



## Real-time plasmonic monitoring of electrocatalysis on single nanorods☆☆☆



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### ABSTRACT

Changes in the optical properties of single gold nanorods during electrocatalytic oxidation of glucose in alkaline media are monitored in real-time by single-nanoparticle dark-field spectroelectrochemistry. The spectral scattering characteristics under dynamic potential scan conditions are closely related to the electrochemical processes, and the electrochemical catalytic mechanism of the process is discussed. Moreover, changes in free-electron density are evaluated using a Drude dielectric function with charge density-modification. The proposed sensing technique based on plasmonic analysis shows significant promise for the design and research of electrochemical catalytic systems at the single-nanoparticle level.

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### 1. Introduction

Localized surface plasmon resonances (LSPR) are collective oscillations of conduction band electrons in a metal nanoparticle [1]. Recently, the study of LSPR properties of noble metal nanostructures has led to significant advances and new applications in nanophotonic devices and circuits [2–4], plasmonic waveguides [5], Fano resonances [6,7], surface enhanced spectroscopy [8–10], plasmonic nanoantennas [11], solar energy conversion [12–14], biological sensing and imaging [15–18], and in life sciences [18–23]. A nanoparticle's size, shape, electron density and dielectric (electronic) properties as well as its dielectric environmental changes can influence its LSPR properties [24]. Charge transfer and storage processes have been a growing focus, and understanding fundamental aspects of the physical and chemical process governing charge transfer at the nanoscale is of paramount importance [25]. Noble metal nanostructures have served as a heterogeneous catalyst in various chemical transformations, from the synthesis of fine chemicals through pollutant removal to electrochemical cells for energy conversion [26,27]. In order to investigate electrochemical catalytic reactions by plasmonic spectroelectrochemistry techniques, bifunctional

noble metal structures that have plasmonic properties and can serve as a catalyst are required [28]. It is critical that nanoparticle size, shape and composition are considered when engineering nanocatalysts. Especially considering that nanocatalysts are often inhomogeneous and this can lead to heterogeneity in the electrochemical catalytic activity. Therefore, only average efficiency is obtained by ensemble catalytic measurements. To effectively study these catalytic processes and eliminate ensemble averaging, single particle spectroscopy techniques are required [29]. This coupled with the fact that it is extremely challenging to study heterogeneous catalytic redox systems on noble metal nanocrystal surfaces means a single particle approach is especially pertinent.

Numerous factors influence catalytic surface reaction processes including surface area, facets and composition [27]. Model systems with single-crystalline facets have been studied under idealised ultrahigh vacuum conditions [30,31]. For instance, gold nanorods have served as model catalysts providing information on aspects of reactions catalyzed by oxidation of ascorbic acid on a gold nanocrystal surface, including features such as charge transfer steps [32,33]. In order to further understand and improve these systems, it is important to monitor catalysis in real time [34]. However, conventional surface interrogation techniques usually require high-vacuum conditions or are limited to ensemble average measurement with high cost [35]. It is a major challenge to correlate the results obtained from model systems or artificial reaction regimes to nanostructure catalysis under real reaction conditions [27].

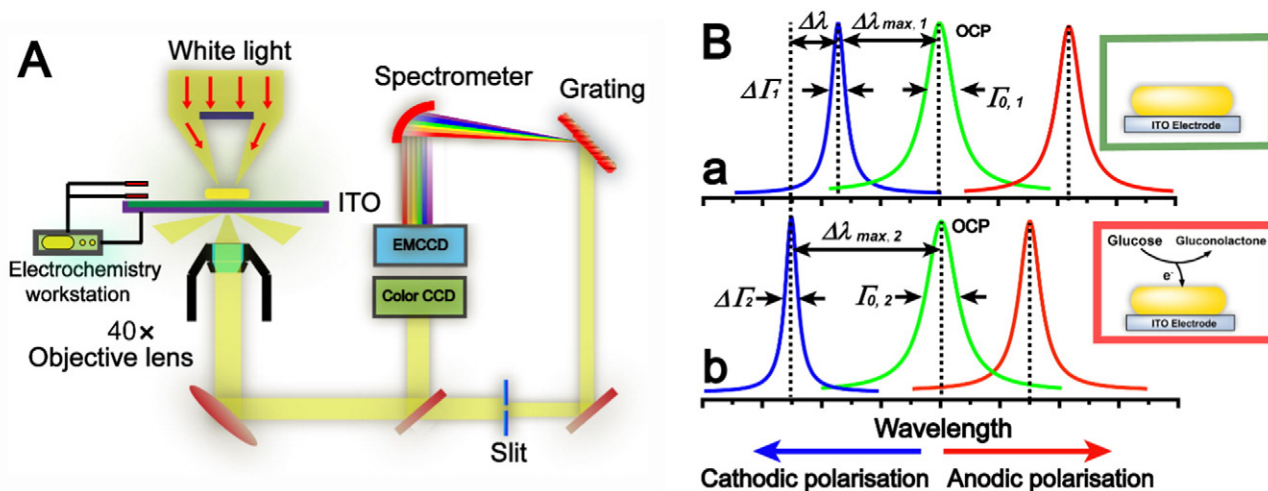
Herein, a novel plasmonic spectroelectrochemistry technique for the study electrocatalytic reactions *in situ* is revealed. Plasmonic

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☆☆ Dedicated to Professor Hong-Yuan Chen on the occasion of his 80th birthday and in recognition of his great contributions to electroanalytical chemistry.

