

Insight into the electrochemical property of TiO_2/AC electrodes prepared by a microwave-assisted ionothermal synthesis method for capacitive deionization

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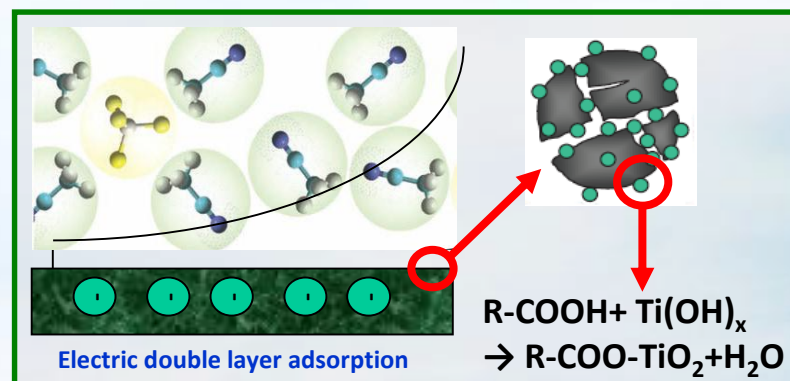
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Purpose of this study

- Nanostructured anatase TiO_2 /activated carbon (AC) composite prepared by a **microwave-assisted ionothermal synthesis method (MAIS)** for CDI electrode.
- The **effect of characteristics of pristine AC**, especially for the **pore structure** and the **surface hydrophilicity** on the electrochemical property of TiO_2 /AC electrodes was investigated using multiple techniques (XPS, TGA, CV, EIS...).

The motive of TiO_2 modification:

1. Increase electrosorptive ability
2. Avoid irreversible adsorption
(reduction of non-electrostatic adsorption)



Ref: Liu et al, Microwave-assisted ionothermal synthesis of nanostructured anatase titanium dioxide/activated carbon composite as electrode material for capacitive deionization, *Electrochimica Acta* 96 (2013) 173.

Microwave-assisted ionothermal synthesis method (MAIS)

Sol-gel method+

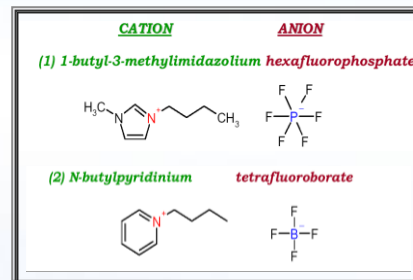
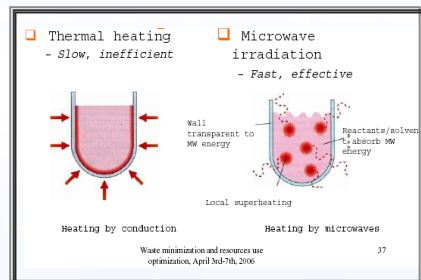
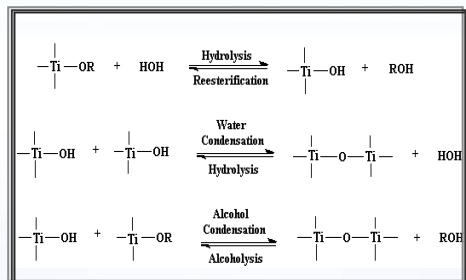
Microwave

+

Ionic liquid

=

MAIS method



Greener heating method

- Molecular homogeneity
- Selective heating
- Less reaction time
- Higher production efficiency

Green reaction medium

- Microwave absorber
- Crystallization at low temperature and ambient atmosphere



In-situ synthesis and immobilization of anatase TiO₂ on AC

Benefits :

- Anatase TiO₂ crystalline (No need for calcination)
- Ambient synthesis condition (<100°C, 1atm)
- Rapid synthesis time (<2hrs)
- TiO₂ nanoparticles uniformly dispersed on activated carbon

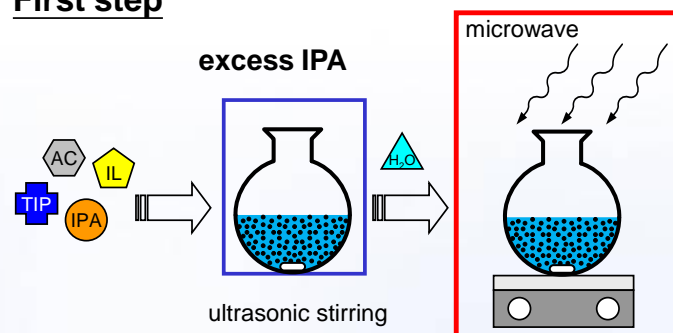
Ref: 1.230th American Chemical Society Meeting & Exposition, 2005 Washington.
2. Waste minimization and resources use optimization, April 3rd-7th, 2006).
3. Non-Crystalline Solids. 1988, 100, 31-50.

