# Tailoring Conductivity of Porous $Ti_4O_7$ Magnéli Phases for Optimized Electrode Properties


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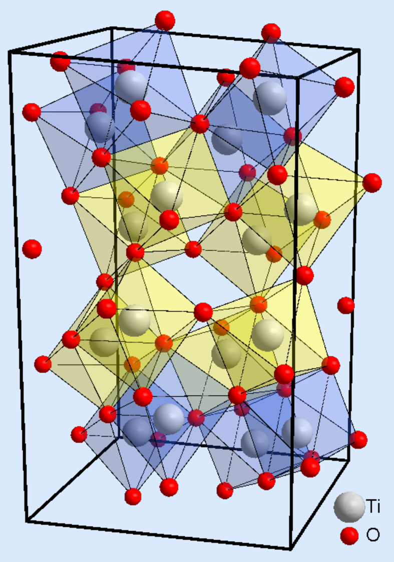
## Introduction

$Ti_4O_7$ belongs to the homologous series of $Ti_nO_{2n-1}$ ($4 \leq n \leq 10$) sub-oxides and exhibits promising properties for the application as electrode material.

- metallic conductivity
- high over potential for $H_2$ evolution
- corrosion-resistance
- stability against re-oxidation



Unit cell of $Ti_4O_7$.

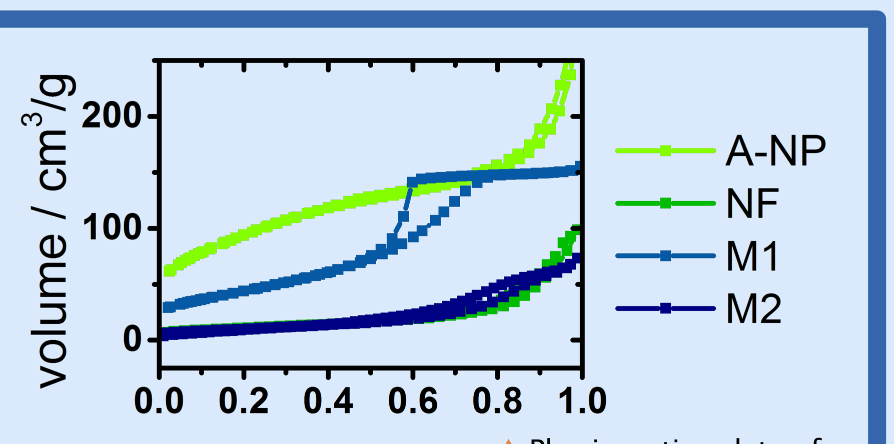
Nanostructured materials are desirable for high surface areas, but the conductivity depends heavily on the morphology.

