Bio-inspired and biomimetic materials towards solar energy utilization

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OUTLINE

■ Bioinspired Materials

■ Bioinspired systems towards solar energy utilization
  ➢ Artificial Leaf for artificial photosynthesis
  ➢ Butterfly wing-inspired efficient NIR harvesting system

■ Summary
Biological systems give us many inspirations to mimic in many areas such as their mechanical, optical, electronic, magnetic properties and so forth.
Bioinspired Materials

How to design NEW materials?

Nature Knows

Natural Materials:
- Simple components
- Complicated structures
- Powerful functions

The functions are highly related to their structures.

Insects
- Light harvesting
- Light manipulation
- Hydrophilic
- Hydrophobic

Plants
- Photosynthesis
- Mass transportation
- Mechanical property
- Hydrophilic/hydrophobic

Fish
- drag reducing
- Self-cleaning
- Hydrophobic
- Light manipulation
Nature mimic

- Hierarchical structures (wood, leaves, etc)
- Periodic structures (butterfly wings, compound eyes, etc)
- Nanostructures (DNA, proteins, viruses, and peptide superstructures)
- Hollow structures (fur and skin of polar bear)

Structures & functions
- energy harvesting and conversion
- antireflection,
- structural coloration,
- superhydrophobicity

Metal Oxides
Three-Dimensional Hierarchical
Morphology
Replace Components
Mimic Functions
Reveal Mechanisms
Build Models
Biomimetic synthesis & Applications

in natural photosynthesis, there are two reactions: water splitting and CO2 fixation.

In artificial systems, there are also two reactions. “CO2 Reduction” is more URGENT than “water splitting”
CO₂ Photoreduction

**Challenges**
- Low efficiencies
- Limited photocatalysts
- Use of sacrificial reducing agents

**Strategies:**
- Band-Structure Engineering
- Nanostructuralization
- Surface Oxygen Vacancy Engineering
- Meso-/Microporous Structuralization
- Crystal Facet Engineering
- Z-Scheme Construction

it's important to develop a **Promising** photocatalysts/or system with:

- **Efficient mass flow network**
- **Unique 3D architectures for light harvesting**
- Suitable catalysts with strong reducing over-potential

**Materials:**
- TiO₂
- Titanates: ATiO₃ (A= Sr, Ca, Ba, Pb), AL₄ Ti₄ O₁₅ (A = Ca, Sr, Ba)
- Niobates: HNb₃ O₈, InNbO₄, ANbO₃ (A = Li, Na, K)
- Tantalates: Ta₂ O₅, InTaO₄, ATaO₃ (A = Li, Na, K)
- Vanadates: BiVO₄, Fe₂V₄O₁₃
- Tungstates: WO₃, W₁₈O₄₉, Bi₂WO₆
- d₁₀ metal oxides includes In(OH)₃
- Gallates: Ga₂O₃, ZnGa₂O₄, CuGaO₂
- Germinates: Zn₂GeO₄, In₂Ge₂O₇,
  solid solutions: (Zn₁+x Ge)(N₂Oₓ) and (Ga₁−x Znx)(N₁−x Oₓ).
- Metal sulfides: CdS and ZnS, MnS,
- Polymers: g-C₃N₄

**Strategies:**
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A natural leaf is a synergy of elaborated structures and functional components in order to produce a highly complex machinery for photosynthesis.
The structure of leaf is favorable for light harvesting.

- The focusing of light by the lens-like epidermal cells
- The multiple scattering and absorbing of light within the veins porous architectures
- The propagating of light in the columnar cells in palisade parenchyma acting like light guides

Bundle sheath extensions can transfer light into deeper layers.

- The enhanced effective light pathlength and light scattering by the less regularly arranged spongy mesophyll cells
- The efficient light-harvesting and fast charge separation in the high surface area three-dimensional constructions of interconnected nano-layered thylakoid cylindrical stacks in chloroplast

another important feature of leaf is that the vein network is favorable for efficient water transportation.
The 3D hierarchical architectures with high porosity, high connectivity and high surface areas are favorable for gas diffusion.
Hierarchical porous perovskite titanates (ATiO₃, A = Sr, Ca, and Pb) with three-dimensional architectures for enhanced mass flow

Typical example
Natural Leaf

General method

CO₂ photoreduction (using Water as an electron donor)
Leaf-architectured 3D Artificial Photosynthetic System of Perovskite Titanates

Comparison between natural system and artificial system

The have similar processes: light harvesting, gas diffusion and gas conversion.

In artificial system, we use water and CO2 to produce hydrocarbon fuels.

Han Zhou et al. Scientific reports, 2013, 3, 1667
Natural Photosynthetic system

Artificial Photosynthetic system

**Synthetic procedure**

- Fresh leaves
- Precursors $A(CH_3COO)_2 + Ti(OC_4H_9)_4$ $A=\text{Sr, Ca, Pb}$
- Diluted Acid
- Wash
- Mix/stir
- Infiltration
- Wash, dry
- Heat 100ºC, 24h
- Calcination 600ºC, 8h, O$_2$ atmosphere

similar morphologies between natural leaves and artificial ones.
Bare SrTiO$_3$

- Bare STO evolve CO and CH$_4$ as the main products in the absence of any sacrificial agents.
- The evolution amount of CO is larger than that of CH$_4$ for bare STO.
- Leaf-architectured APS of STO has about 2 fold improvement in activities than the corresponding powder constituents of APS and referenced STO synthesized without templates.
The APS of STO and the powder constituents have the same surface area, but different morphology because of grounding and sonication. The activity enhancement could be attributed to the Enhanced light harvesting and Efficient gas diffusion introduced by the large quality of macropores.
- Au serves as a suitable cocatalyst while Pt not working.
- Control experiment (without light, catalysts, H2O and CO2) prove that H2O supplies protons, CO2 offers a carbon source, and the photocatalyst gives the redox potentials for the whole reaction to finally produce CO and CH4.