Schematic description for two-step MAIS method

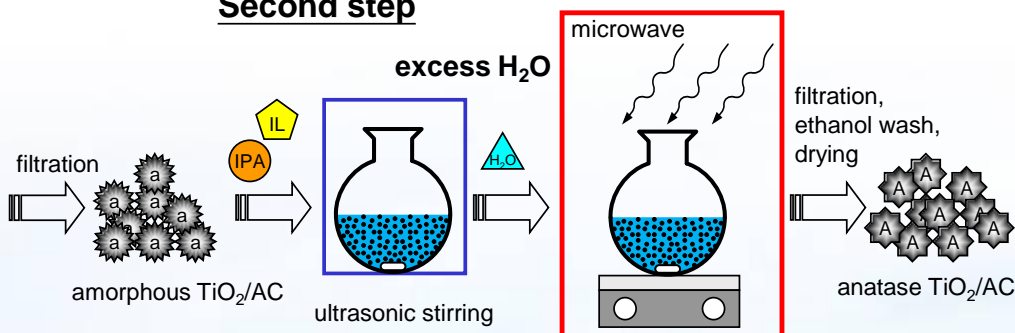
Two step :

1. Sol-gel reaction step
2. crystallization step

First step



Second step



AC activated carbon, TIP titanium tetraisopropoxide, IL ionic liquid, [Bmim]⁺[BF₄]⁻, IPA isopropyl alcohol, H₂O Water, a amorphous TiO₂/AC, A anatase TiO₂/AC

Ionic liquid plays a **hydrothermal analogy** role in driving the surface anatase crystallization of amorphous TiO₂ nanoparticles formed in the matrix of AC.

Ref:

1. Liu et al. The hydrothermal analogy role of ionic liquid in transforming amorphous TiO₂ to anatase TiO₂: elucidating effects of ionic liquids and heating method. *J Mater Sci* 43(2008) 5005.
2. Liu et al. New insights into anatase crystallization behavior in ionothermal synthesis of nanostructured TiO₂. *J Mater Sci* 45(2010)369.
3. Liu et al. Diverse effects of microwave heating on anatase crystallization in ionothermal synthesis of nanostructured TiO₂. *J Mater Sci* 46(2011)4826.

Experimental

Fabrication of electrode for capacitive deionization experiment

- Electrode composition: Active material: PVDF: Graphite=80:10:10 (wt%).
- Fabrication: slurry casted onto a titanium foil by applying a doctor-blade technique (wet thickness 300 μm) and dried at 140 $^{\circ}\text{C}$ for 2 h.

Cyclic voltammetry (CV)

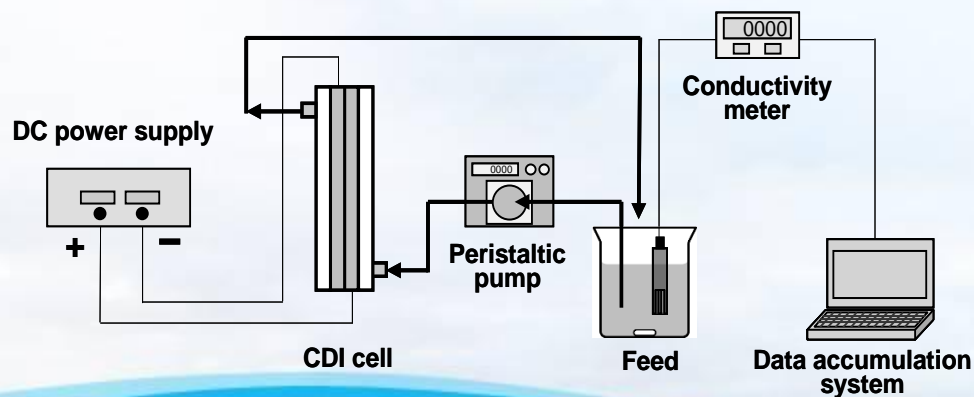
- Test cell: three-electrode cell at room temperature.
- Potential range: -0.5 to 0.5 V (vs. Ag/AgCl) at scan rate of 10 mV/s.
- Electrolyte: 0.5 M NaCl solution.

