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ABSTRACT

The formation of methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) perovskite into mesoporous titania (TiO$_2$) scaffold via a sequential deposition method is known to offer high quality films for good photovoltaic device performance. The local kinetics at the lower interface between the mesoporous TiO$_2$ film and the collecting electrode govern perovskite growth and formation. Here, we have used a NanoPlasmonic Sensing (NPS) approach with gold (Au) nanosensors to monitor the formation of CH$_3$NH$_3$PbI$_3$ perovskite at the lower interface of up to 650 nm mesoporous TiO$_2$ films. This technique provides time-resolved spectral shifts of the localized surface plasmon resonance at different operating temperatures and methylammonium iodide (CH$_3$NH$_3$I$_3$) concentrations by recording changes in the local vicinity of the Au nanosensors at the mesoporous TiO$_2$ film interface. Analytical studies included ellipsometry, scanning electron microscopy, X-ray diffraction, and photoluminescence spectroscopy. The results show that both the intensity of the NPS response and NPS rate constants are correlated with the operating concentrations and temperatures of CH$_3$NH$_3$I as well as CH$_3$NH$_3$PbI$_3$ perovskite growth in mesoporous TiO$_2$.

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I. INTRODUCTION

Perovskite solar cells based on alkylammonium metal trihalide light-absorption layer offer the promise for a breakthrough for next generation solar devices. Particularly, the attractive class of methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$; MAPbI$_3$) exhibit several advantages of unique optical characteristics with bandgap tunability, high mobility and long carrier lifetime, and long-range electron-hole diffusion lengths. Perovskite films have been deposited via either thermal evaporation or solution processing. The two common pathways often applied during film formation are the one-step method in which the reactants are thoroughly mixed prior to deposition and the two-step route where the precursors are sequentially deposited. Remarkably, much better control over the perovskite morphology was observed using the two-deposition route to either thick or thin mesoscopic metal oxides. The growth and fabrication conditions of these films significantly affect the performance of the fabricated photovoltaic devices.

In the pioneering work of Burschka et al., they have applied a sequential solution deposition protocol to deposit a thin film of PbI$_2$ into ~350 nm thick mesoporous TiO$_2$, followed by an appropriate dipping in a CH$_3$NH$_3$I/isopropanol solution for perovskite conversion. The small crystallite size of PbI$_2$ deposited in the mesoporous TiO$_2$ host matrix allows remarkable perovskite conversion upon diffusion of CH$_3$NH$_3$I. The complete conversion of crystalline perovskite was notably obtained within a few seconds. They monitored the perovskite formation integrally by optical
absorption emission and X-ray diffraction (XRD) spectroscopy, without providing insight into reaction dynamics of perovskite formation at the interface between the mesoporous TiO\textsubscript{2} film and the collecting electrode.

In this paper, we demonstrate the use of nanoplasmonic sensing (NPS) to detect the formation kinetics of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite at the interface of up to \~650 nm compact/mesoporous TiO\textsubscript{2} films with Au nanodisks. We monitor time-resolved spectral shifts of the Localized Surface Plasmon Resonance (LSPR) peak induced by the embedded plasmonic Au sensors. We assess the formed materials at the interface according to analytical results obtained by NPS and other characterization techniques.

II. EXPERIMENTAL

A. Materials

Insplorion sensors with a dense TiO\textsubscript{2} coating were purchased from Insplorion AB (Gothenburg, Sweden). TiO\textsubscript{2} paste (average particle size of 20 nm) was acquired from Dyesol. Lead iodide (PbI\textsubscript{2}) and methyl ammonium iodide (CH\textsubscript{3}NH\textsubscript{3}I: MAI) were purchased from Solaronix. Dimethylformamide (DMF), propanol, and ethanol were purchased from Sigma-Aldrich.