→ ideal structure for optimized electrode performance

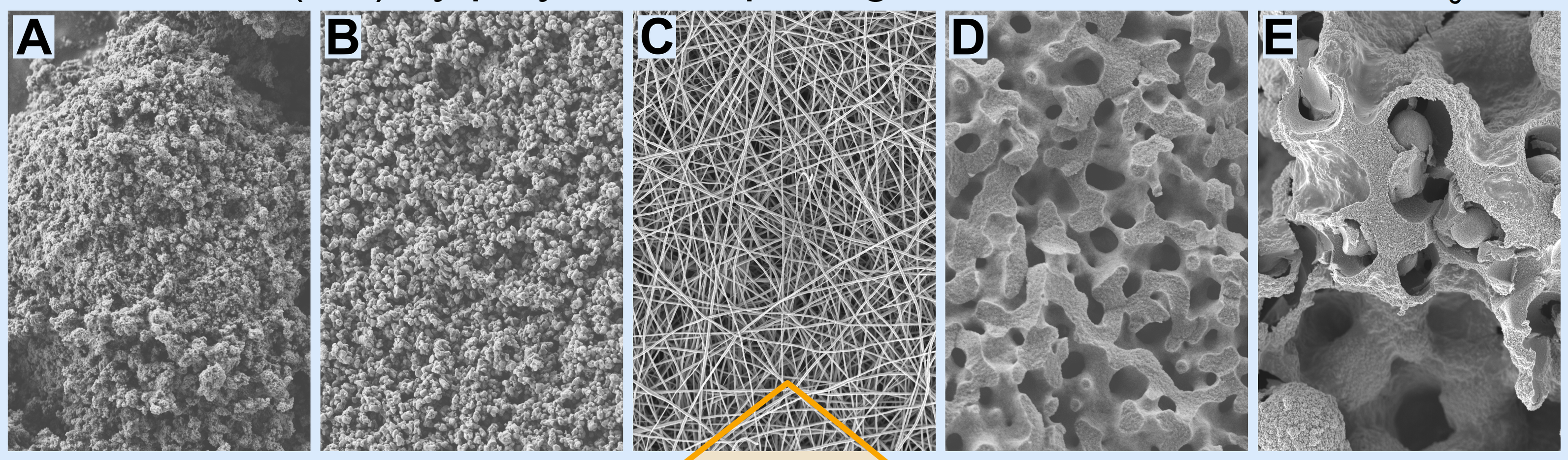
## Precursor Materials

Different $TiO_2$ nanomaterials were investigated.

- Anatase and rutile nanoparticles (NP)
- Nanofibers (NF) by electro spinning
- Monoliths (M1) by phase separation
- Monoliths (M2) by polymer templating



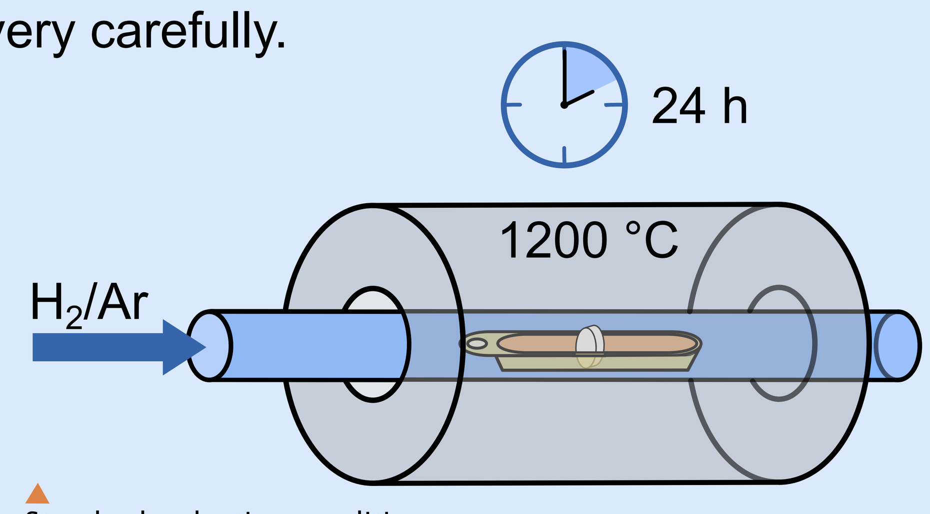
Physisorption data of the precursor materials.



SEM pictures of the morphology of the used $TiO_2$ NPs (A, B), NFs (C), and Ms (D, E).

## Reduction Parameters

Due to only small differences in the composition of $Ti_nO_{2n-1}$ ($4 \leq n \leq 10$), phase-pure syntheses are difficult. Thus, the reduction parameters need to be controlled very carefully.



