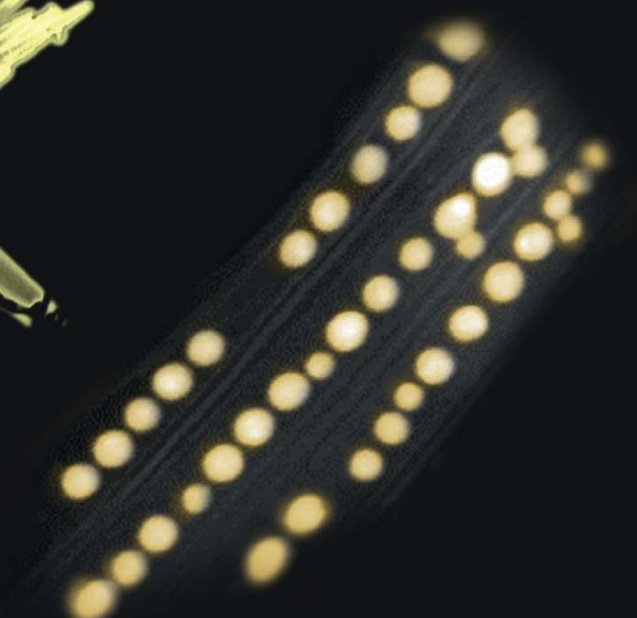
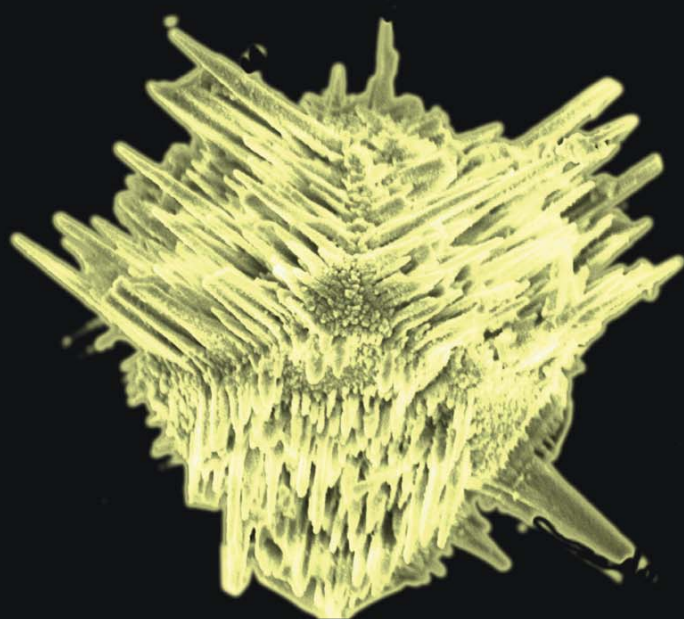


Ying-Chu Chen

Advanced Nanoarchitectures with Photocatalytic Functionality



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Die vorliegende Arbeit wurde von Oktober 2013 bis Januar 2018 am Institut für Anorganische Chemie des Karlsruher Instituts für Technologie (KIT) unter Anleitung von Prof. Dr. Claus Feldmann angefertigt.

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Abstract

Two novel nanoarchitectures – including the highly branched spikecube exemplified by β -SnWO₄ and the biomimetic nanopeapod manifested in Au@Nb@H_xK_{1-x}NbO₃ –were put forward for the first time in this thesis, particularly aiming at enriching the library of pattern designs for sunlight-driven photo(electro)chemical applications.

Specifically, β -SnWO₄ spikecubes were entitled on the basis of the peculiar morphology, wherein bundles of nanopillars were self-aligned with quasi-periodicity onto each sharp face of hexahedral cube cores. The reinforced surface roughness stemmes from the nanoarms with a well-defined length(spike)-to-diameter(cube) aspect ratio of 0.3 and gives rise to a nearly 5-fold increase in specific surface area, suggesting more solid surface readily accessible to the reactants to trigger desirable catalytic reactions under illumination of a photoflux. Noteworthily, this geometric engineering was particularly carried out on a Scheelite-type (ABO₄) β -SnWO₄ crystal in terms of the characteristic twisted coordination structure mediated by the stereoactive electron lone pair, allowing additional textural modifications. Specifically, the interaction between the “non-bonding” electron pair on Sn(II) and the O-2p orbitals tailored the electronic band structure of β -SnWO₄ with a visible-light-active band gap of 2.91 eV and a subtle conduction and valence band positions, endowing the photoexcited electron-hole pairs on β -SnWO₄ with strong reducing and oxidizing power, respectively. Consequently, an outstanding photocatalytic activity in degrading organic dyes was observed for the β -SnWO₄ spikecubes with an enhancement more than 150% in comparison with a benchmark visible-light-active WO₃ photocatalyst, which originated mostly from the synergy of the aforementioned effects.