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**Fig. 1.** (A) Experimental setup for single nanoparticle plasmon spectroelectrochemistry: dark-field microscopy coupled with an electrochemical workstation. (B) Schematic representation of the direct localized plasmon sensing strategy and real-time monitoring of single-nanoparticle electrochemical catalysis. Scattering spectra versus wavelength at different polarisation potentials are shown in the absence (a) and presence (b) of glucose, respectively. The scattering spectrum (green line) of a single gold nanorod shown in (a) and (b) was obtained at open circuit potential (OCP). Scattering spectra (red and blue lines) were obtained under anodic polarisation and cathodic polarisation, respectively. Spectral shifts,  $\Delta\lambda_{max}$ , and changes in the peak full-width at half maximum ( $\Delta\Gamma$ ) induced by catalysis serve as a readout providing information on the electrocatalytic oxidation of glucose on the single gold nanorod. The  $\lambda_{max}$  and  $\Gamma$  obtained at OCP in the absence and presence of glucose serve as reference points to calculate the  $\Delta\lambda_{max}$  and  $\Delta\Gamma$ .

spectral characteristics are used to ascertain information on electrocatalytic reactions occurring at noble metal nanoparticles under dynamic potential control (Fig. 1). Electrocatalytic oxidation of glucose in alkaline media was chosen as a suitable and important model reaction, not least due to the potential for exploitation of glucose as a next generation energy source [34,36]. As such the electrocatalytic oxidation of glucose at single particle level is investigated for the first time. LSPR spectral changes are correlated to catalytic reaction steps, which can be used to postulate the electrochemical redox reaction mechanism at single-nanoparticle level.

## 2. Experimental

### 2.1. Materials

Indium tin oxide (ITO)-coated glass sheets (sheet resistances  $20\text{--}30\ \Omega\ \text{sq}^{-1}$ ; 1 mm thickness) purchased from Shenzhen Laibao Hi-tech Co. Ltd. (Shenzhen China), were cut into small pieces ( $20\ \text{mm} \times 20\ \text{mm}$ ) and coated with a polydimethylsiloxane (PDMS) cell to serve as the working electrode. Potassium hydroxide (KOH), acetone (AR), isopropanol (AR), ethanol (AR) and potassium chloride (KCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai China). Glucose was purchased from Sigma-Aldrich Co. Gold nanorods (40 nm; 65 nm; 10 O.D.) were purchased from Nanoseedz (Hong Kong, China). The dimensions of the gold nanorod used in this study were  $44 \pm 3\ \text{nm}$  in length and  $98 \pm 6\ \text{nm}$  in diameter ( $n > 150$ ) as characterised by transmission electron microscopy (TEM, JEOL JEM-2100, Japan). All reagents were of analytical grade and used as received without any further purification. Ultrapure water, filtered by a Milli-Q reagent water system at a resistivity of  $>18\ \text{M}\Omega\ \text{cm}$ , was used throughout the experiments. The ITO-coated glass was cleansed first by ethanol, and then washed successively in acetone, isopropanol and pure water with at least 30 min sonication. Lastly they were dipped in a mixture of pure water, hydrogen peroxide and ammonium hydroxide (volume ratio, 5:1:1) and heated to boiling for at least 30 min [10], and then dried with nitrogen gas. Gold nanorods were immobilised on the ITO electrodes through electrostatic adsorption by placing the ITO electrode in the diluted gold nanorod solution (300 times) for 5 min. Then, the gold nanorod modified ITO electrodes were rinsed with copious amounts of water prior to dark-field measurements. The gold nanorod

modified ITO electrodes were stable to cyclic voltammetric scanning, as shown in Fig. S1.

### 2.2. Instrumentation

#### 2.2.1. Electrochemistry

All electrochemical experiments were performed on a CHI660E electrochemical workstation (CH Instruments Inc.) in a conventional one-compartment cell in conjunction with a standard three-electrode system. A PDMS microelectrochemical flow cell was used in the electrochemical experiments (Schematic S1). ITO electrodes modified with gold nanorods served as the working electrode. A Pt wire electrode served as the counter electrode and another Pt wire electrode functioned as reference electrode. The potential of the Pt reference electrode was calibrated through a cyclic voltammetry scan of potassium ferricyanide (Fig. S2, Supporting information). The  $\Delta E_0^{1/2}$  was 0.4 mV between using Pt quasi-reference electrode and saturated calomel reference electrode (SCE) in 5.00 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution, respectively. Ensemble gold nanorods modified ITO electrodes were prepared by spin-coating three drops of gold nanorods solution onto an ITO electrode (geometry area ca.  $0.50\ \text{cm}^2$ ). Experiments were carried out with KOH as the supporting electrolyte, and the solutions were purged with nitrogen (20 min) before electrochemical experiments. All solutions were stored under an atmosphere of nitrogen and all experiments were performed at room temperature  $25 \pm 2\ ^\circ\text{C}$ .

#### 2.2.2. Dark-field microscopy

Optical dark-field spectrum measurements were recorded using a Nikon eclipse Ti-U inverted microscope equipped with a dark-field condenser ( $0.8 < \text{NA} < 0.95$ ) and a  $40\times$  objective lens ( $\text{NA} = 0.8$ ). Illumination was provided by a 100 W halogen lamp which was used to excite the gold nanorods generating the local plasmon resonance scattering light. The scattering light was focused onto the entrance port of a monochromator (Isoplane SCT 320) that was equipped with a grating (grating density: 300 lines/mm; blazed wavelength: 500 nm) to disperse the scattering light. Then, the scattering light was recorded by a  $400 \times 1600$  pixel cooled spectrograph CCD camera (ProEM+: 1600eXcelon3, Princeton Instruments, USA). A true-colour digital camera (Nikon, DS-f), Japan) was used to record the field of the microscope for coregistration with the monochromator. Adjustable entrance slits can

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