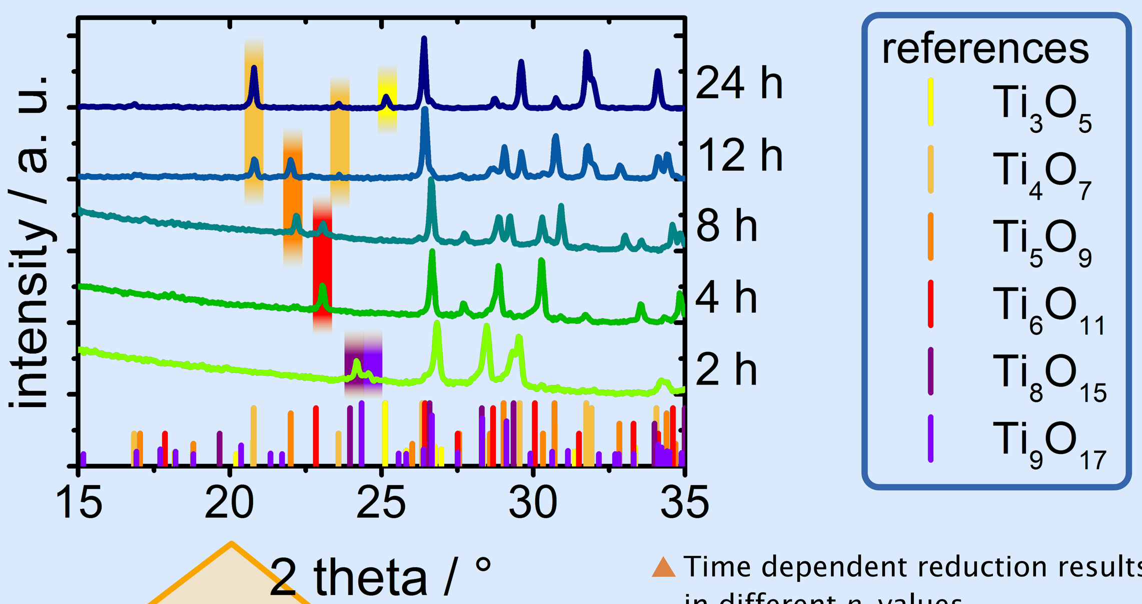
Standard reduction conditions.


Photographs of a $TiO_2$ monolith before the reduction (above) and the obtained $Ti_4O_7$ monolith (below).

### Time dependence

- All suboxides are present during the reduction at different times

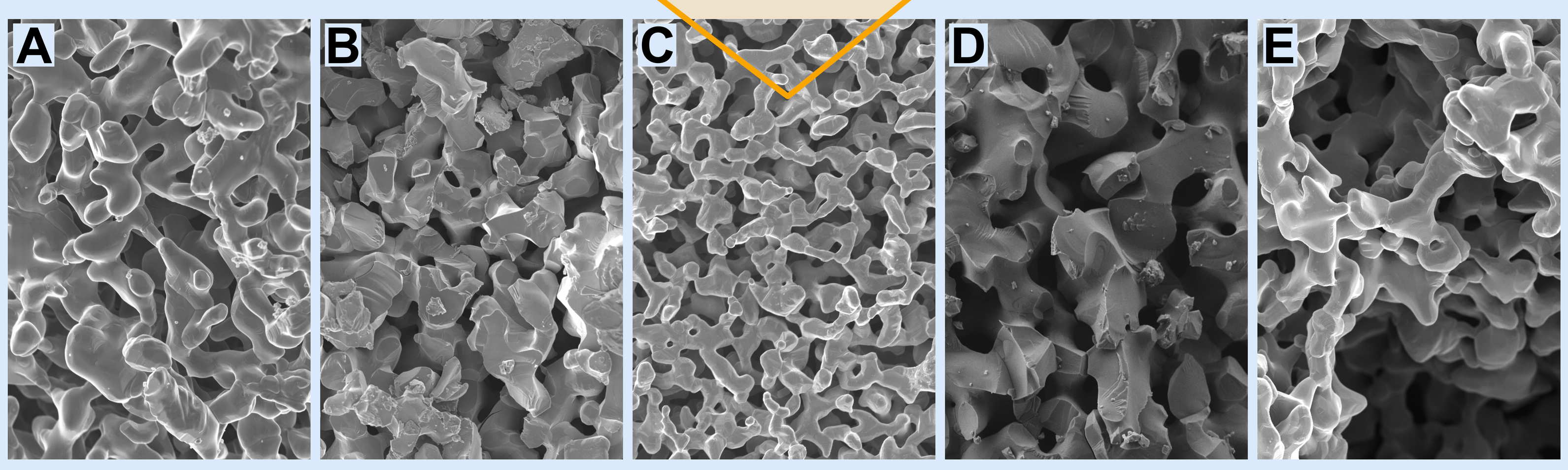
→ stepwise reduction



Time dependent reduction results in different $n$-values.

## Morphology Dependent Conductivity

The morpholgy changes during the reduction.