Moreover, the biomimetic peapod-analogous blueprint additionally introduced in this dissertation aims at further subduing photoelectrocatalytic response over a longer wavelength regime far beyond ultraviolet (UV) and blue light. Metal-specific plasmonic nanoantennas were alternatively employed in this design in terms of the straightforward adaptability in light harvesting ability via size, geometry and configuration. Particularly, semi-infinite sub-10 nm Au@Nb core-shell nanoparticle (CS-NP) chain with nanometric breaks residing unidirectionally inside the cavity of tubular H_xK_{1-x}NbO₃ nanoscrolls (NSs). This biomimicry endowes Au@Nb@H_xK_{1-x}NbO₃ nanopeapods (NPPs) with broadband light responses, wherein the niobate NSs and the Au@Nb CS-NP absorb UV and visible light *via* interband transition and surface plasmon resonance, respectively. More importantly, the strong near-field plasmon coupling between neighboured Au@Nb CS-NPs allows the Au@Nb@H_xK_{1-x}NbO₃ NPPs to absorb near-infrared (NIR) light.



Consequently, the characteristic absorption spectrum matches well with the full solar spectrum. Moreover, the 3D Schottky junction in the NPP structure additionally favors the transfer of plasmon-promoted “hot” electrons from bimetallic Au@Nb to $H_xK_{1-x}NbO_3$ to participate in the subsequent chemical conversion. Overall, a quadruple enhancement relative to an antenna-less photocatalyst and NIR-triggered water splitting as the proof-of-concepts manifest that the Au@Nb@ $H_xK_{1-x}NbO_3$ NPPs can readily convert the photon energy into useful chemical fuels.

Zusammenfassung

Zwei neuartige Nanoarchitekturen – darunter β - SnWO_4 als hoch verzweigter Spikecube und die biomimetischen „Nanoerbsen“, die durch $\text{Au@Nb@H}_x\text{K}_{1-x}\text{NbO}_3$ repräsentiert werden – wurden in dieser Arbeit zum ersten Mal erwähnt und stellen eine Erweiterung der Bibliothek aus Morphologien für die mit Sonnenlicht angetriebenen photo(elektro)chemischen Anwendungen dar. Insbesondere β - SnWO_4 -Spikecubes sind aufgrund ihrer eigenartigen Morphologie, bei welcher Bündel aus „Nano-säulen“ durch Selbstanordnung regelmäßig auf den Flächen der Würfel gewachsen sind. Die hohe Oberflächenrauheit rührt vom wohldefinierten Länge(Spitze)-zu-Durchmesser(Würfel)-Seitenverhältnis von 0,3 der Nanoarme her und ruft eine nahezu 5-fache Zunahme der spezifischen Oberfläche hervor, was viel Oberfläche andeutet, die für Reaktionspartner zum Initiieren der erwünschten katalytischen Reaktionen unter einer Photoflux-Beleuchtung leicht zugänglich ist. Darüber hinaus wird diese geometrische Besonderheit insbesondere an einem scheeliteartigen (ABO_4) β - SnWO_4 -Kristall hinsichtlich der charakteristisch verdrillten Koordinationsstruktur, welche durch das einzelne stereoaktive Elektronenpaar induziert wird, erzielt. Dies ist die Voraussetzung für zusätzliche strukturelle Modifikationen ermöglicht. Die Wechselwirkung zwischen dem „nicht-bindenden“ Elektronenpaar bei Sn(II) und bei den O-2p-Orbitalen verändert die elektronische Bandstruktur des β - SnWO_4 zu einer im sichtbaren Licht aktiven Bandlücke von 2,91 eV, was für die Erzeugung Lichtangeregter Elektron-Loch-Paare bei β - SnWO_4 , sehr hilfreich ist. Daraus folgend konnte eine Erhöhung von mehr als 150% im Vergleich mit einem im sichtbaren Licht aktiven WO_3 -Photokatalysator als Bezugspunkt festgestellt werden, die von der Synergie der obengenannten Bandstruktur-Effekte herrührt. Folglich wurde an den β - SnWO_4 -Spikecubes eine herausragende photokatalytische Aktivität beim Abbau der organischen Farbstoffe festgestellt.

