Institute of Robotics and Intelligent Systems

NANOROBOTICS 2015
Exercise Session 2

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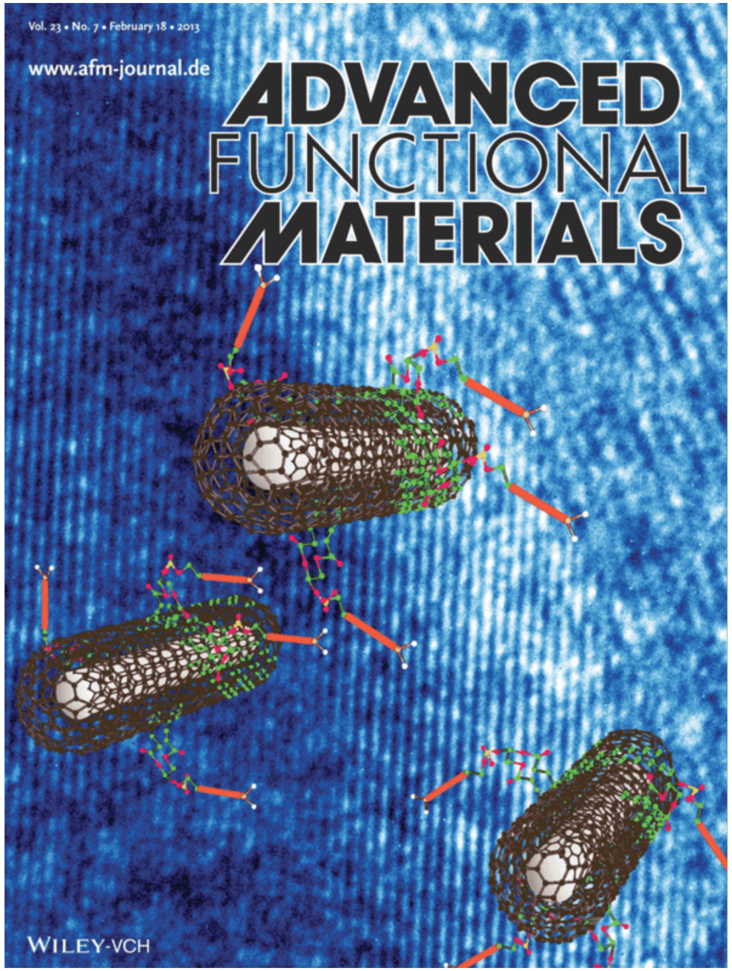

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Article

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Piezoelectrochemical Effect: A New Mechanism for Azo Dye Decolorization in Aqueous Solution through Vibrating Piezoelectric Microfibers

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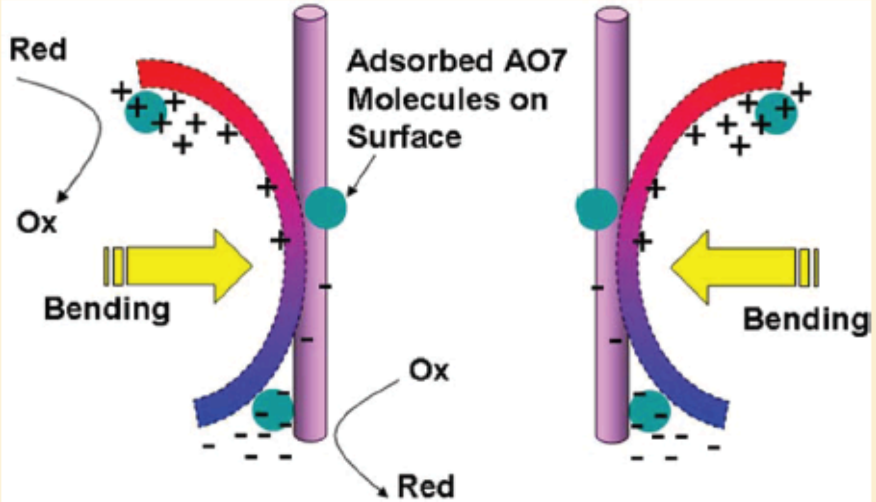
Abstract

ABSTRACT: A newly discovered piezoelectrochemical (PZEC) effect for the direct conversion of mechanical energy to chemical energy is applied for the mechanically induced degradation of a dye of C.I. Acid Orange (AO7) from aqueous solution in the presence of $BaTiO_3$ microdendrites. The mechanism of the PZEC degradation of the dye depends on the ultrasonic vibration used, in which the formation of the strain-induced electric charges on the dendrite surface is due to the deformation and local charge accumulation on the $BaTiO_3$. With sufficient applied electric potential, strained piezoelectric dendrites in AO7 aqueous solution triggered the decomposition reaction. The process is monitored by following the decolorization rate of AO7. The effects of pH, catalyst loading, and initial dye concentration on dye degradation were also studied. Kinetic analyses reveal that the PZEC degradation rates of AO7 can be approximated in terms of the Langmuir–Hinshelwood model. The value of the adsorption equilibrium constant, K_{AO7}, was 0.149 $(mgl^{-1})^{-1}$, and the value of the kinetic rate constant of the surface reaction, k_c, was 0.50 $mgl^{-1}\ min^{-1}$. These new strain-induced chemical reactions can provide a simple and cost-effective technology for decomposing organic pollutants in aqueous solution by scavenging waste energy such as noise or stray environmental vibrations.