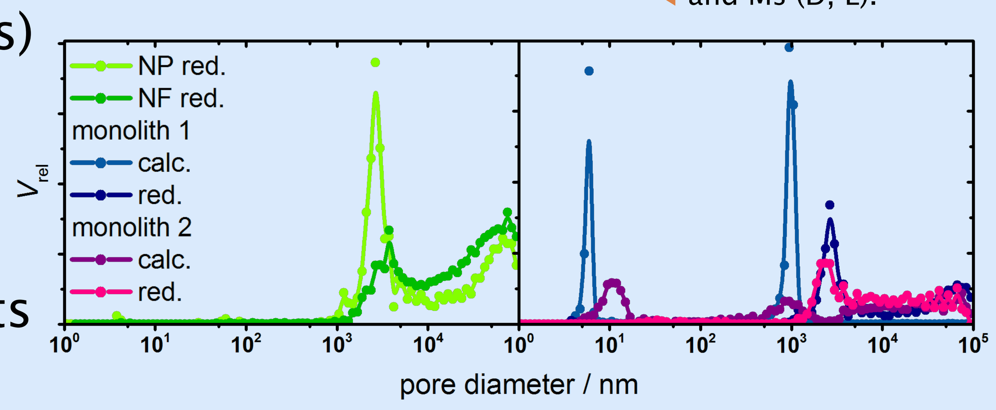
SEM pictures of the obtained morphology depending on the precursor material: NPs (A, B), NFs (C), and Ms (D, E).

- Small structures (NP, NF, mesopores) vanish

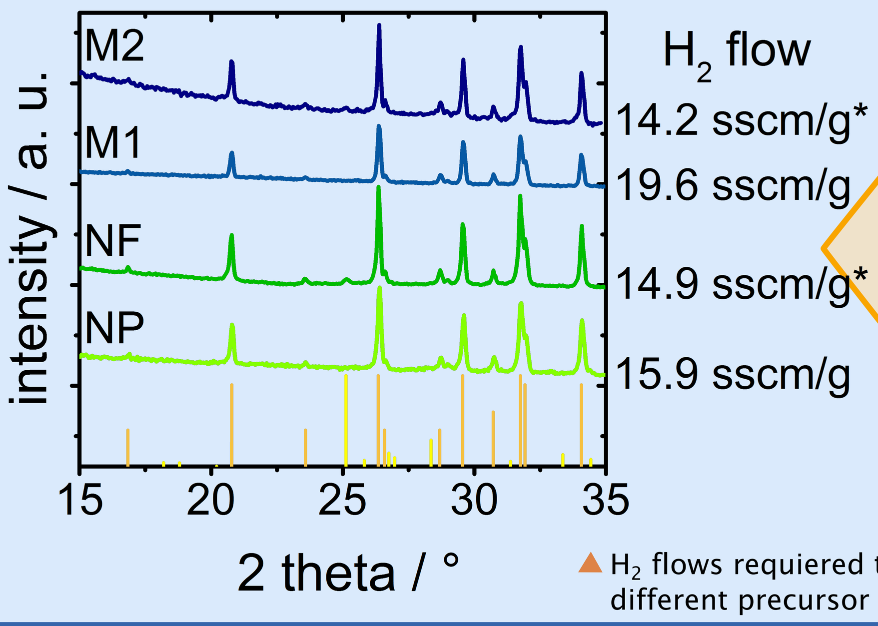
→ Sintering

→ Crystallographic rearrangements

Changes in the porosity in the NPs, NFs, and monoliths measurend by Hg intrusion porosimetry.

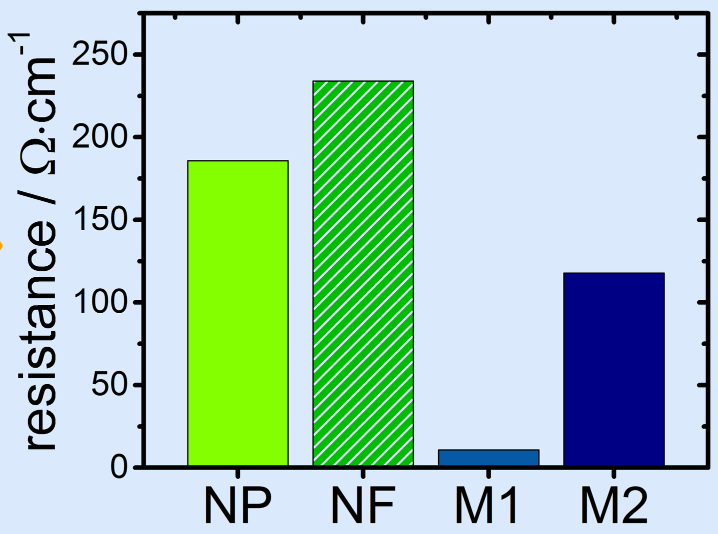



- The $H_2$ flow needs to be optimized for each precursor structure



$H_2$ flows requiered to reduce the different precursor morphologies.