B. Film formation

The NPS sensors monitor changes taking place on the surface of spacer layer (a 10 nm dielectric layer aimed to tailor surface chemistry and protect Au nanosensors) via locally, strongly enhanced electromagnetic (EM) field that often extends a few tens of nanometers. Standard films comprising fused silica coated with Au nanodisks (100 nm diameter and 20 nm height) and 10 nm dense layer of compact TiO\textsubscript{2} as a dielectric spacer layer have been used in various NPS experimental system arrangements. In our work, these films were used following a procedure adapted from the pioneer work in Ref. 1. We spin-coated an additional layer of mesoporous TiO\textsubscript{2} prepared by mixing a commercial TiO\textsubscript{2} paste from Dyesol and ethanol (2:7 wt. %) at 5000 rpm for 30 s. The films are calcined at 500 °C for 30 min. The thickness of mesoporous TiO\textsubscript{2} films was 650 nm, which is measured using the VASE Ellipsometer VB-400. Then, 1M (462 mg/ml) of lead iodide (PbI\textsubscript{2}) in dimethylformamide (DMF) was prepared under stirring at 70 °C. The mesoporous TiO\textsubscript{2} films were consequently infiltrated with PbI\textsubscript{2} by spin coating at 6000 rpm for 90 s and dried at 70 °C for 30 min. Different concentrations of CH\textsubscript{3}NH\textsubscript{3}I (MAI) in 2-propanol ranging from 5 to 15 mg/ml at various temperatures (25–53 °C) were prepared for \textit{in situ} monitoring of perovskite formation.

C. \textit{In situ} nanoplasmonic sensing of MAPbI\textsubscript{3} perovskite formation

Insplorion Xnano was used to monitor nanoplasmonic peaks during MAPbI\textsubscript{3} perovskite formation.

Initially, a blank measurement was taken for a fused silica substrate for subtraction. The coated Au sensor film was placed inside the system chamber, and the wavelength scan shows that the nanoplasmonic peak position of a sensor is located at 800 nm –900 nm depending on the Au disk size and distribution of the gold nanoparticles. The Au nanodisks, which act as optical antennas, respond to events occurring at the interface between the sensor surface and the sample material [Figs. 1(a), 1(c), and 1(d)].
As a result, it is possible to probe the kinetics of the reactions occurring at the lower interface. A peak-fitting method proposed by Dahlin et al. is applied to enable monitoring the spectral shifts on the order of 1 nm or less with a 0.01 nm resolution limit.

A fresh pure solvent was injected via the system pump to flush the tubes and to take a baseline measurement as settings are set at a continuous, optimum flow rate of 0.1 µl/min to avoid the bulk concentration gradient. At this point, minor spectral shifts were observed in both the nanoplasmonic peak position and extinction due to the change in the dielectric constant of the medium near the sensors. Upon diffusion of CH₃NH₃I into the mesoporous TiO₂ film at different concentrations and temperatures, the refractive index at Au nanodisks changes with the film color change (dark brown), known as perovskite reaction, as major spectral shifts of resonance wavelength and extinction due to the change in the dielectric constant of the previously located, sensor-specific peak are simultaneously, in real time, collected and monitored via the Insplorer software [Fig. 1(b)].

For comparison, fresh solvent can be pumped again for rinsing the films. The sensors were removed for characterization. A set of 5 sensors were used for each experimental condition. Additionally, X-ray diffraction (XRD) Bruker AXS D4 Endeavour X diffractometer using Cu Ka/2, λ₁ = 154.060 pm, λ₂ = 154.439 pm radiation and room temperature photoluminescence (PL) (RF-5301 PC, SHIMADZU, 400 W, 50/60 Hz) average spectra were obtained. Scanning electron microscopy (SEM) (JEOL-6300F, 5 kV) images were analyzed using the Image J software to generate histograms of average particle size distributions.

III. RESULTS AND DISCUSSION

The nanoplasmonic sensor peak position [Fig. 2(a)] and extinction shifts [Fig. 2(b)] occur as a result of changing the sensor environment at the coated Au sensors prior and post injection of the MAI containing solvent. The mesoporous TiO₂/PbI₂ coated Au sensors were run without postrinsing. However, a fast rinsing at stagnant conditions has been reported with almost no effects on the perovskite phase formed. Additionally, the coated Au sensors were found to be sensitive to the change in the heating program (25–53 °C) prior to the MAI injection (Fig. S1, supplementary material); however, the actual sensor peak position and extinction shifts detected in this work are tailored to present the sensor response after MAI injections as addressed hereafter.