Questions

1. Describe in your own words the smart material presented in this paper and explain its working principle.

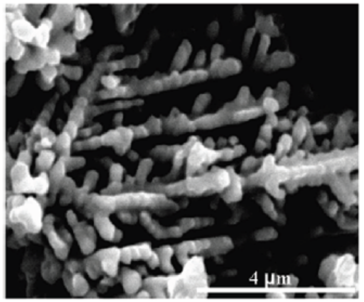
2. Explain the piezoelectrochemical effect used for the decolorization of the solution.

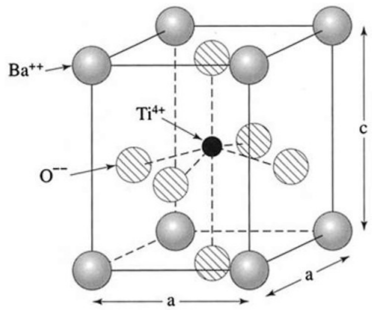
3. Name a possible improvement of the present structure (e.g. think about material properties).

Question 1

Describe in your own words the smart material presented in this paper and explain its working principle.

$BaTiO_3$ microdendrites:

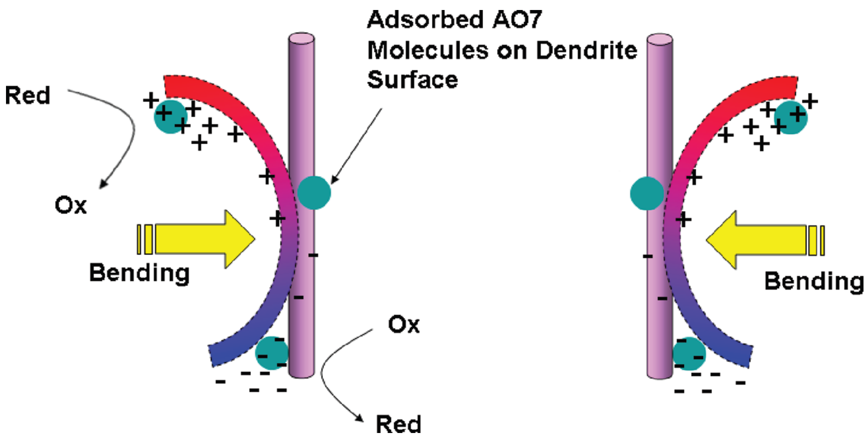




Piezoelectric Material:

- Generation of electrical charge upon applied mechanical stress (ultrasonification)
- $BaTiO_3$ with non-centrosymmetric unit cell structure in the crystal lattice → off centered Ti^{4+}, which creates an electric dipole
  - Upon mechanical stress the Ti^{4+} ion shifts further → change in dipole moment → influencing the polarization strength of the crystal

Explain the piezoelectrochemical effect used for the decolorization of the solution.



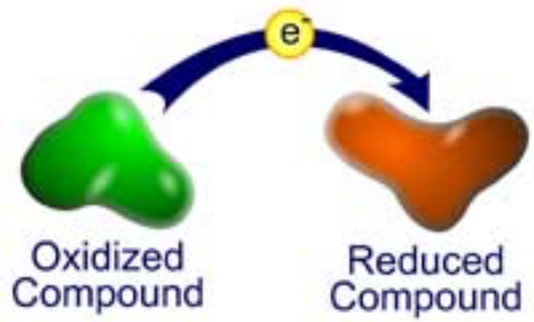
- Ultrasonification causes bending of microdendrites → charge generation on surface
- Photocatalytic decomposition - **Redoxreaction**

Definition:

Chemical Reaction involving the exchange of electron between two different species.

Half Reactions:

1. **Oxidation:** Loss of e^-; increase of oxidation state
2. **Reduction:** Gain of e^-; decrease of oxidation state



Example: $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

Ionic Equation: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Oxidation: $Zn \rightarrow Zn^{2+} + 2\ e^-$

(Zn is loosing neg. charged electrons; increases in overall oxidation state)

Reduction: $Cu^{2+} + 2\ e^- \rightarrow Cu$

(Cu ions gain the free neg. charged electrons; decrease in overall oxidation state)