- The precursor morphology has an influence on the conductivity

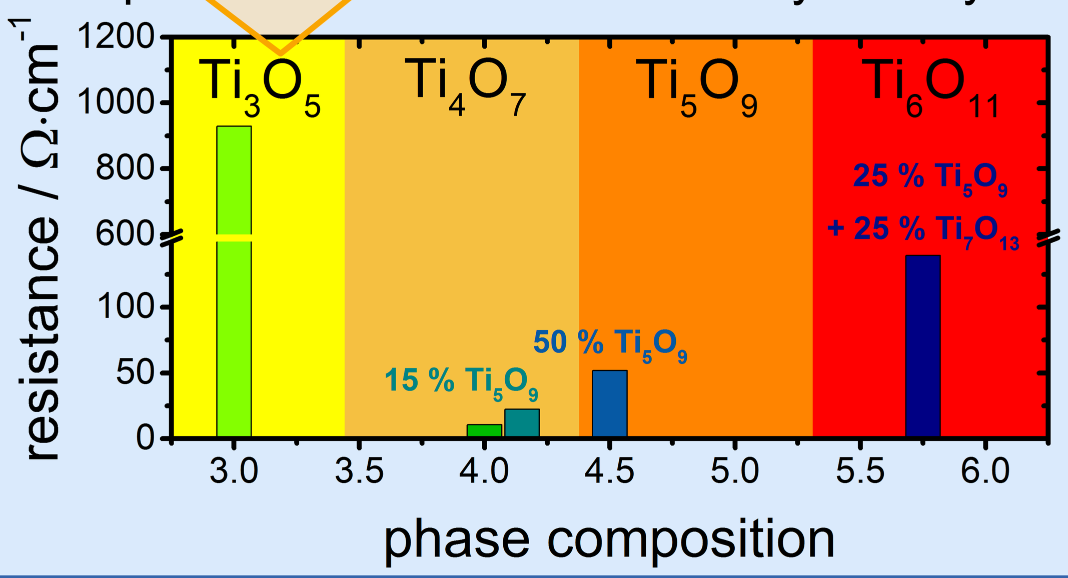


The resistance differs for the investigated $Ti_4O_7$ structures.

## $Ti_nO_{2n-1}$ Conductivity

The conductivity depends heavily on the precursor structure and the reductive treatment.

- monoliths exhibit the highest conductivity
- impurities reduce the conductivity heavily




Measured resistances for different phase composition.

| composition | resistance |
|---|---|
| $Ti_3O_5$ | 930 Ω/cm |
| $Ti_4O_7$ | 10.7 Ω/cm |
| $Ti_4O_7$ + 15 $\%_{wt.}$ $Ti_5O_9$ | 22.5 Ω/cm |
| $Ti_4O_7$ + 50 $\%_{wt.}$ $Ti_5O_9$ | 52 Ω/cm |
| $Ti_6O_{11}$ + 25 $\%_{wt.}$ $Ti_5O_9$ + 25 $\%_{wt.}$ $Ti_7O_{13}$ | 22.5 Ω/cm |

Even though all $Ti_nO_{2n-1}$ monoliths show much lower resistances than the $Ti_3O_5$ monolith, the phasepure $Ti_4O_7$ monolith exhibits by far the best conductivity.

## Conclusion

Different precursor materials were successfully reduced to $Ti_4O_7$ under structure depending reduction conditions.

- Stepwise reduction from $TiO_2$ to $Ti_4O_7$

→ **Phase control via reduction time**

- Even small impurities reduce the conductance significantly

→ **Phase-pure synthesis of $Ti_4O_7$ is essentiell**

- Precursor structure has a huge influence

→ **Monoliths exhibit the highest conductance**

The results show the importance of choosing the correct precursor as well as carefully controlling the reduction parameters for optimized electrode properties.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