Zudem zielt der biomimetische Entwurf einer Erbsenschote, den diese Doktorarbeit beinhaltet, auf eine weitere Adaption der photoelektrokatalytischen Reaktion an eine größere Wellenlänge weit hinter ultravioletten (UV) und blauen Licht. Metallspezifische plasmonische Nanoantennen wurden in diesem Design eingesetzt. Hinsichtlich der unkomplizierten Anpassungsfähigkeit in der Einstellung des Lichtertrages über Größe, Geometrie und Konfiguration sind diese einfach einsetzbar. Insbesondere ist eine Sub-10 nm Au@Nb Core-Shell-Nanopartikelkette (CS-NP) mit nanometrischen Brüchen in eine Richtung im Innern der Kavität der rohrförmigen $\text{H}_x\text{K}_{1-x}\text{NbO}_3$ -Nanoschnecken (NSs) vorhanden. Diese Biomimikry erlaubt den $\text{Au@Nb@H}_x\text{K}_{1-x}\text{NbO}_3$ -Nanopeapods (NPPs) Breitband-Lichtreaktionen, wobei das Niobat NSs



und das Au@Nb CS-NP das UV- und sichtbare Licht durch einen Interband-Übergang bzw. durch die Oberflächenplasmonenresonanz absorbieren. Darüber hinaus ermöglicht die starke Nahfeld-Plasmonenkupplung zwischen dem benachbarten Au@Nb CS-NPs im Au@Nb@H_xK_{1-x}NbO₃ NPPs, das nahe Infrarotlicht (NIR) zu absorbieren. Folglich ist das charakteristische Absorptionsspektrum nach dem vollen Sonnenspektrum ausgerichtet. Zudem bevorzugt die 3D-Schottky-Verbindung in der NPP-Struktur den Übergang der plasmonengeförderten “heißen” Elektronen vom bimetallicen Au@Nb zum H_xK_{1-x}NbO₃ um diese mit in die nachfolgende chemische Umwandlung einzubinden. Alles in allem zeigt die vierfache Erweiterung eines antennenlosen Photokatalysators zu einer mit NIR initiierten Wasserspaltung, dass Au@Nb@H_xK_{1-x}NbO₃ NPPs die Photonenenergie leicht in nützliche chemische Brennstoffe umwandeln kann.



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1. Introduction and Brief History

Nature is the starting point for advancing science and technology. Replication and adaption of natural systems including elements, structures and processes, so-called biomimicry, routinely help humans to solve problems throughout their existence.^[1] One of the extensively studied themes in this field is the photosynthesis in plants. The featured solar-to-chemical energy conversion involved in this course has triggered worldwide scientists and engineers to emulate using man-made materials. This is generally called artificial photosynthesis. The first demonstration was performed in 1839 by Becquerel.^[2] In his study, the charge transfer involved in a sunlight-driven chemical reaction was manifested in an electric current flowing from an illuminated silver chloride electrode immersed in an acidic chemical medium to a metallic counter electrode *via* an external circuit (Fig. 1.1). Extensive studies followed up his unprecedented work with a systematic investigation on such photoelectrochemical phenomena in other semiconducting materials, such as Si, Ge, GaAs, ZnO, CdSe, KTaO₃, SrTiO₃ and TiO₂.^[3-28] These pioneering works prior to 1970 substantially established the fundamentals of photoelectrochemistry. Afterwards, the work by Fujishima and Honda in 1972 was of particular importance.^[29] They used TiO₂ as the electrode material, which was irradiated under a photoflux to split water (H₂O) and which is similar in many respects to natural photosynthesis. The significance of their results lies in reinforcing the availability of oxygen (O₂) and especially of hydrogen (H₂), which is the next-generation clean fuel, upon water cleavage under renewable sunlight casting. More importantly, the sustainability and environmental benignity in the context of this photoelectrosynthesis effectively alleviate contemporary public concerns with the oncoming exhaustion of fossil fuel and global temperature increases.

Although the solar fuel generation is of primary importance, other nowadays critical issues in addition to the global warming including food crisis and water stress can also be mitigated *via* artificial photosynthesis. In particular, the reduction of primary greenhouse gas carbon dioxide (CO₂) to carbohydrates,^[30] the production of ammonium (NH₄⁺) and nitrate (NO₃⁻) fertilizers from atmospheric nitrogen (N₂)^[31] and the remediation of raw and waste water^[32] are all possible *via* photoelectrocatalysis, thus stimulating a tremendous research activity in this realm. Further important early contributions emerged between 1978 and 1979 by Bard,^[33] who established the principles of photoelectrocatalysis (PEC) not only applicable to a cell configuration but also appropriate for a particulate system (miniaturized metallic counter electrode granulates the semiconductor colloids), and by Nozik,^[34] who formulated such concept of a short-circuited photoelectrocatalytic cell as a “photochemical diode”.