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Potential for the realization of carbon cycle.

Artificial systems

Chemical transformation

Photosynthesis

Light

Carbon cycle

Artificial Photosynthesis

Sustainable hydrocarbon fuels (CH₄, CO, H₂…)

Biomass, food, fossil fuels

CO₂+H₂O

O₂

CO₂+H₂O
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  - Artificial Leaf for artificial photosynthesis
  - Butterfly wing-inspired efficient NIR harvesting system

- Summary
Butterfly wing-inspired Plasmonic Nanoarchitectured Hybrid System for efficient NIR utilization

NIR (near infrared light) accounts for about 40% of solar spectrum,

The utilization of NIR light is very important.

Problems

- **limited NIR active photocatalysts** (e.g. Cu$_2$(OH)PO$_4$, WS$_2$, BiErWO$_6$, defect-induced Bi$_2$WO$_6$, H-WO$_3$, H-TiO$_2$, etc.),
- **low efficiency**
- **restricted mechanisms**
  - upconversion process
  - carbon quantum dots doping
  - heterostructure design
  - oxygen vacancies induction
  - localized surface plasmon resonance nanoparticles modification etc.

One main challenge is the development of novel strategies for activity promotion and new basic mechanisms for NIR response.
Some photosynthetic bacteria can use NIR light for photosynthesis.

Black scales of some snake skins can absorb NIR light because of their hierarchical patterns.

However, these NIR harvesting mechanisms in biology have never been applied for the design of new efficient NIR responsive systems.
Butterfly wings have optical properties (e.g. structural color, circular polarization, etc.) because of their unique, structures (e.g. multilayer, photonic crystals, double-facet microlens and so forth).

Certain colored scales of butterfly wings are able for NIR harvesting due to their photonic crystals.

Thus, the exploration and understanding of the NIR responsive mechanisms and further integration of bio-inspired 3D architectures with NIR-active photocatalysts for biomimetic design are highly appealing.
Plasmonic metallic nanostructures

- Plasmonic metallic nanostructures can serve as antennas to absorb visible-to-NIR light through localized surface plasmon resonance (LSPR).
- The absorption wavelength could be adjusted by tuning the morphologies and sizes of the nanostructures.

Nat. Mater., 2015, 14(6), 567-576
we propose a new strategy, inspired by nature’s NIR light responsive architectures prototypes for an efficient far red-to-NIR plasmonic hybrid photocatalytic system. The system is based on controlled assembly of light-harvesting plasmonic gold nanorods onto a typical photocatalytic unit (bismuth vanadate) with biological 3D architecture designs.

- Study the structural effects on the activity promotion
- Investigate light-matter interaction between plasmonic metal nanostructures and semiconductors with unique 3D micro/nanoarchitectures
finite-difference time-domain (FDTD) simulations are performed to investigate the optical property.

compared with the slab model, the absorption enhancement at far red-to-NIR wavelengths (700~1200 nm) reaches about 12%, 25%, 15% and 5% respectively.
Development of Bio-inspired Far Red-to-NIR Photocatalytic System

we controlled assemble Au nanorods onto the surfaces of the butterfly wing derived BVO (BiVO4, bismuth vanadate) system.
Simulative and Experimental Optical Absorption Properties of Bio-inspired Systems

The absorption peak of Au NRs on BVO wing reaches almost twice that of non-structured counterparts, suggesting the remarkable enhancement of optical absorption caused by the butterfly wings’ 3D architectures. (experiment accords with simulation).

The Au nanorods we synthesized have an absorption peak around 750 nm.
The electric field intensity is extremely strengthened by the architecture ($R_E = |E|/|E_0|$):

- $R_E$ reaches 75.89 in the holes of the structure (blue line);
- $R_E$ reaches 30.6 on the surface of the structure (red line);
- $R_E$ reaches 20.83 on the surface of BVO slab (black line).

the rate of electron-hole formation is proportional to the local intensity of the electric field
Photocatalytic Properties

IPA Photodegradation and photoelectrochemical performance of materials with the structure inherited by butterfly wings approximated $2.85$ times and $2$ times than the non-structural ones.

**Structural effects:**

1. Enhancing far red-to-NIR harvesting, up to 25%;

2. Enhancing electric-field amplitude of localized surface plasmon to more than 3.5 times than that of the nonstructural one, which promotes the rate of electron-hole pair formation, thus substantially reinforcing photocatalysis.

Artificial Leaf for artificial photosynthesis

Bioinspired Design

Butterfly wing-inspired efficient NIR utilization system
Design is Nature!

Thank you!

Welcome to State Key Lab of Metal Matrix Composites
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