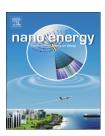


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#### RAPID COMMUNICATION

# Heterogeneous bacteriorhodopsin/gold nanoparticle stacks as a photovoltaic system



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#### **KEYWORDS**

Bacteriorhodopsin; Stack system; Photocycle; Photoelectric performance

#### **Abstract**

To mimic the stack structure of granum, for the first time we demonstrate bacteriorhodopsin (bR)/gold nanoparticles (AuNPs) heterogeneous multilayers to perform as a novel photovoltaic stack system with improved photoelectric performance. Upon a cooperative control of the diameter of AuNPs and the stacking layers, the photocurrent can be effectively regulated to reach about 350 nA cm $^{-2}$ . The possible mechanism for enhanced photocurrent recorded in our system is revealed by analyzing the flash kinetics of photocycle intermediates  $M_{412}$ ,  $O_{640}$ , and  $J_{600}$  of bR layers, which are accelerated under proper AuNPs in this stacking structure. A bypass photocycle model of bR photocycle from  $M_{412}$  to  $B_{570}$  state is proposed and supported by tested accumulation of  $M_{412}$  and  $O_{640}$  intermediate during the bR photocycle process. Interestingly, with this stack system, the input flickering light can be effectively modulated into regular photoelectric signals that are well controlled under different flickering frequency and proton concentration gradient. Based on above results, this system potentially serves as solar energy converter to power nano-devices. © 2014 Elsevier Ltd. All rights reserved.

#### Introduction

Photosynthetic systems in nature are green and efficient energy technologies for solar energy conversion over millions of years. It includes two main different photosynthetic systems [1], well-developed chloroplast system in green plant and bacteriorhodopsin (bR) system in *Halobacterium halobium*. Green plants, meanwhile, exhibit a process for light-to-charge conversion that provides a useful model for using solar energy efficiently. Granum [2], the core organ in photosynthesis, consists of a stack of  $\sim$ 10-100 thylakoids containing pigments and electrons acceptors, which provide a larger surface area to capture solar radiation efficiently. Upon light stimulated the antenna pigment molecules, electrons are excited and transferred to accomplish photoelectric conversion process (Figure 1a). Recent investigation has reported that this

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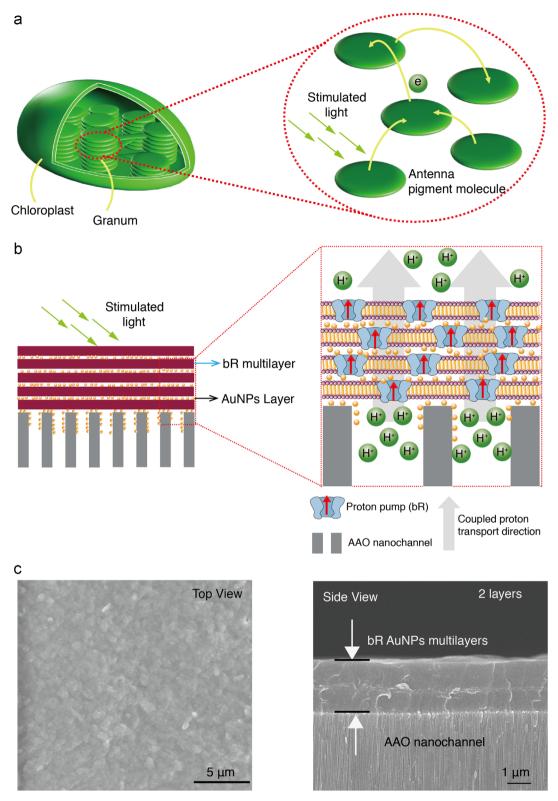


Figure 1 Design and mimic of the stacking structure of granum. a, Diagram of chloroplast in green plant. The granum contained disc-like photoreceptors. Evolution has frequently used chloroplast to complete the photosynthetic process in green plant. After light is captured through the antenna pigment molecules, electrons are excited and transferred. b, Scheme of the bR/AuNPs heterogeneous structure. The bR and Au nanoparticles were designed to deposit alternatively on the AAO nanochanels. After light illumination, the protons were transferred from CP side to EC side directionally. Owing to the surface plasmonic effect of AuNPs, the photocycle path was shortened to pump more protons in a fixed time. The pore size of the AAO nanochanels is  $59\pm6$  nm and keeps constant in all experiments mentioned in this article. c, Top view of the stacking structure from the bR side and the side view of bR/AuNPs stacks. bR layers densely packed at the surface of AAO nanochannel. In our bR/AuNPs stack, the bR layers are densely covered the surface of AAO nanochannels to maintain the proton gradient between two half cells.

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