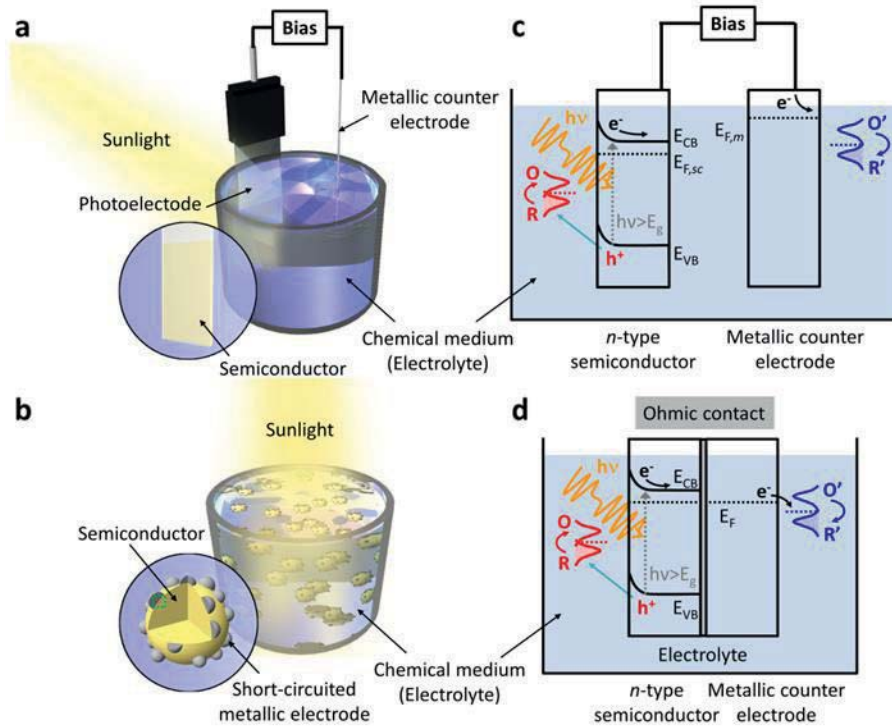


Figure 1. (a) Electrochemical cell and (b) suspended metallized powder configurations for carrying out photoelectrocatalysis using *n-type* semiconductor. Energetics of the (c) photoelectrochemical cell and (d) photochemical diode (framed region in Fig. 1.1b). Abbreviations used: $h\nu$, photon energy; E_g , bandgap of the semiconductor; E_{CB} , conduction band edge of the semiconductor; E_{VB} , valence band edge of the semiconductor; $E_{F,sc}$, Fermi level of the semiconductor; $E_{F,m}$, Fermi level of the metallic counter electrode; E_F , Fermi level of the metallized semiconductor.

Their formulations advanced the development in many aspects, including i) the material scope branching out into semiconductors having high electrical resistivity that cannot work as an electrode, ii) the synthetic field opened up to additional more facile but less expensive protocols, and iii) the efficiency record of solar-to-chemical conversion going up to a new plateau owing to strong light scattering within the suspended particles (Fig. 1.2). Later in the early eighties, Grätzel's group excellently exemplified their argumentation with a series of experimental evidences using a variety of semiconducting colloids.^[35-37] More importantly, most colloids were characterized by a particle size of few tens of nanometers, rendering these reports acknowledged as another significant milestone highlighting the fusion of modern nanoscience with photoelectrochemistry. The use of nanomaterials in the *bias-free* photochemical diode brings numerous advantages, including shortening the migration pathway of photogenerated carriers (electrons (e^-) and holes (h^+)) within semiconducting materials and increasing the surface area for carrier transfer across the solid/liquid

interface.^[33,34] Most significantly, the specific size quantization effect renders the optoelectronic properties, e.g. the bandgap, the carriers' lifetime and the catalytic activity of these nanoscale granules, size-adaptable.^[38-40]

