4d75-ae1f-7cecbb5a6a64@redis&vid=0&format=EB&rid=1

10) Manganese | Uses, Facts, & Compounds | Britannica [Internet]. [cited 2023 Sep 24]. Available from: https://www.britannica.com/science/manganese

Citations

11) ChemicalBook [Internet]. [cited 2023 Sep 24]. Manganese carbonate | 598-62-9. Available from: https://www.chemicalbook.com/ChemicalProductProperty_EN_CB5135235.htm

12) Haldar SK. 1.3.2.19 Rhodochrosite. In: Introduction to MIneralogy and Petrology [Internet]. 2nd ed. 2020 [cited 2023 Sep 24]. p. 39–40. Available from: https://app-knovel-com.libproxy.aalto.fi/web/view/khtml/show.v/rcid:kpIMPE0003/cid:kt012LG476/viewerType:khtml//root_slug:introduction-mineralogy/url_slug:rhodochrosite?b-toc-cid=kpIMPE0003&b-toc-root-slug=introduction-mineralogy&b-toc-title=Introduction%20to%20Mineralogy%20and%20Petrology%20%282nd%20Edition%29&b-toc-url-slug=rhodochrosite&b-toc-within=rhodochrosite&toc-within=rhodochrosite&view=collapsed&zoom=1&page=39&q=rhodochrosite

13) China Agriculture Grade and Fertilizer Grade CAS 598-62-9 Manganese (II) Carbonate Manganese Carbonate Photos & Pictures - Made-in-china.com [Internet]. [cited 2023 Sep 24]. Available from: https://dydkchemical.en.made-in-china.com/productimage/tZKGuVPchvpU-2f1j00TJwhSCGzYEgY/China-Agriculture-Grade-and-Fertilizer-Grade-CAS-598-62-9-Manganese-II-Carbonate-Manganese-Carbonate.html

14) user:Gribeco KB. ‘Alma King’, largest known rhodochrosite crystal, Denver Museum of Nature and Science [Internet]. 2006 [cited 2023 Sep 24]. Available from: https://commons.wikimedia.org/wiki/File:Alma_King_rhodochrosite.jpg

15) Cannon WF. Manganese—It Turns Iron Into Steel (and Does So Much More) [Internet]. USGS; 2014 [cited 2023 Sep 21]. (Fact Sheet). Report No.: 3087. Available from: https://pubs.usgs.gov/fs/2014/3087/pdf/fs2014-3087.pdf

16) indiamart.com [Internet]. [cited 2023 Sep 25]. Mno2 Powder. Available from: https://www.indiamart.com/proddetail/mno2-powder-19760566488.html

17) Batteries and Fuel Cells | Chemistry: Atoms First [Internet]. [cited 2023 Sep 24]. Available from: https://courses.lumenlearning.com/suny-chem-atoms-first/chapter/batteries-and-fuel-cells-2/

18) Testbook [Internet]. [cited 2023 Sep 24]. Supercapacitor: Definition, Types, Working, and Applications. Available from: https://testbook.com/physics/supercapacitor

19) Yu Y, Zhai Y, Liu H, Li L. Single-layer MnO2 nanosheets: From controllable synthesis to free-standing film for flexible supercapacitors. Materials Letters. 2016 Aug 1;176:33–7.

20) Hu C xing, Wei L gang, Wu T, Yue C mei, Guo R tang. Minireview and Perspective of One-Dimensional Manganese Oxide Nanostructures for the Removal of Air Pollutants. Energy Fuels. 2023 Aug 3;37(15):10886–96.

Thank you!

Comments or Questions?
Please Ask!