Electrochemical impedance spectroscopy (EIS)

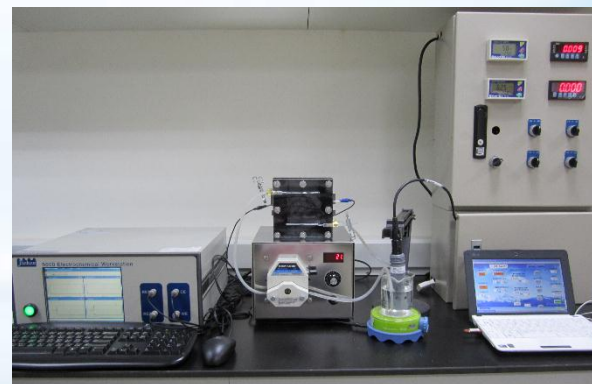
- Test cell: three-electrode cell at room temperature.
- Potential range: 0 V \pm 5 mV (vs. Ag/AgCl).
- Electrolyte: 0.5 M NaCl solution.

CDI performance test

- Electrode area: 8 \times 5 cm^2 .
- Measurement: batch or continuous-type apparatus.
- Operation: influent rate 12 ml/min, 100 mg/l NaCl solution, applied voltage 1.2 V.

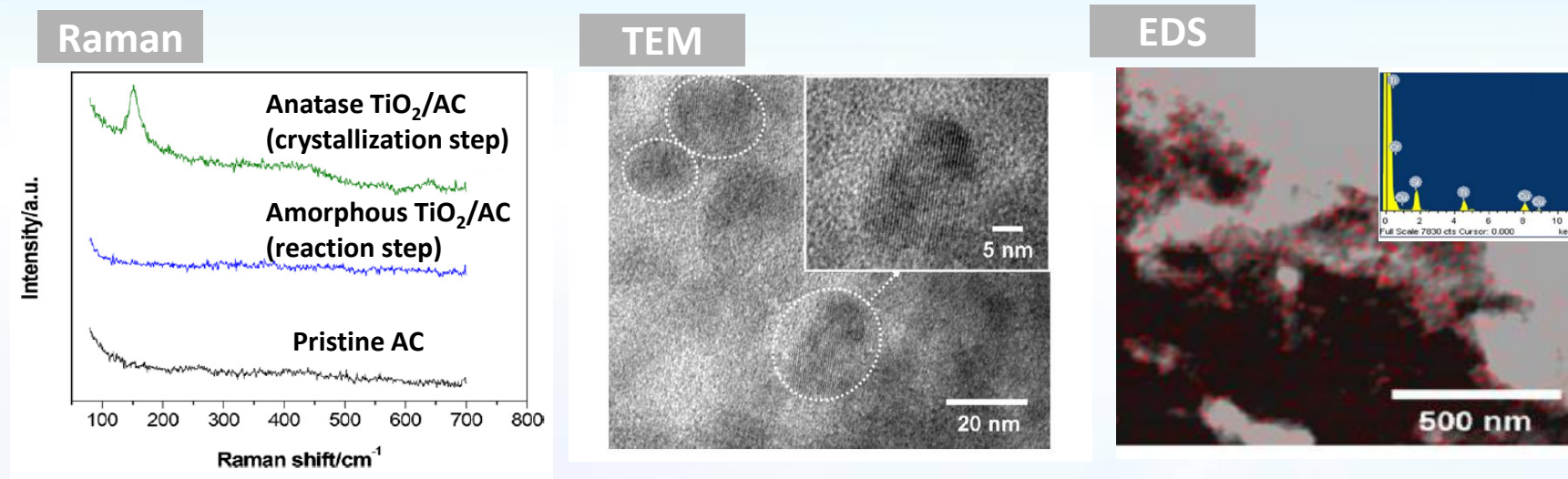


Schematic diagram of capacitive deionization experiments.



Characteristic of anatase TiO₂/AC prepared by MAIS method

1. Even dispersion of the anatase TiO₂ nanoparticles in AC matrix



2. Significant improvement in capacitance of AC after anatase TiO₂ modification

| Electrode material | Specific capacitance (F/g) | Increment (%) |
|-----------------------------------|----------------------------|---------------|
| AC | 44.9 | - |
| Degussa-P25 TiO ₂ /AC | 45.9 | 2.2 |
| Amorphous TiO ₂ /AC | 47.5 | 5.8 |
| Anatase TiO₂/AC | 51.5 | 14.7 |