Question 2

Anode: Reduction

$$4e^- + 4H_2O \rightarrow 4OH^- + 4H^\bullet$$

$$4H^\bullet \rightarrow 2H_2$$

Overall:

$$4e^- + 4H_2O \rightarrow 4OH^- + 2H_2$$

Cathode: Oxidation

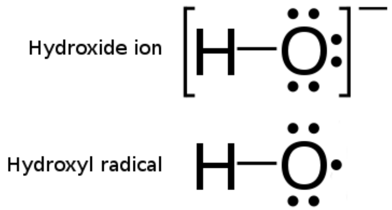
$$4OH^- \rightarrow 4e^- + 4OH^\bullet$$

$$2(OH^\bullet + OH^\bullet) \rightarrow 2H_2O + 2O^\bullet$$

$$2O^\bullet \rightarrow O_2$$

Overall:

$$4OH^- \rightarrow 4e^- + 2H_2O + O_2$$



Semiconductors contain narrow gaps between the valence and conduction bands. Photocatalysis occurs when the produced energy is equal to or more than the energy gap. Induction of electron movement creates e^-/h^+ (neg. electron/pos. hole pairs). The holes will attract electrons from neg. charged OH^- **(Oxidation)** forming Hydroxil radicals (atom with unpaired valence electrons/unfilled electron shell).

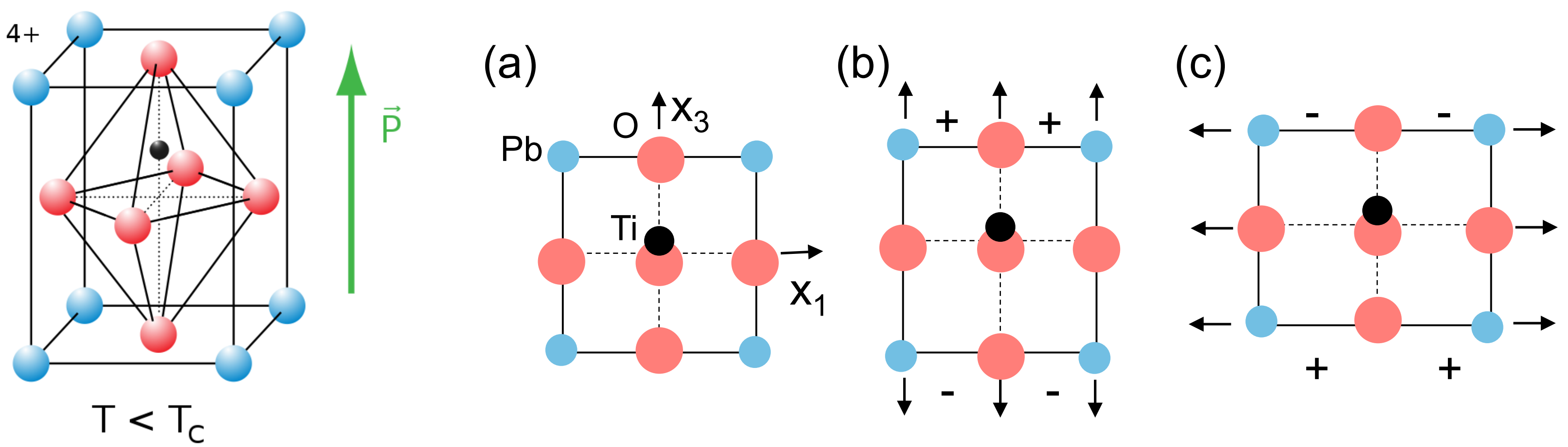
Dye degradation:

$$OH^\bullet + \text{dye} \rightarrow \text{degradation product of dye}$$

$$e^- + \text{dye} \rightarrow \text{degradation product of dye}$$

$$h^+ + \text{dye} \rightarrow \text{degradation product of dye}$$

Piezoelectric Coefficients:



d_{33} ~ 120 pC/N d_{31} ~ 50 pC/N

d_{33}: induced polarization in direction 3 (parallel to direction in which ceramic element is polarized) per unit stress applied in direction 3 **or** induced strain in direction 3 per unit electric displacement applied in direction 3.

d_{31}: induced polarization in direction 3 (parallel to direction in which ceramic element is polarized) per unit stress applied in direction 1 (perpendicular to direction in which ceramic element is polarized)
or induced strain in direction 1 per unit electric field applied in direction 3

http://onlinelibrary.wiley.com/doi/10.1002/0471216275.esm076/full
https://www.americanpiezo.com/knowledge-center/piezo-theory/piezoelectric-constants.html

Typical Properties of Some Piezoelectric Materials

material	T_c(°C)	d_{31}	d_{33} p$^{C/N}$
α-Quartz[a] [b]	—	—	—
$BaTiO_3$	130	−79	190
PZT A[c]	315	−119	268
PZT B[c]	220	−234	480
$PbNb_2O_6$	560	−11	80
$Na_{0.5}K_{0.5}NbO_3$	420	−50	160
$LiNbO_3$[b]	1210	−0.85	6
$LiTaO_3$[b]	665	−3.0	5.7
$PbTiO_3$	494	−7.4	47

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