A. Nanoplasmonic sensing of perovskite formation in mesoporous TiO₂ films

The effect of changing MAI concentrations (from 5 to 15 mg/ml at 25 °C) and temperature (from 25 to 53 °C at MAI concentration of 10 mg/ml) on NPS position and extinction shifts using Au sensors/compact TiO₂/650 nm mesoporous TiO₂/PbI₂ are shown in Figs. 3(a)–3(c) and Figs. S2(a) and S2(b). The response of NPS is inherently dependent on the thickness of the support structure. For the 650 nm mesoporous TiO₂, NPS extinction shifts are inversely proportional to MAI concentrations and proportional to temperatures. This implies that diffusion at the lower interface is not limited under these conditions. Rate constants of perovskite formation are obtained from the corresponding NPS extinction shifts where the slope values (point of rise, initial point after plateau, duration of time in seconds) are accurately obtained from the Insplorer software. The reaction rates are dependent on the concentrations of MAI at the lower interface and the obtained rate constants. According to the results in the sequential work by Rajab, when the morphology of mesoporous titanatia structure is changed as in a mimic photoelectrode of solar cells using Au sensors/compact TiO₂/350 nm mesoporous TiO₂/PbI₂, the NPS extinction shifts follow different trends reflecting different perovskite structural formation.

The effect of operating temperature (from 25 to 53 °C at MAI concentration of 10 mg/ml) on NPS extinction shifts using Au sensors/compact TiO₂/650 nm mesoporous TiO₂/PbI₂ is shown in Fig. 3(c) and Fig. S2(b), which shows an increase in NPS extinction with higher temperature (except for the highest temperature of 53 °C). The highest extinction increase was observed for the TiO₂/PbI₂ film temperature of 41 °C.

The change in dielectric constants of the materials upon injection of MAI into the Au sensor-coated TiO₂/PbI₂ films provides insight into the interface interactions. The conversion of PbI₂ with a dielectric constant (ε∞ ≈ 6) to MAPbI₃ perovskite with much higher (ε∞ ≈ 20) explains the red shifts observed in NPS extinction. The structural, optical, and morphological details of the MAPbI₃ materials were thus investigated by XRD, PL, and SEM measurements. First, the XRD patterns on different substrate surfaces were acquired.
FIG. 3. Characteristic MAI concentration curves measured for Au sensors/compact TiO$_2$/650 nm mesoporous TiO$_2$/PbI$_2$ prepared by the step spin coating program showing (a) the nanoplasmonic peak position shifts and (b) the rate constant vs MAI concentration obtained from the nanoplasmonic peak extinction shifts for MAI concentrations ranging from 5 to 15 mg/ml at 25°C. The slowest reaction is recorded for the 10 mg/ml of MAI compared with the other concentrations highlighted in the dashed box. The rate constant is nonlinear with temperature as shown in (c), which is obtained from the nanoplasmonic peak extinction shifts for temperatures ranging from 25 to 53°C at 10 mg/ml of MAI.

FIG. 4. (a) XRD patterns of MAPbI$_3$ perovskites prepared into Au sensors/compact TiO$_2$/650 nm mesoporous TiO$_2$ structures at different concentrations at a temperature of 25°C. (b) The corresponding photoluminescence spectra measured at room temperature with 400 nm excitation wavelength. [(c-1)–(c-5)] Typical SEM images of as-formed perovskites at different MAI concentrations: 5, 7.5, 10, 12.5, and 15 mg/ml, respectively. As revealed, the PL peaks detected at ~1.631 eV show correlation in intensity with particle size distribution. Films of larger particle size distribution show higher PL intensity: 15 > 12.5 > 10 > 7.5 > 5 mg/ml.
as control samples. As revealed in Fig. S3, peaks of tetragonal MAI at $2\theta = 19.74^\circ$ and $29.79^\circ$ along with a hexagonal PbI$_2$ at $2\theta = 12.8^\circ$ were identified. Figures 4 and 5 show the XRD patterns and the PL spectra of MAPbI$_3$ perovskites prepared into Au sensors/compact TiO$_2$/650 nm mesoporous TiO$_2$ at different MAI concentrations and temperatures, respectively, with the corresponding SEM images.

B. The effect of MAI concentration on perovskite formation in mesoporous TiO$_2$ films

As revealed from Fig. 4(a), a series of diffraction peaks (at $2\theta = 14.25^\circ$, $28.57^\circ$, and $31.95^\circ$) corresponding to the tetragonal phase of MAPbI$_3$ perovskite has been detected at all MAI concentrations but with different extents, consistent with the literature data.\textsuperscript{17,26} Furthermore, the PL spectral lines of Fig. 4(b) exhibited characteristic PL bands at 1.631 eV, attributed to the near-band-edge (NBE) transition in tetragonal MAPbI$_3$ perovskite,\textsuperscript{27,28} but with different PL intensities. Additionally, the SEM images taken at different MAI concentrations for the 650 nm films revealed well-crystalline phase formation with different crystal morphologies [Figs. 4(c-1)]. Correlation in PL intensity [Fig. 4(b)] with crystal size distribution [Figs. S4(a)–S4(e)] can be seen as films of larger particle size distribution show higher PL intensity.

