Washington University in St. Louis

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LOW-COST, ENVIRONMENTALLY FRIENDLY SYNTHESIS OF DELTA-MNO2 NANOSHEETS FOR BATTERY CATHODES, CATALYSTS AND REMEDIATION

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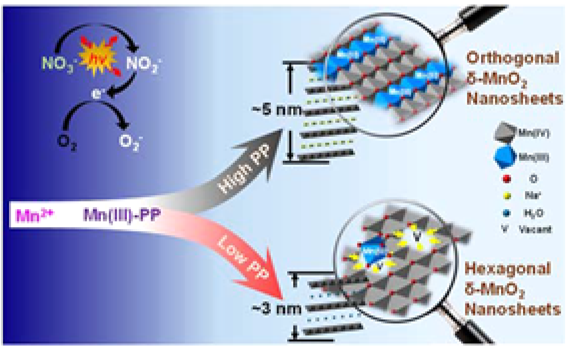
Technology Description

Engineers in Prof. Young-Shin Jun's laboratory have developed a cost-effective, fast, green chemistry process to produce birnessite (δ-MnO_2) nanosheets with naturally abundant resources. This method uses sunlight and nitrate to oxidize Mn^{2+} (aq) to Mn (IV) and has potential applications for remediating aqueous manganese or creating tunable nanosheet materials for battery cathodes or water oxidation.



Schematic overview of fast, green chemistry for δ-MnO_2 tunable nanosheet formation

Disordered (turbostatic) δ-MnO_2 is highly redox active and naturally forms a 2D layer structure that could potentially be used in applications such as catalysts for photo chemical water oxidation and cathodes for Li-ion batteries. Previous attempts to oxidize δ-MnO_2 from aqueous Mn either relied on microbes or slow abiotic synthesis that required heat energy. To improve this process, the inventors developed a simple, one-pot synthesis that uses photolysis of nitrate to oxidize Mn^{2+} (aq), mimicking the natural system without microorganisms or organic matter. This environmentally benign, energy efficient, fast reaction harnesses sunlight as the energy source with no external heat or pressure. Furthermore, the process can also be controlled by adjusting the ligands (e.g., pyrophosphate) and reaction rates to manipulate the thickness and structure for specific applications. This inexpensive, fast, energy-efficient method could be used for water remediation to remove harmful Mn^{2+} (aq) while creating δ-MnO_2 nanosheets with a variety of potential engineering applications.

Stage of Research

- **Proof of Principle:** The inventors demonstrated that this new abiotic oxidative pathway can form δ-MnO_2 (birnessite) nanosheets within ~5 hours using natural sunlight to oxidize Mn^{2+} (aq) to Mn(IV) via nitrate photolysis.
- **Tunable Features**: The inventors showed that a pyrophosphate (PP) ligand can be used to adjust the stacking behavior and structure of the disordered δ-MnO_2 nanosheets. With increasing PP concentration, the nanosheets had better stacking (thicker) layers and the structure changed from hexagonal to orthogonal (with more Mn (III) in the layers).

Applications

- **Battery material** - δ-MnO_2 nanosheets can be used as a cathode material for Li ion, Li air, Na or dry cell batteries
- **Water oxidation** - δ-MnO_2 can be used as a cost-effective catalyst for water oxidation
- **Remediation** – this process could be used for fast, efficient, inexpensive remediation of aqueous manganese while also generating useful materials for other applications

Key Advantages

- **Cost-effective, environmentally friendly process:**
  - sunlight is energy source, with no external heat or pressure
  - reusable nitrate system reduces operation costs as well as waste materials from production
  - simple pathway with easy one-pot synthesis
  - utilizes naturally abundant resources (nitrate and sunlight)
- **Fast reaction:**
  - nanosheets formed in ~5 hours with abiotic process using sunlight as the energy source (oxidation rate comparable to bacterial process)
  - significantly enhanced reaction rates with Xe lamp light source
- **Tunable properties –** thickness and structure of nanosheets can be engineered to meet the requirements of diverse applications by adjusting reaction rates and ligands (for example, increasing Mn (III) to enhance water oxidation)

Publications

- Jung, H., Chadha, T. S., Kim, D., Biswas, P., & Jun, Y. S. (2017). Photochemically assisted fast abiotic oxidation of manganese and formation of δ-MnO 2 nanosheets in nitrate solution. *Chemical Communications*, 53(32), 4445-4448.
- Jung, H., Chadha, T. S., Min, Y., Biswas, P., & Jun, Y. S. (2017). Photochemically-assisted synthesis of birnessite nanosheets and their structural alteration in the presence of pyrophosphate. *ACS Sustainable Chemistry & Engineering*, 5(11), 10624-10632.

Patents: U.S. Patent Application Pending

Website: Jun Lab