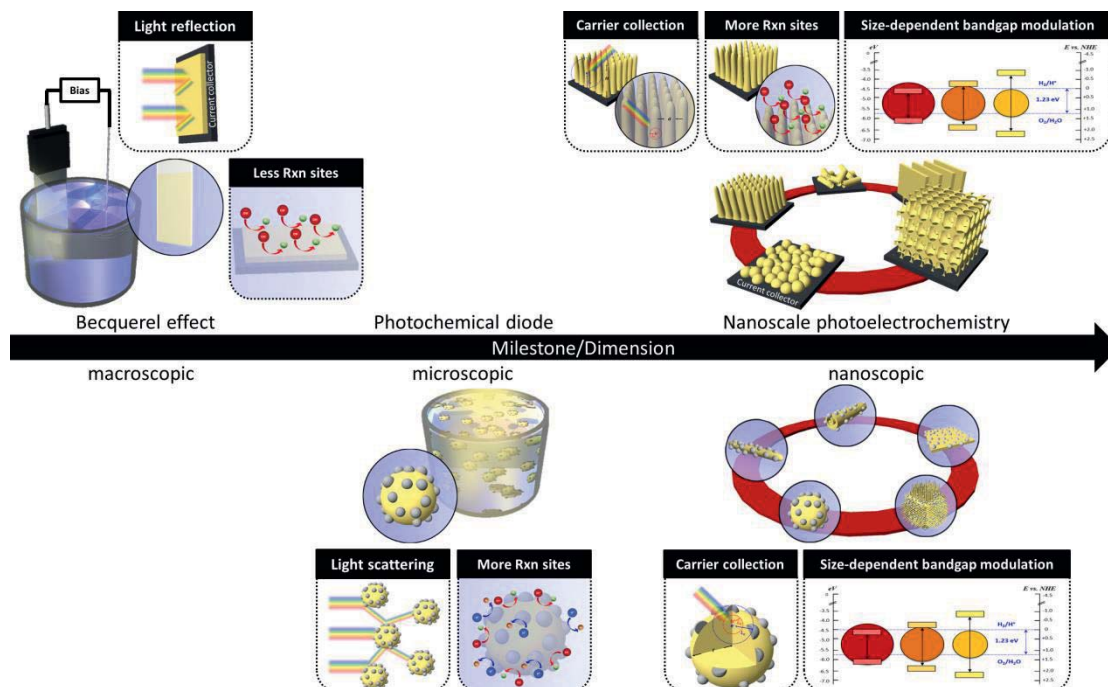


Figure 1. 2. Chronological summary of significant milestones, including dimensional migration and nanostructuring strategies, in photoelectrochemistry. Abbreviations used: L_h , mean free diffusion length of the hole (h^+); L_e , mean free diffusion length of the electron (e^-). Geometries of the exemplary nanoparticle and nanotip are characterized by the radius (r), the diameter (d) and the height (H).

The intriguing consequences of nanoengineering likewise work well in photoelectrochemical cell and lead to the exploitations in advanced nanoarchitecture that are extensively studied in bilateral classes.^[41-44] This study deals with such burgeoning interests via putting forward two modern nanoarchitectures including the highly branched spikecubes exemplified by β - SnWO_4 and the biomimetic nanopeapods manifested in $\text{Au@Nb@H}_x\text{K}_{1-x}\text{NbO}_3$ for the first time to enrich the library of pattern designs for photoelectrocatalysis (Fig. 1.3).^[45,46] In-depth discussions on these hierarchical structures begin with an argumentation on the interplay between the textural properties and the local chemical bonding between the constituent elements. The elaborations of the dependency of the architectural geometry on the coordination environment of these chemical systems and the synthetic methodologies follow up to gain a substantial insight into making and especially integrating the nanomaterials at a satisfactory precision level. All in all, this thesis

contributes to the synergism of overall atomic and nano-/micro-scopic treatments on the macroscopically photoelectrocatalytic activity.

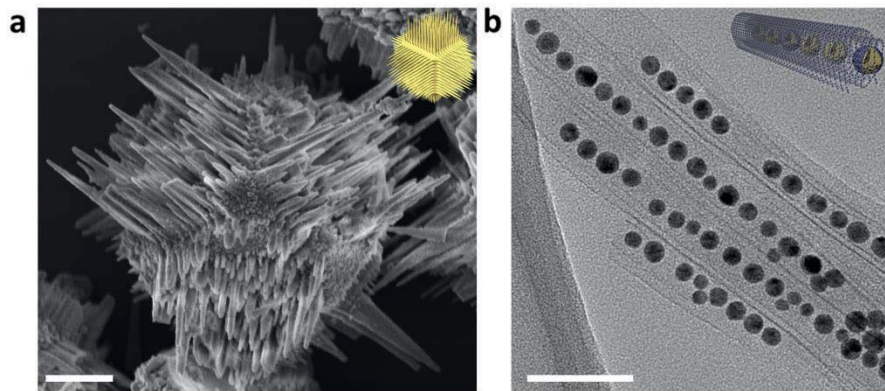


Figure 1. 3. (a) SEM image of multiarmed β -SnWO₄ spikecube (scale bar: 2 μ m) and (b) TEM image of bioinspired Au@Nb@H_xK_{1-x}NbO₃ nanopeapods (scale bar: 50 nm) (*adapted from reference[45,46]*).