*Pristine carbon: AC-w

*TiO₂ synthesis: AC/TIP weight ratio of 1:0.25, TIP/H₂O molar ratio of 1:30

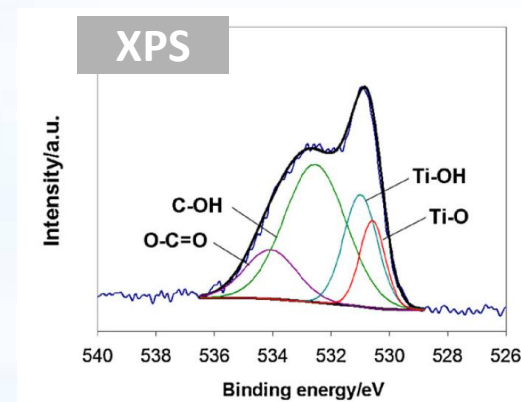
TiO₂/AC electrodes prepared with different TIP/H₂O

| TIP/H ₂ O (molar ratio) | TiO ₂ content (%) | Electrode resistivity (μΩ cm) | Specific capacitance (F/g) |
|---------------------------------------|---------------------------------|----------------------------------|-------------------------------|
| AC | 0 | 80.8 | 44.9 |
| 1:5 | 4.65 | 71.3 | 66.4 |
| 1:15 | 5.41 | 65.6 | 84.7 |
| 1:30 | 7.62 | 91.1 | 51.5 |

*Pristine carbon: AC-w

*TiO₂ synthesis: AC/TIP weight ratio of 1:0.25

| TIP/H ₂ O (molar ratio) | O-C=O (%) | C-OH (%) | Ti-OH (%) | Ti-O (%) |
|---------------------------------------|-------------|-------------|-------------|-------------|
| 1:5 | 17.9 | 52.4 | 18.5 | 11.2 |
| 1:15 | 14.9 | 49.8 | 22.3 | 13.0 |
| 1:30 | 17.8 | 41.8 | 19.3 | 21.1 |

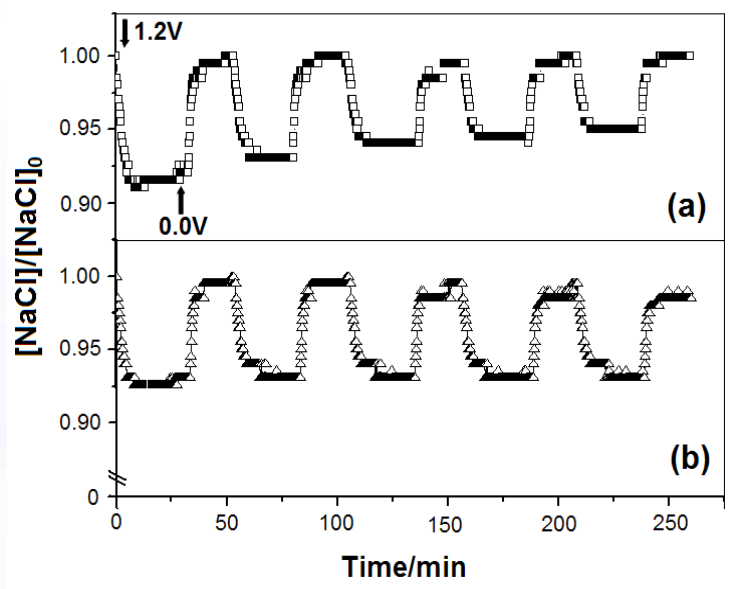


The features of TiO₂/AC prepared under the TIP/H₂O of 1:15-

1. Anatase TiO₂ : Faster electron transfer
2. Higher content of Ti-OH group: Better ionic access ability

CDI performance

The ion electrosorption process of the nanostructured anatase TiO₂/AC composite electrode is a **reversible process**.



The adsorption-desorption cycles of AC electrode (a) and the nanostructured anatase TiO₂/AC electrode (b) at [NaCl]₀ of 100 mg l⁻¹ and applied potential difference of 1.2 V (at TIP/H₂O molar ratio of 1:15).

| Electrode material | NaCl electrosorption capacity (mg/g) |
|----------------------|--------------------------------------|
| AC | 5.43 ± 0.91 |
| TiO ₂ /AC | 8.05 ± 0.34 |

Conclusions

- **TiO₂ modification of AC with microwave-assisted ionothermal synthesis method (MAIS) for CDI was developed to enhance electrosorption capacity resulting from reduction of irreversible adsorption and electrode resistance.**
- **The effect of TiO₂ on the capacitance of nanostructured anatase TiO₂/AC composite is dependent on the characteristics of pristine AC, especially for the pore structure and the hydrophilicity.**

ITRI

Thank you for your attention