Complete conversion of MAPbI$_3$ formation, confirmed by film XRD testing at an MAI concentration of 10 mg/ml, in Fig. 4(a), corresponds with the lowest NPS rate constant of 2.5–3.0 ms$^{-1}$ in Fig. 3(b), smallest particle size (90 nm) and smallest particle size distribution (<500 nm) in Fig. S4(c) and lowest PL spectra in Fig. 4(b). Other MAI concentrations ranging from 5 to 15 mg/ml which indicate the presence of reactants correspond with higher NPS rate constants of 4.8–5.3 ms$^{-1}$ and larger particle size distributions, due to crystallization of MAI [peaks of tetragonal MAI at $2\theta = 19.74^\circ$ and $29.79^\circ$ for MAI concentration of 7.5, 12.5, and 15 mg/ml, Fig. 4(a)] and the presence of unreacted PbI$_2$ [peak of hexagonal PbI$_2$ at $2\theta = 12.8^\circ$ for MAI concentration of 5 mg/ml in Fig. 4(a)], as well as higher PL spectra shift. Although the extinction shifts are inversely proportional to MAI concentration, the lowest NPS rate constant for the intermediate MAI concentration is a criterion of complete MAPbI$_3$ perovskite formation which happens at a lower time scale compared with incomplete conversion. Hence, the local kinetics at the lower interface between the mesoporous TiO$_2$ film and the collecting electrode govern perovskite growth and formation.

C. The effect of temperature on perovskite formation in mesoporous TiO$_2$ films

Similarly, as revealed from Fig. 5(a), a series of diffraction peaks (at $2\theta = 14.25^\circ$, $28.57^\circ$, and $31.95^\circ$) corresponding to the tetragonal phase of MAPbI$_3$ perovskite has been detected at all temperatures ranging from 25 to 53 $^\circ$C at a concentration of 10 mg/ml. However, the MAPbI$_3$ formation at temperatures of 25 $^\circ$C corresponds with rate constants of $\sim$2.5 to 3.0 ms$^{-1}$, seen in Fig. 3(c) with a median particle size of 165 nm. The MAPbI$_3$ formation at other temperatures of 31–41 $^\circ$C corresponds with higher NPS rate constants of around 6.8–8.9 ms$^{-1}$, larger median particle size, and...
smaller particle size distributions. MAPbI₃ formation at a temperature of 53 °C corresponds with a NPS rate constant of ∼3.0 ms⁻¹ with spread out particle size distribution. This behavior of perovskite formation is highly non-Arrhenius as higher temperatures beyond the optimum conditions lead to slower rate constants and spread out growth regions. In summary, MAPbI₃ perovskite particle size distribution is reduced as temperature is increased to 53 °C [Figs. S5(a)–S5(e)], which correlate well with PL intensity in Fig. 5(b). Here, the NPS rate constant from the NPS technique is a direct indicator of MAPbI₃ perovskite crystal growth as higher rates indicate faster conversion as well as smaller particle size distribution, which can be utilized in solar cell applications using Au sensors/compact TiO₂/350 nm mesoporous TiO₂/PbI₂, as illustrated in the sequential work by Rajab.⁵

IV. CONCLUSIONS

The formation of MAPbI₃ perovskite at the lower interface of mesoporous TiO₂ films via a sequential deposition method was performed in situ using a nanoplasmonic sensing approach. We used nanoplasmonic sensing to detect CH₃NH₃PbI₃ perovskite formation at the interface of thick TiO₂ films with Au nanodisks, where complete conversion of perovskite formation was characterized by slow NPS red shifts, while incomplete reactions were characterized by fast methylammonium iodide (CH₃NH₃I) crystallization. When complete reaction activation energies were reduced, perovskite formation was characterized by relatively fast NPS red shifts. The research findings lead to the pursuit of utilizing the NPS approach to characterize CH₃NH₃PbI₃ perovskite formation in a mimetic photoelectrode of solar cells.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional NPS characterization, XRD, and SEM particle size distribution histograms.

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